



Universidade de Brasília
Instituto de Geociências
Programa de Pós-graduação em Geologia

Caracterização de materiais de referência de titanita e monazita para microanálises isotópicas de U-Pb e Sm-Nd por LA-ICP-MS

Characterisation of titanite and monazite reference materials for U-Pb and Sm-Nd isotopes microanalysis by LA-ICP-MS

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Tese de Doutorado Nº 208

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RESUMO

O uso da técnica LA-ICP-MS tem aumentado em vários laboratórios ao redor do mundo, assim como a demanda por materiais de referência (MRs) para calibração e controle de qualidade em análises de datação U-Pb e de composição isotópica de Sm-Nd. Nesta pesquisa, investigamos dois novos potenciais MRs de titanitas (Bear Lake e Khan River) para geocronologia U-Pb por meio de métodos de alta precisão (ID-TIMS e solução MC-ICP-MS) e alta resolução espacial (SHRIMP e *laser ablation*-MC-ICP-MS). Utilizamos a técnica de abrasão química para minimizar as áreas imperfeitas dos fragmentos. As análises U-Pb ID-TIMS produziram idades de intercepto não corrigidas para Pb_c de 516.3 ± 1.3 Ma (2s) e 1067.81 ± 0.74 Ma (2s) para as titanitas Khan River e Bear Lake, respectivamente. Análises múltiplas de U-Pb LA-SF/MC-ICP-MS e SHRIMP em ambas as amostras de titanitas apresentaram idades consistentes dentro da incerteza com os valores de ID-TIMS. As análises de LA-SF-ICP-MS, usando as titanitas Khan River e Bear Lake como calibrantes para corrigir a razão $^{206}Pb/^{238}U$ em análises matriz não-compatíveis, reproduziram as idades de outros MRs estabelecidos dentro de $<1\%$ de desvio. Neste estudo, também caracterizamos a monazita Vermilion como MR para geocronologia U-Pb e para microanálise de Sm-Nd. A monazita Vermilion apresentou média ponderada da idade $^{207}Pb^*/^{206}Pb^*$ obtida via ID-TIMS em dois laboratórios (2668.6 ± 1.8 Ma e 2666.8 ± 1.8 Ma; 2s) ligeiramente discordante. Os dados de U-Pb em SHRIMP e LA-(Q-SF-MC)-ICP-MS estão de acordo com os valores de ID-TIMS. Isótopos de Nd obtidos via ID-TIMS e solução MC-ICP-MS retornaram razões consistentes de $^{143}Nd/^{144}Nd$ de 0.510694 ± 0.000040 (2s) e 0.510726 ± 0.000014 (2s), respectivamente. Para realizar uma aplicação do material de referência da monazita Vermilion, um estudo de caso foi realizado em metapelitos do Cinturão Limpopo - África do Sul, para investigar a fonte de fluidos que causaram a retrogressão de granulitos da Zona Marginal Sul (SMZ) em condições de fácies anfibolito. Idades U-Pb de monazitas variaram de 2741-2707 Ma e indicam o pico metamórfico em fácies granulito. Os dados de U-Pb em apatitas apresentaram idades mais jovens (2056-2048 Ma). A isócrona Sm-Nd indica que a monazita e apatita cristalizaram em ca. 2.7 Ga durante a fusão parcial da fácies granulito dos metapelitos da SMZ e que os anfibólios cristalisaram durante a hidratação da SMZ no Neoarqueano. Propomos que a zona retrogridida da SMZ experienciou metamorfismo de fácies granulito Neoarqueano seguido por retrogressão em fácies anfibolito em ca. 2.7 Ga, em que um fluido derivado internamente interagiu com os metapelitos. Um evento

Paleoproterozóico posterior de reaquecimento de baixa temperatura em ca. 2.05 Ga foi responsável pelo *reset* do sistema U-Pb de apatita por perda de Pb por difusão.

Palavras-chave: espectrometria de massa; geocronologia; geoquímica isotópica; isótopos traçadores

ABSTRACT

The use of the LA-ICP-MS technique has increased in several laboratories around the world as has the demand for reference materials (RMs) for calibration and quality control in U-Pb dating and Sm-isotopic composition analyses. In this research, we investigated two new potential titanite RMs (Bear Lake and Khan River) for U-Pb geochronology through high-precision (ID-TIMS and solution-MC-ICP-MS) and high spatial resolution methods (SHRIMP, and laser ablation-MC-ICP-MS). The chemical abrasion technique was applied on titanite to minimise the fragment imperfections. U-Pb ID-TIMS analyses yielded Pb_c-uncorrected intercept ages of 516.3 ± 1.3 Ma (2s) and 1067.81 ± 0.74 Ma (2s) for the Khan River and Bear Lake titanites, respectively. Multiple U-Pb LA-SF/MC-ICP-MS and SHRIMP analyses on both titanite samples returned ages consistent within uncertainty with the ID-TIMS values. LA-SF-ICP-MS analyses, using Khan River and Bear Lake titanites as calibrants to correct the $^{206}\text{Pb}/^{238}\text{U}$ ratio in non-matrix-matched analyses, reproduced the ages of other established RMs within <1% deviation. In this study, we also characterised the Vermilion monazite as RM for U-Pb geochronology and Sm-Nd microanalysis. Vermilion monazite presented a weighted average $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ age obtained via ID-TIMS in two laboratories (2668.6 ± 1.8 Ma and 2666.8 ± 1.8 Ma; 2s) slightly discordant. The U-Pb data in SHRIMP and LA-(Q/SF/MC)-ICP-MS are consistent with the ID-TIMS values. Nd isotopes obtained via ID-TIMS and solution and MC-ICP-MS returned consistent $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.510694 ± 0.000040 (2s) and 0.510726 ± 0.000014 (2s), respectively. To demonstrate an application of the Vermilion monazite reference material, a case study was carried out on metapelites from the Limpopo Belt - South Africa, to investigate the source of fluids that caused the retrogression of former granulites from the South Marginal Zone (SMZ) in amphibolite-facies conditions. U-Pb ages of monazites ranged from 2741-2707 Ma and indicate peak metamorphism in granulite-facies. U-Pb data in apatite yielded younger ages (2056-2048 Ma). The Sm-Nd isochron indicates that monazite and apatite crystallised at ca. 2.7 Ga during the partial melting of the granulite facies of the SMZ metapelites and that amphibole grew during the hydration of the SMZ during the Neoarchean. We propose that the hydrated portion of the SMZ experienced Neoarchean granulite-facies metamorphism followed by amphibolite-facies retrogression at ca. 2.7 Ga, which an internally derived fluid interacted with the metapelites. A later Paleoproterozoic low-temperature re-heating event at ca. 2.05 Ga was responsible for the reset of the apatite U-Pb system by Pb loss by diffusion.

Keywords: mass spectrometry; geochronology; isotopic geochemistry; tracer isotopes

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CAPÍTULO 1

INTRODUÇÃO

1.1 Apresentação

Esta tese de doutorado contempla metodologia aplicada, dados, interpretações das análises, e resultados de composição química, da geocronologia U-Pb e dos estudos isotópicos de Sm-Nd realizados em potenciais materiais de referência de titanita e monazita caracterizados. Este trabalho apresenta dois potenciais materiais de referência de titanita e um de monazita para serem utilizados como calibrantes e/ou controle de qualidade para análises U-Pb e Sm-Nd por LA-ICP-MS (*laser ablation - inductively coupled plasma - mass spectrometry*). Além disso, o material de referência de monazita foi utilizado como material de referência primário em um estudo de caso realizado na área do Cinturão Limpopo, na África do Sul, para investigar o período e a origem de fluidos responsáveis por um evento de hidratação de granulitos na porção retrogredida em fácies anfibolito na Zona Marginal Sul. A tese foi estruturada em sete capítulos e contém dois artigos científicos publicados e um terceiro em preparação.

No primeiro capítulo, é apresentada uma introdução sobre geocronologia U-Pb e os estudos isotópicos de Sm-Nd por LA-ICP-MS vinculados à natureza do problema deste estudo, a justificativa da pesquisa, assim como os objetivos e localização das amostras analisadas.

O segundo capítulo apresenta um resumo sobre o conceito de um material de referência e suas possíveis aplicações e importância nos estudos geocronológicos. Além disso, é exibida uma revisão sobre a geocronologia U-Pb e o sistema isotópico Sm-Nd.

No terceiro capítulo, são descritas as metodologias empregadas neste estudo, desde a revisão bibliográfica e preparação das amostras, até os instrumentos utilizados para avaliar a composição química dos materiais de referência de titanita e monazita. Os métodos analíticos foram utilizados para medir os elementos traços e os isótopos de U-Pb e Sm-Nd nos materiais de referência caracterizados. Este método foi aplicado no estudo de caso da Zona Marginal Sul – Cinturão Limpopo, em minerais acessórios como monazita e apatita e fases minerais de granada e anfibólio. Além disso, é mostrada uma breve descrição das características principais e funções dos espectrômetros de massa utilizados.

O quarto capítulo é apresentado na forma de artigo científico intitulado “*Khan River and Bear Lake: Two Natural Titanite Reference Materials for High-Spatial Resolution U-Pb Microanalysis*” (Mazoz et al., 2022) publicado na revista *Geostandards and Geoanalytical Research*. Este artigo aborda a caracterização de dois novos materiais

de referência de titanita (Khan River e Bear Lake) para geocronologia U-Pb e com elevado potencial para serem utilizados em análises isotópicas de Sm-Nd. O destaque deste artigo é voltado para a utilização de materiais de referência de titanita, que mesmo contendo Pb comum em sua estrutura, apresenta uma pequena variação, o que permite sua aplicação em estudos petrocronológicos.

O quinto capítulo, na forma de artigo científico, propõe um novo material de referência de monazita Arqueano. Atualmente, não há nenhum material de referência mais antigo que 1.76 Ga disponível e/ou bem caracterizado para a comunidade científica. “*The Vermilion Monazite: A New Archean Monazite Reference Material for U-Pb and Sm-Nd Microanalysis by LA-ICP-MS*” (Mazoz et al., 2024) publicado na revista *Chemical Geology*, este artigo apresenta a caracterização completa deste mineral por meio de diversas técnicas de alta resolução espacial e de alta precisão. A homogeneidade isotópica também é discutida e avaliada, comparando a composição química e isotópica com outros materiais de referência de monazita existentes. A monazita Vermilion pode ser utilizada como material de referência primário ou secundário para geocronologia U-Pb e apresenta um potencial para ser utilizada como material de referência secundário para estudos de composição isotópica de Sm-Nd.

O sexto capítulo está elaborado na forma de artigo científico (em preparação). Este capítulo aborda o trabalho elaborado durante o estágio internacional realizado na Universidade de Stellenbosch na África do Sul. Com o título “*Unravelling fluid interaction processes in the hydrated zone of the Southern Marginal Zone of the Limpopo Belt - South Africa: implications for U-Pb and Sm-Nd systematics using monazite and apatite in metapelites*”, este artigo aborda a investigação da fonte dos fluídos que causaram a hidratação de granulitos retrogradados em fácies anfibolito, da Zona Marginal Sul do Cinturão Limpopo, e o período que este evento ocorreu, após a colisão continental e acreção de arco entre os crátons Kaapvaal e Zimbabwe em ca. 2.7 Ga. Este estudo nos metapelitos permitiu a obtenção de novas informações acerca da origem dos fluídos por meio do uso da técnica LA-MC-ICP-MS para investigar a geocronologia U-Pb e a composição isotópica de Sm-Nd em monazitas e apatitas, e Sr-Sr em apatitas integradas com a composição de elementos traços destas fases minerais e gerações distintas de granadas. Análises de Sm-Nd em ortoanfibólios foi feita por meio de solução-MC-ICP-MS. Por meio da geoquímica isotópica associada à composição química das fases minerais investigadas, este estudo permitiu concluir que os fluídos eram derivados internamente da cristalização de *melts* provenientes dos granulitos que experienciaram

fusão parcial, no qual nenhum fluido externo contribuiu com esta retrogressão em fácies anfíbolito.

Por último, o sétimo capítulo apresenta as conclusões do trabalho realizado ao longo da pesquisa de doutorado, destacando os pontos mais relevantes de cada material de referência caracterizado e do estudo de caso realizado no estágio internacional.

1.2 Natureza do problema

Estudos recentes em minerais acessórios (e.g., titanita, monazita, zircão), focados em análises geocronológicas de U-Pb via *laser ablation-inductively coupled plasma-mass spectrometry* (LA-ICP-MS), evoluíram nas últimas décadas, proporcionando uma aquisição de dados mais acurada e precisa. Os processos de preparação de amostras são simples, a resolução espacial do furo a laser é alta e os custos são mais acessíveis (Simonetti et al., 2006). É importante ressaltar que esta técnica analítica é destrutiva por construção e requer constantemente a reposição de materiais de referência naturais homogêneos, bem caracterizados para serem utilizados na calibração e controle de qualidade.

Um desafio para realizar as análises por LA-ICP-MS é a necessidade de um material de referência matriz-compatível (composição química e estrutura similar) com a amostra, ideal para realizar a correção do fracionamento das razões U-(Th)-Pb, mas também de outros pares isotópicos, induzido pelo sistema de laser (Horstwood et al., 2016). Assim, os dados geocronológicos e isotópicos adquiridos por LA-ICP-MS serão precisos e acurados, além de garantir a estabilidade do sistema durante as análises (Schoene, 2014).

O zircão é um mineral acessório refratário e abundante em rochas crustais, comumente utilizado nos estudos geocronológicos por LA-ICP-MS. Entretanto, outros minerais acessórios também podem ser utilizados (monazita, xenotima, badeleita, titanita), assim como minerais formadores de rocha (calcita, aragonita; Woodhead et al., 2006). Apesar da análise destes minerais ser analiticamente possível, a falta de materiais de referência matriz-compatíveis é um desafio para a maioria dos laboratórios brasileiros e internacionais. Além disso, para se obter um material de referência adequado para calibrar o equipamento e estabelecer o controle de qualidade das análises, devem seguir os seguintes pré-requisitos (Slàma et al., 2008): baixo teor de Pb comum; composição química homogênea; estrutura cristalina livre de imperfeições; ausência de qualquer complexidade nas razões de U/Pb radiogênico; apresentar tamanho considerável para

realizar repetidas análises de ablação; e apresentar ampla disponibilidade para ser distribuído para a comunidade científica. Portanto, é necessária uma caracterização química e isotópica meticulosa de cada material de referência a ser investigado.

O sistema isotópico de Sm-Nd também vem sendo muito utilizado em análises terrestres e planetárias, atuando como um geocronômetro e como um traçador isotópico (e.g., Lugmair and Carlson, 1974; O'Nions et al., 1977; Lugmair and Carlson, 1978; De Paolo, 1981). Pesquisas recentes apontam que, a partir da técnica de LA-MC-ICP-MS (multicoletor), é possível adquirir análises *in-situ* precisas e acuradas dos isótopos de Sm-Nd em minerais acessórios (e.g., titanita, monazita, apatita, alanita, peroviskita) enriquecidos em elementos terras raras leves (ETRL) (Foster and Vance, 2006; McFarlane and McCulloch, 2007; Yang et al., 2008, 2009). Os obstáculos para esse tipo de estudo incluem a necessidade de corrigir a interferência isobárica de ^{144}Sm , a determinação de um fator de correção instrumental do *mass bias* para o Sm e Nd e dados acurados de $^{147}\text{Sm}/^{144}\text{Nd}$. Dessa forma, é necessário utilizar materiais de referência que apresentam composição isotópica de Nd e Sm-Nd homogênea com o intuito de corrigir esses fatores limitantes (Fisher et al., 2011).

1.3 Justificativa

Existem alguns materiais de referência de titanitas na comunidade científica disponíveis para utilização na geocronologia U-Pb por LA-ICP-MS, por exemplo, MKED1 (Spandler et al., 2016), OLT1 (Kennedy et al., 2010), BLR-1 (Aleinikoff et al., 2007) e Khan (Kinny et al., 1994). Eles apresentam valores concordantes nas idades obtidas via ID-TIMS, entretanto, alguns possuem Pb comum variável, podendo apresentar algumas variações que influenciam na idade $^{207}\text{Pb}/^{206}\text{Pb}$ (e.g., Khan, BLR-1), e outros podem apresentar porções com perda de Pb radiogênico (e.g., MKED1). É importante notar que esses materiais de referência apresentam quantidades significativas de U para serem datados e podem apresentar algumas áreas zoneadas (e.g., Khan, MKED1), podendo influenciar na concentração dos elementos traços. Em análises de Sm-Nd, esses calibrantes apresentam bons resultados, porém não há uma grande variedade disponível aos laboratórios.

Para estudos isotópicos em monazita, poucos materiais de referência são distribuídos de forma ampla e internacional, pois existe apenas um pequeno número disponível, além de destacar o fato da técnica de geocronologia por LA-ICP-MS ser destrutiva. Alguns dos materiais de referência de U-Pb mais utilizados e que estão

disponíveis são a monazita 44069 (Alenikoff et al., 2006), TS (Budzyń et al., 2021) e as monazita Managountry (Paquette et al., 1994), Itambé (Gonçalves et al., 2016) e Diamantina (Gonçalves et al., 2018) que também são utilizadas como materiais de referência para Sm-Nd. Estes minerais são homogêneos, possuem idade ID-TIMS (*Isotope Dilution–Thermal Ionisation Mass Spectrometry*) concordante e, além disso, costumam não apresentar quantidades significativas de Pb comum nem áreas com perda Pb radiogênico.

Para caracterizar um material de referência e distribuir aos laboratórios nacionais e internacionais é necessária uma completa caracterização química e isotópica de cada cristal do mineral em estudo. Após esta etapa, realizou-se um estudo de caso na África do Sul, no Cinturão Limpopo, na Zona Marginal Sul, para poder investigar a origem de fluídos que proporcionaram a retrogressão de granulitos da região em fácies anfibolito por meio do estudo químico e isotópico de U-Pb e Sm-Nd em minerais acessórios como apatita e monazita e fases minerais silicáticas, como ortoanfibólio e granada. A monazita Vermilion foi utilizada como material de referência primário para analisar as amostras desconhecidas de monazitas dos metapelitos.

1.4 Objetivo

O estudo geocronológico de isótopos de U-Pb e Sm-Nd via LA-ICP-MS necessita de uma ampla disponibilidade de minerais isotopicamente homogêneos e bem caracterizados para serem utilizados como materiais de referência. Além disso, o estudo isotópico de amostras desconhecidas permite investigar os processos geológicos desencadeados na região em estudo. Portanto, este projeto de doutorado teve como objetivo a caracterização química e isotópica de novos materiais de referência para a comunidade científica, avaliando o potencial desses minerais para serem utilizados em microanálises de alta resolução espacial para datação U-Pb, composição isotópica de Sm-Nd e elementos traços por LA-ICP-MS para gerar dados acurados e precisos. Foram selecionados duas amostras de titanita, Khan River e Bear Lake, e a monazita Vermillion para serem cuidadosamente caracterizadas a partir de análises químicas e isotópicas. Com isso, os objetivos deste estudo basearam-se em:

- 1) Avaliar a homogeneidade química e isotópica das titanitas Khan River e Bear Lake e da monazita Vermilion, demonstrando o potencial para serem utilizadas como materiais de referência para análises isotópicas de U-Pb e Sm-Nd e elementares (ETR e outros traços) por LA-ICP-MS.

- 2) Apresentar a técnica de abrasão química desenvolvida em titanitas, com o intuito de aprimorar as regiões dos fragmentos a serem ablados, permitindo a eliminação de áreas danificadas/fraturadas com potencial perda de Pb e, consequentemente, uma melhoria na acurácia e precisão dos dados geocronológicos.
- 3) Utilizar as técnicas obtidas nos minerais caracterizados para investigar, por meio de análises isotópicas, os eventos de interação de fluídos na região retrogredida da Zona Marginal Sul, Cinturão Limpopo, África do Sul, em parceria com a Universidade de Stellenbosch. Esta pesquisa buscou investigar quando os granulitos da região foram hidratados e retrogredidos para fácies anfibolito e qual a fonte dos fluídos que interagiram com os metapelitos. Além disso, também foi utilizado o material de referência de monazita Vermilion como uma aplicação do trabalho desenvolvido nesta tese.

1.5 Localização das amostras

1.5.1 *Titanita Khan River*

Os fragmentos da titanita Khan River utilizados neste estudo foram amostrados em um pegmatito no deserto da Namíbia, situado próximo à mina de cobre Khan, a nordeste de Swakopmund, na costa do sudoeste da África (Sohnge et al., 1939). A mina se encontra na região central do Orógeno Damara próxima ao rio Khan, nas coordenadas 22° 30' 29" Sul, 14° 59' 30" Leste, na cidade de Arandis, região de Erongo. A figura 1.1 representa a localização da região da mina de cobre Khan, e o local aproximado de coleta das amostras da titanita Khan River.

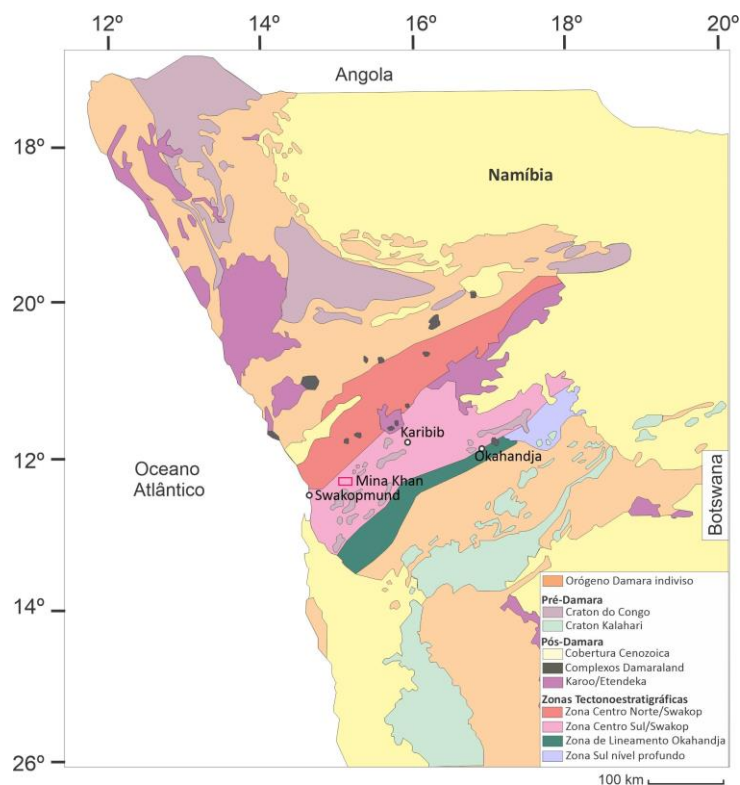


Figura 1.1: Mapa de localização da região onde foram extraídos os grãos de titanita, próximos à mina de cobre Khan (destacado em rosa) na Namíbia, sudoeste da África.

1.5.2 Titanita Bear Lake

Os fragmentos da titanita Bear Lake analisados neste trabalho foram coletados na região de Bear Lake Diggings, próximo a cidade de Tory Hill, Ontário, Canadá. Esta região se localiza na porção sudeste do Complexo Gnaissico Glamorgan na província geológica Grenville. A Figura 1.2 destaca a região aproximada do local de extração das amostras.

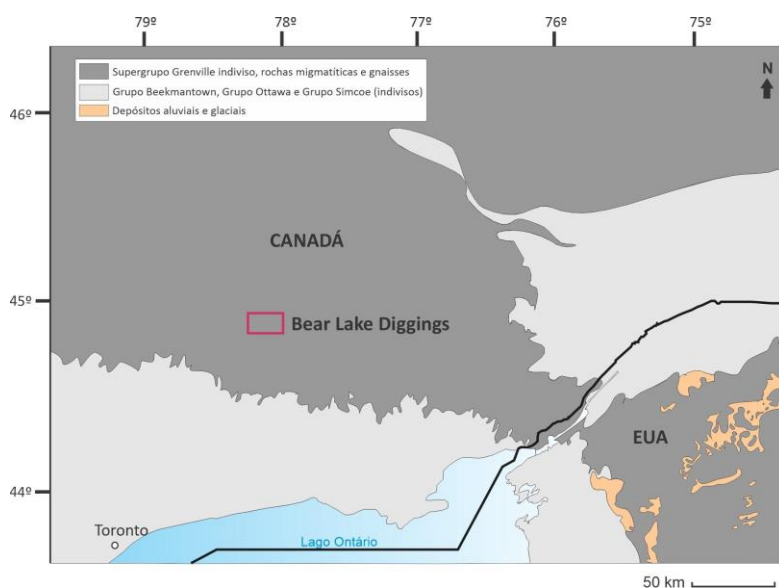


Figura 1.2: Mapa da região onde foi amostrada a titanita Bear Lake, na região de Bear Lake Diggings (destacado em rosa), em Ontário, Canadá.

1.5.3 Monazita Vermilion

As amostras da monazita Vermilion foram coletadas no Complexo Granítico Vermilion (VGC), na região nordeste do Minnesota (EUA), situado na Subprovíncia Quetico (Figura 1.3) na Província Superior do Escudo Canadense. Os cristais da monazita Vermilion foram separados de amostras de um biotita-xisto.

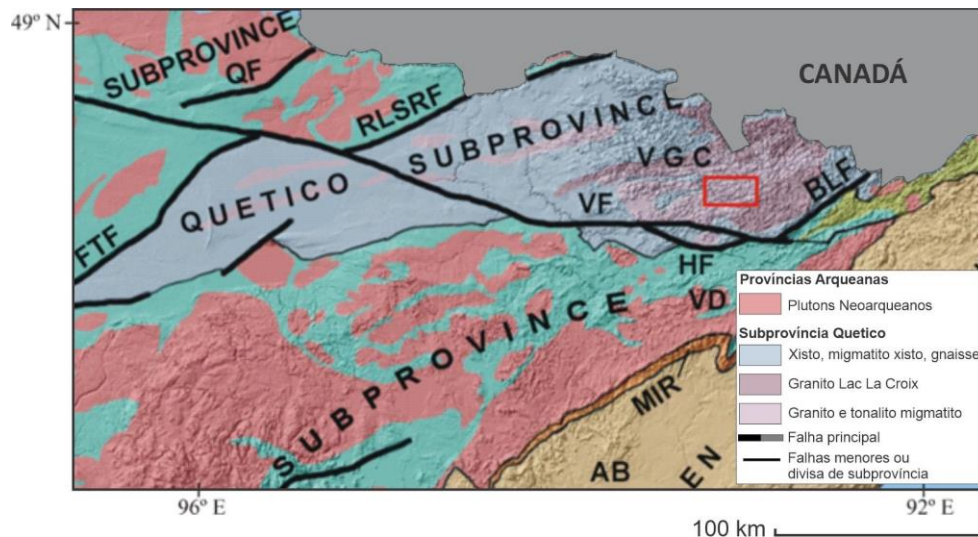


Figura 1.3: Mapa da região nordeste do Minnesota, EUA, onde foi amostrada a monazita Vermilion (destacado em Vermelho), na Subprovíncia Quetico. Na figura pode-se observar as demais subprovíncias da região. Extraído e modificado de “The Archean Terranes of Minnesota” em US Geology and Geomorphology. Fonte: U.S. Geological Survey, Minnesota Geological Survey.

1.5.4 Estudo de caso – Zona Marginal Sul, Cinturão Limpopo

Este estudo de caso foi realizado na Zona Marginal Sul do Cinturão Limpopo, na África do Sul. O Cinturão Limpopo se localiza na divisa da África do Sul-Zimbabwe-Botsswana na porção norte do cráton Kaapvaal (Figura 1.4a). A Zona Marginal Sul se formou durante um evento de formação de arco acrescionário e colisão continental entre os crátons Kaapvaal e Zimbabwe em ca. 2.7 Ga. Este terreno consiste em metapelitos que registram fácies granulito na região mais ao norte e que foram retrogradados em fácies anfibolito na porção sul da Zona Marginal Sul, localizada ao norte do cráton Kaapvaal. As amostras de metapelitos foram coletadas na porção hidratada e retrogradada em fácies anfibolito (Figura 1.4b).

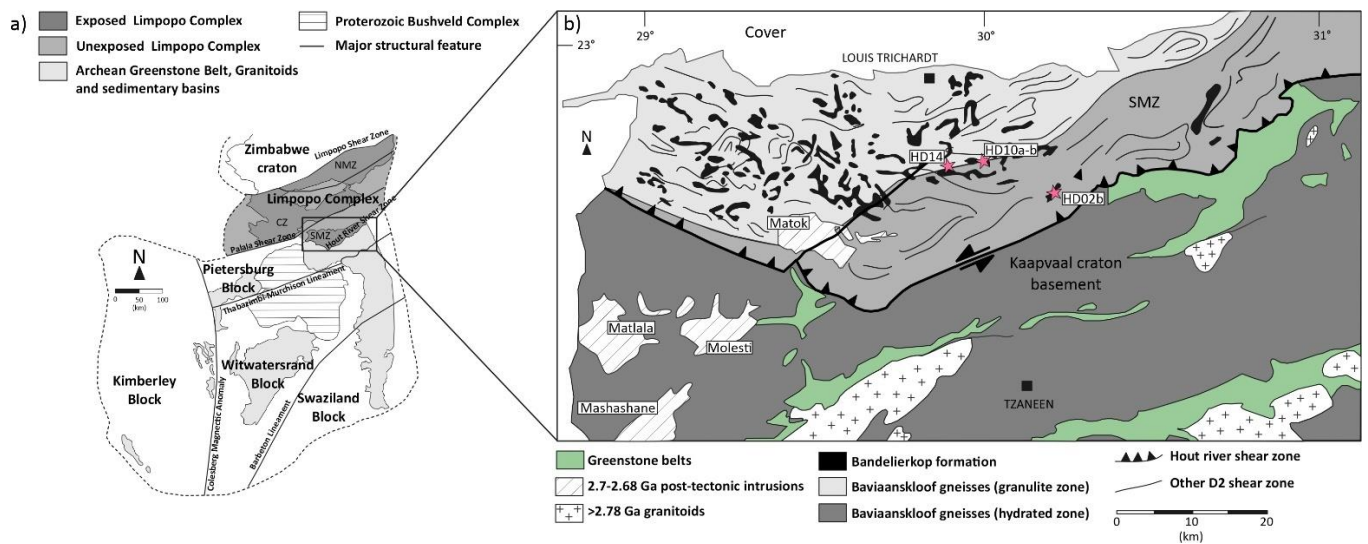


Figura 1.3: a) Mapa simplificado do cráton Kaapvaal e terrenos localizados ao norte (modificado de Hunter, 1974; de Wit et al., 1992c; Poujol et al., 2003; Eglington and Armstrong, 2004; Vezinet et al., 2018); b) Mapa geológico da Zona Marginal Sul localizada no Cinturão Limpopo na porção norte do cráton Kaapvaal (modificado de Stevens, 1997; Nicoli et al., 2015; Vezinet et al., 2018; Carranza, 2018).

CAPÍTULO 2

ARCABOUÇO TEÓRICO

Este capítulo irá abordar os aspectos relevantes sobre geocronologia U-Pb, análises isotópicas de Sm-Nd e elementos traços, e descrever o uso de materiais de referência de titanita e monazita como geocronômetros. Além disso, será apresentada uma breve abordagem acerca do uso de minerais acessórios para investigar processos de interação de fluido-rocha associada ao período de evolução crustal das rochas.

2.1 Materiais de referência para LA-ICP-MS

2.1.1 O que é um material de referência?

Nas análises obtidas por meio do equipamento LA-ICP-MS, é necessário o uso de materiais de referência, bem caracterizados e matriz-compatíveis, que podem ser naturais ou artificiais, utilizados para fazer a calibração e o controle de qualidade dos dados das amostras investigadas. Para realizar a calibração das análises, utiliza-se um material de referência primário, de preferência matriz-compatível com as amostras, para corrigir as razões U/Pb e Pb/Pb medidas. Esta etapa proporciona a correção simultânea para *mass bias*, *drift* instrumental e fracionamento elementar induzido pelo laser (e.g., Eggins et al., 1998). Esse procedimento é realizado medindo essas razões do material de referência antes e depois de um número de amostras, durante a rodada analítica. Desta forma, é determinado um fator de correção em relação ao valor medido e o valor aceito para essas razões. Assim, aplica-se esse fator de correção nas razões medidas das amostras, considerando que não há efeito matriz entre o material de referência e a amostra (e.g., Jackson et al., 2004).

Para realizar o controle de qualidade das análises, é preciso um material de referência secundário. Este possui a função de conferir os dados adquiridos com os valores aceitos, de modo que, se o valor obtido (após ter sido calibrado pelo material de referência primário) estiver dentro das incertezas dos valores certificados, entende-se que as razões estão sendo medidas corretamente. Consequentemente, os valores obtidos das amostras em estudo também estarão precisos e acurados.

Além disso, podemos utilizar na rotina das análises os materiais de referência *in-house*, que são materiais de referência caracterizados ou parcialmente caracterizados por um determinado laboratório, mas que não apresentam os dados publicados e/ou não há quantidade suficiente para ampla distribuição. Muitos laboratórios fazem a calibração externa desse material de referência em outros laboratórios para certificar o valor utilizado, contudo, estes dados ainda não estão disponíveis na literatura e, portanto, são dados utilizados apenas para uso interno.

2.1.2 Investigações da composição geoquímica e isotópica em titanita e monazita

2.1.2.1 Titanita

O mineral mais utilizado em estudos geocronológicos é o zircão, entretanto, não é o mais adequado para relacionar as texturas e a petrogênese da paragênese mineral de uma determinada rocha em estudo. Esse fator está associado principalmente às rochas que passaram por eventos de alteração hidrotermal e metamorfismo (Storey et al., 2006). Neste contexto, podemos avaliar a titanita ($\text{CaTi}_2\text{SiO}_5$) como um mineral comumente presente em fases ígneas, metamórficas e hidrotermais. Além disso, este mineral apresenta uma clara relação textural e mineralógica com o histórico de pressão e temperatura que a rocha foi submetida (Carswell et al., 1996; Frost et al., 2000; Piccoli et al., 2000). É importante destacar que, a titanita apresenta uma alta temperatura de fechamento de 650-700 °C (Frost et al., 2000; Pidgeon et al., 1996; Scott and St-Onge, 1995) e, com isso, pode suportar eventos de altas temperaturas, assim como o zircão. Entretanto, como muitas rochas apresentam fases ricas em Ti e Ca, as titanitas presentes podem ser muito mais reativas comparadas ao zircão em altas temperaturas (Scott and St-Onge, 1995), podendo apresentar vários processos de crescimento no mineral. Dessa forma, é necessário compreender os eventos que ocorreram na rocha em estudo para avaliar o momento em que este mineral se cristalizou, no qual os fatores envolvidos podem estar associados à processos ígneos, metamórficos e de deformação (Frost et al., 2000).

A titanita apresenta um alto potencial de incorporar quantidades significativas de U em sua estrutura cristalina (Frost et al., 2000). Isso permite uma boa aquisição de dados de U-Pb a partir do estudo destes geocronômetros. Também é importante considerar que a titanita pode incorporar Pb comum durante sua cristalização e, assim, é necessária uma análise cautelosa dos dados (Frost et al., 2000).

Como a titanita apresenta um alto potencial em incorporar elementos terras raras (ETR), principalmente os ETR médios, torna-se possível analisar a composição química de Sm-Nd e as razões isotópicas deste sistema (Kohn, 2017). Esse método analítico permite a interpretação de processos ígneos e metamórficos distintos a partir das razões iniciais de cada fase mineral analisada associada à composição dos ETR, podendo também obter idades a partir da isócrona de Sm-Nd em minerais cogenéticos (Kohn, 2017).

2.1.2.2 Monazita

Outro mineral acessório utilizado na geocronologia é a monazita (Ce, La, Nd, Th)PO₄, um fosfato rico em elementos terras raras leves. Devido à sua composição química variável, o estudo deste mineral permite interpretar os diversos processos da história evolutiva da rocha hospedeira (*e.g.*, Zhu & O'Nions 1999; Spear & Pyle 2002; Harrison et al., 2002; Paquette et al., 2004; Williams et al., 2007). A monazita é comumente encontrada em rochas ígneas, como pegmatitos e rochas graníticas, veios hidrotermais, rochas em diferentes graus metamórficos e em rochas sedimentares (Parrish 1990). Como a monazita também pode ser considerada um mineral diagenético e se cristaliza pouco tempo depois da deposição dos sedimentos, pode ser aplicada para interpretar as idades de sedimentação dessas rochas (*e.g.*, Evans and Zalasiewicz, 1996; Evans et al., 2002).

A monazita vem sendo amplamente utilizada em estudos isotópicos por diversas razões. Este mineral pode ser encontrado em vários ambientes, como em rochas ígneas, metamórficas e sedimentares (Williams et al., 2007), e pode agregar altas concentrações de U e Th, baixa concentração de Pb comum e apresenta elevada temperatura de fechamento para Pb (~900°C; Cherniak et al., 2004; Gardes et al., 2006). Além disso, como a monazita apresenta uma baixa taxa de difusão de U-Th-Pb, dificilmente o sistema será reiniciado por difusão no estado sólido desses elementos (Cherniak et al., 2004). Ademais, mesmo apresentando elevadas concentrações de U-Th, dificilmente esse mineral se torna metacmítico visto que sua estrutura é capaz de recuperar dos danos causados pelo decaimento em baixa temperatura (Harrison et al., 2002; Seydoux-Guillaume et al., 2002). Em casos de interação com fluidos, a monazita pode se recrystalizar ou dissolver, o que ocasionará o reinício do sistema e, consequentemente, o registro de quando ocorreu esse evento (Poitrasson et al., 2000, Janots et al., 2008, Kirkland et al., 2009, Allaz et al., 2013). A monazita possui altas concentrações de Sm e Nd, o que permite a determinação das razões isotópicas de Sm-Nd (Evans e Zalasiewicz, 1996; Tomascak et al., 1998).

2.1.3 *Uso de minerais acessórios em estudos petrocronológicos para investigar processos de interação de fluidos integrados no tempo*

A geocronologia e a caracterização geoquímica de minerais acessórios enriquecidos em ETR integrados à petrologia da rocha, podem proporcionar uma interpretação mais aprofundada de processos geológicos complexos (*e.g.* McFarlane and

McCulloch, 2007; Mottram et al., 2015; Parrish, 1990; Rubatto et al., 2013; Spear and Pyle, 2002; Williams et al., 1999). A distribuição de ETR pode ser presenciada em rochas félsicas e metapelitos durante processos subsolidus em condições metamórficas (Bea and Montero, 1999; Bingen et al., 1996; Hammerli et al., 2014, 2016; Janots et al., 2008; Spear and Pyle, 2002; Villaseca et al., 2007; Wing et al., 2003). Estudos anteriores mostraram que em condições de metamorfismo de fácies granulito, a abundância de monazita pode diminuir e o teor de ETR pode ser incorporado em apatitas (Bingen et al., 1996; Hansen and Harlov, 2009). Bea and Montero (1999) reportaram que com o aumento de condições de pressão e temperatura, monazita e zircão se mantêm preservados quando não são consumidos em reações de formação de minerais principais, sendo relativamente insolúveis no *melt*, enquanto apatita pode ser amplamente dissolvida em *melts* anatéticos. Janot et al. (2018) reportou que apatitas em condições metamórficas de fácies anfibolito podem se reequilibrar quimicamente em processos de dissolução-precipitação somente quando tem uma quantidade significativa de fluidos envolvidos. Isso permite que apatitas podem ser utilizadas como um *fingerprint* das condições metamórficas experienciadas pela rocha.

Os sistemas U-Pb e Sm-Nd também podem ser afetados por eventos distintos, no qual estes permanecem registrados em alguns minerais acessórios de acordo com o comportamento do sistema isotópico. Corfu and Stone (1998) mostraram que, em um estudo envolvendo duas gerações de titanitas com idades distintas, as idades da primeira geração de titanita indicam a idade de cristalização do plúton, apresentado um espalhamento, possivelmente associado a eventos termais ou hidrotermais mais jovens na região. As idades mais jovens da segunda geração de titanita concordam com idades de apatitas, e refletem cristalização em eventos mais recentes de retrogressão causadas por atividade termais ou de fluidos. Gillespie et al. (2022) demonstraram que um estudo envolvendo idades U-Pb em zircão e apatita e dados de Sm-Nd em apatita registrou uma evolução termal Arqueana-Paleoproterozoica. Análises de U-Pb em zircão proporcionaram interpretar uma idade de cristalização para as rochas magmáticas e as idades de U-Pb e juntamente com dados isotópicos de Sm-Nd e Lu-Hf em apatitas permitiram investigar a história evolutiva das rochas e os diversos eventos metamórficos. Portanto, por meio da combinação da composição química elementar e dos pares isotópicos de U-Pb e Sm-Nd, é possível reconstruir os diversos eventos geológicos ocorridos nas rochas em estudos a partir da análise de minerais acessórios enriquecidos nestes elementos.

2.2 Geocronologia – Sistema isotópico U-Pb

2.2.1 Introdução

O conceito de geocronologia envolve o uso do decaimento radioativo e sua constante de decaimento para determinação do tempo de processos geológicos. Como o isótopo radioativo-pai decai para o radiogênico-filho de acordo com uma taxa constante, é possível determinar o tempo a partir do número de núclídeos que decaíram (White, 2015). O início dos estudos envolvendo geocronologia ocorreu em 1907 a partir do descobrimento do elemento Pb ser o último produto do decaimento do U pelo cientista Bertram Boltwood (White, 2015). Ele descobriu que a partir da análise de minerais com altos teores de U, a razão Pb/U era a mesma para minerais do mesmo período geológico, no qual esta razão aumentava ao longo do tempo (White, 2015). O desenvolvimento de técnicas envolvendo o decaimento de U e a geocronologia U-Th-Pb (e.g., Barrell, 1917; Bateman, 1910; Boltwood, 1907; Holmes and Lawson, 1927 *in* Schoene, 2014), tornou possível a criação do método de datação de isótopos, que apresenta alto potencial em medir idades de eventos ocorridos desde o início do sistema solar em torno de ~4.57 Ga até o Pleistoceno (Schoene, 2014).

O sistema U-Th-Pb apresenta um elevado potencial nas análises devido a abundância de minerais com alto teor de U na maioria das rochas, assim como a resistência ao intemperismo químico e físico. O zircão é o mineral mais utilizado para a geocronologia U-Pb (Hanchar and Hoskin, 2003), porém minerais acessórios como titanita, monazita, apatita, xenotima, rutilo, badeleíta, alanita e peroviskita vem demonstrando um elevado potencial em estudos isotópicos de U-Pb. A abundância de zircões em rochas ígneas félsicas permitem determinar a idade de cristalização da rocha, porém para investigar eventos metamórficos ou processos hidrotermais, outros minerais acessórios são mais indicados (e.g., titanita, monazita, rutilo – Storey et al., 2006; Gonçalves et al., 2018; Bracciali et al., 2013).

A partir da década de 1960, a aquisição de um dado preciso e acurado tornou-se cada vez maior, principalmente após o aprimoramento da técnica de geocronologia por espectrômetros de massa pelo sistema U-(Th)-Pb. As análises realizadas em minerais com alto teor de U passaram a ser obtidas com mais facilidade por meio desse sistema, porém, a obtenção de um resultado de alta precisão por ID-TIMS ainda é a técnica no qual os outros métodos (SHRIMP - *Sensitive High Resolution Ion Microprobe*, SIMS - *Secondary Ion Mass Spectrometer*, LA-ICP-MS) são comparados.

2.2.2 O sistema de decaimento U-Th-Pb

No núcleo atômico do U e do Th, a força nuclear que atua unindo os prótons e os nêutrons é elevada. Isso ocorre devido à instabilidade gerada em átomos com aproximadamente 100 prótons, em que a força apresentada é 100 vezes mais forte que a repulsão eletromagnética existente. Para diminuir a energia e alcançar a estabilidade, o U e Th decaem por emissão de partículas alfa (núcleo de ^4He) (Harrison et al., 2002). A geocronologia do U-(Th)-Pb se baseia no decaimento dos isótopos-pai para os isótopos radiogênicos estáveis de Pb, em que cada um apresenta um determinado período de meia-vida (Faure, 1986). Este processo de decaimento radioativo passa por etapas de emissão de partículas alfa e beta, criando uma série de isótopos filhos que levam ao mesmo isótopo estável de Pb (Bateman 1910, *in* Schoene, 2014). Os pares isotópicos pai-filho pode ser observado na Tabela 1, no qual o isótopo de maior massa decai para o de menor massa (e.g., ^{238}U para ^{206}Pb) (Jaffey et al., 1971).

Tabela 2.1: Pares isotópicos pai-filho para U e Th e o decaimento para Pb

Rota de decaimento	$t_{1/2}$ (Ga)	Constante de decaimento λ , anos ⁻¹
$^{238}\text{U} \rightarrow ^{206}\text{Pb}$	4.47	1.55125×10^{-10}
$^{235}\text{U} \rightarrow ^{207}\text{Pb}$	0.704	9.8485×10^{-11}
$^{232}\text{Th} \rightarrow ^{208}\text{Pb}$	14.01	0.49475×10^{-12}

As idades U-Pb são consistentes com a idade de cristalização dos minerais após estarem em equilíbrio secular, ou seja, é necessário um período decorrido de cinco meia-vida dos isótopos-filho intermediários. Esse fator ocorre quando a constante de decaimento de um isótopo e sua abundância geram um produto igual entre todos os isótopos-filho e isótopos-pai. É importante considerar que este equilíbrio não ocorre de forma rápida ao longo do tempo geológico, e por haver a incorporação ou exclusão preferencial dos isótopos intermediários devido à partição de elementos durante a cristalização do mineral, o teor de isótopos-filho será variado (Faure, 1986). Entretanto, em relação aos isótopos de ^{232}Th , estes atingem um equilíbrio secular em um menor intervalo de tempo, pois decaem para ^{208}Pb em um curto período de meia-vida diferentemente dos outros isótopos.

O mecanismo de decaimento radioativo de três sistemas distintos permite a elaboração de três equações de idades a partir de um equilíbrio secular estabelecido (Faure, 1986):

$$\left(\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}}\right) = \left(\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}}\right)_0 + \left(\frac{{}^{238}\text{U}}{{}^{204}\text{Pb}}\right)(e^{\lambda^{238}t} - 1) \quad [A]$$

$$\left(\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}}\right) = \left(\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}}\right)_0 + \left(\frac{{}^{235}\text{U}}{{}^{204}\text{Pb}}\right)(e^{\lambda^{235}t} - 1) \quad [B]$$

$$\left(\frac{{}^{208}\text{Pb}}{{}^{204}\text{Pb}}\right) = \left(\frac{{}^{208}\text{Pb}}{{}^{204}\text{Pb}}\right)_0 + \left(\frac{{}^{232}\text{U}}{{}^{204}\text{Pb}}\right)(e^{\lambda^{232}t} - 1) \quad [C]$$

em que o índice 0 representa o valor da razão do teor isotópico de Pb quando houve o fechamento do sistema (Pb inicial), t se refere ao tempo decorrido desde o fechamento do sistema e λ^{238} , λ^{235} e λ^{232} são as constantes de decaimento de ${}^{238}\text{U}$, ${}^{235}\text{U}$ e ${}^{232}\text{Th}$, respectivamente. Por último, a equação é dividida pelo ${}^{204}\text{Pb}$, que não é um isótopo nem radioativo nem radiogênico, considerado o chumbo comum (Pb_c), que entra na estrutura cristalina durante a cristalização de determinados minerais (Faure, 1986). Essas equações permitem a criação de diagramas de isócronas desde que o sistema permaneça fechado para U e Pb. Em casos em que o sistema de um mineral incorpora quantidades significativas de U, mas não incorpora o Pb inicial, é possível se obter valores concordantes da idade de formação do mineral (equações [A] e [B]), desde que o sistema se permaneça fechado.

2.2.3 Diagrama concórdia de Wetherhill

Uma das formas mais eficientes utilizadas para representar o decaimento dual de U para Pb e interpretar os resultados e suas aplicações é o diagrama concórdia de Wetherhill (1956) (Figura 2.1). A partir dos cálculos das equações [A] e [B], é possível criar o diagrama de concórdia de Wetherill, que apresenta as razões ${}^{206}\text{Pb}^*/{}^{238}\text{U}$ versus ${}^{207}\text{Pb}^*/{}^{235}\text{U}$ a partir de uma mesma análise do mineral. Este diagrama é não-linear devido às distintas meia-vidas dos isótopos de ${}^{238}\text{U}$ e ${}^{235}\text{U}$. Neste diagrama, para amostras que permaneceram em um sistema fechado, ou seja, sem terem sido submetidas a uma perturbação no sistema, os dados caem em cima da curva da concórdia. Entretanto, para as amostras que sofreram alguma abertura no sistema, os dados são alinhados em uma curva chama discórdia (Schoene, 2014).

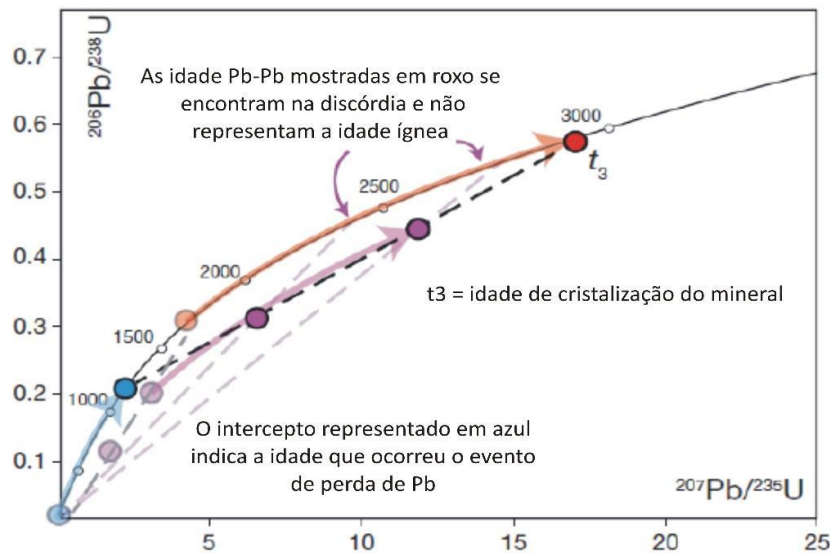


Figura 2.1: Representação do diagrama de Wetherhill indicando a idade de cristalização de um mineral em t_3 , a linha de discordância com as amostras em roxo após um evento de perda de Pb e o intercepto inferior em azul representando a idade em que a abertura do sistema ocorreu (extraído e modificado de Schoene et al., 2014).

Estudos envolvendo os processos de perda/ganho de U e Pb podem auxiliar em diversas interpretações geológicas de acordo com cada condição analisada no diagrama de concordância (e.g., Sinha et al., 1992; Williams et al., 1984). A cristalização de um mineral acumula Pb^* (Pb radiogênico), proveniente do decaimento do U, em que, em um sistema fechado, permite apresentar as razões $^{207}\text{Pb}^*/^{235}\text{U}$ e $^{206}\text{Pb}^*/^{238}\text{U}$ no diagrama de concordância. Em casos de perda de Pb radiogênico, o Pb que sairá do mineral de acordo com a abundância natural de cada isótopo, terá uma razão $^{207}\text{Pb}/^{206}\text{Pb}$ do mineral naquele tempo, que será equivalente à sua idade Pb-Pb. Os distintos processos que vários minerais de uma rocha foram submetidos, a partir de diferentes concentrações de perda de Pb, permitem a obtenção de um diagrama na linha de discordância, no qual o intercepto inferior representa o período em que ocorreu um evento que gerou abertura do sistema isotópico e, o intercepto superior, que se refere à idade de cristalização do mineral (Schoene, 2014). Dessa forma, é possível interpretar e extrair várias informações geológicas que ocorreram em diversos eventos ao longo do tempo.

2.2.4 Diagrama concordância de Tera-Wasserburg

Outros tipos de diagramas de concordância são utilizados para plotar os dados de U-(Th)-Pb (Searle et al., 2007; Steiger and Wasserburg, 1966; Villeneuve et al., 2000). Especialmente para minerais que contém Pb comum (ou inicial, Pb_0), o diagrama de Tera-Wasserburg (TW) é o mais apropriado, em que as razões $^{238}\text{U}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ são apresentadas respectivamente nos eixos x e y (Tera e Wasserburg, 1972a, b).

Em análises onde as razões $^{238}\text{U}/^{206}\text{Pb}^*$ e $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ (corrigidas para Pb comum) são plotadas em um diagrama de TW, a interpretação é igual ao diagrama de Wetherhill (Figura 2.2). Em casos em que as amostras que contém Pb comum, a verdadeira idade será apresentada no intercepto inferior da concórdia a partir de uma linha de regressão formada pelas amostras no diagrama, e o intercepto com o eixo $^{207}\text{Pb}/^{206}\text{Pb}$ irá representar a composição de Pb inicial no mineral analisado (Figura 2.2). O método de representação dos dados no diagrama de TW, entretanto, pode ser comprometido se uma amostra analisada tiver se submetido a eventos de perda de Pb ou apresentar porções do mineral com idades distintas (Schoene 2014).

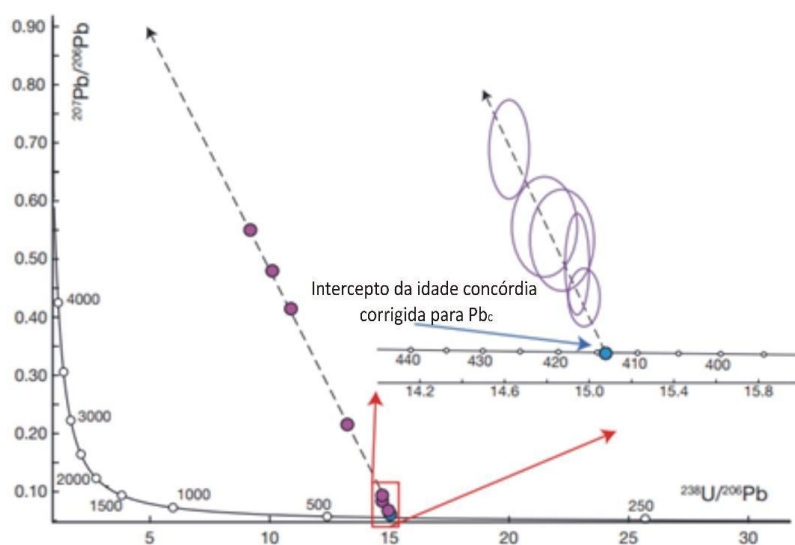


Figura 2.2: Diagrama de Tera-Wasserburg, mostrando a discordância causada pelo Pb comum inicial, o que resulta em uma linha que intercepta o eixo $^{238}\text{U}/^{206}\text{Pb}$ que mostra a idade de cristalização do mineral (extraído e modificado de Schoene et al., 2014).

2.2.5 Mecanismos de difusão de Pb

Alguns minerais acessórios apresentam baixa solubilidade em processos de fusão da crosta, podendo migrar da rocha de origem através de uma fração do *melt*. Esse processo permite investigar as informações da fonte que os originou a partir de análises dos elementos traços e de registros nos minerais, como zoneamento isotópico (Cherniak, 1993). Entretanto, para investigar e restringir o histórico dos processos de temperatura e tempo, é necessário interpretar os dados e parâmetros de difusão de Pb para estabelecer de forma precisa a temperatura de fechamento do mineral (Cherniak, 1993; Dodson, 1973).

Minerais que apresentam elevadas concentrações de U podem sofrer processos significativos de perda de Pb por difusão em temperaturas baixas/médias da crosta, mas

que permanecem retidos próximo a superfície terrestre. Esses minerais apresentam um elevado potencial como termocronômetros de U-Pb, pois associados à temperatura e o volume da difusão de Pb da estrutura cristalina, permitem interpretar as condições de tempo e temperatura vivenciadas pelo mineral durante um evento geológico (Cherniak, 1993; Cherniak and Watson, 2000, 2001; Cherniak et al., 1991).

A perda de Pb é um processo comum de ocorrer em titanitas e monazitas, assim como em zircões, conforme publicado em alguns estudos. Minerais metamíticos e fraturados podem ter passado por eventual perda de Pb, principalmente se estiverem retidos próximos à superfície da crosta por uma longa escala de tempo (Corfu et al., 1994). Neste contexto, pode haver a migração de Pb para fora do mineral devido à percolação de fluidos com baixas temperaturas (Pidgeon et al., 1996), alteração química de corpos metamíticos (Krogh and Davis 1975) ou aquecimento e recristalização de estruturas metamíticas durante um metamorfismo progressivo (Gebauer and Grünenfelder 1976). A migração do Pb está associada à temperatura, na qual em altas temperaturas, o Pb tende a migrar da estrutura cristalina rapidamente por difusão. Na medida em que a temperatura decresce, a perda de Pb do sistema cristalino também tende a diminuir. Algumas idades aparentes, apresentadas por minerais que tiveram a abertura do seu sistema, representam o momento em que cessou a difusão de Pb do mineral (Cherniack et al., 1991; Cherniack et al., 1993; Cherniack et al., 2004).

2.2.6 Temperatura de fechamento do sistema U-(Th)-Pb

De acordo com alguns estudos realizados sobre a cinética da difusão de Pb (Cherniak, 1993; Cherniak and Watson, 2000, 2001; Cherniak et al., 1991), foi determinada a temperatura de fechamento nominal (T_c ; Dodson, 1973, 1986) para alguns minerais, como, apatita em ($T_c=450-550^\circ\text{C}$), rutilo ($T_c=400-500^\circ\text{C}$) e titanita ($T_c=550-650^\circ\text{C}$). Devido a essa temperatura de fechamento moderada a alta desses minerais, é possível identificar o resfriamento de rochas que passaram por processos metamórficos e a exumação da crosta inferior à média durante bilhões de anos. A temperatura de fechamento pode ser encontrada a partir da fórmula apresentada por Dodson (1973), em que R representa a constante dos gases, dT/dt caracteriza a razão de resfriamento, A é um fator geométrico e a é o raio da difusão efetiva:

$$T_c = \frac{E_A/R}{\ln\left(\frac{ART_c^2(D_0/a^2)}{E_A(dT/dt)}\right)} \quad (D)$$

A temperatura de fechamento representa o momento em que cessou a difusão de Pb do mineral durante o período de resfriamento. Segundo estudos realizados por Cherniak (1993), foi encontrada uma temperatura de fechamento em torno de 600-800°C para titanitas. Esse valor pode representar situações onde esse mineral foi aquecido suficientemente a ponto de restaurar o estrago de radiações acumuladas ou quando ocorreu um resfriamento lento após passar por processos com altas temperaturas. Em casos onde a temperatura de aquecimento não é suficientemente alta para reestruturar o cristal, a migração de Pb para o ambiente pode ser maior durante o processo de resfriamento, o que resultará em uma menor temperatura de fechamento. É importante considerar que, para calcular a temperatura de fechamento, alguns fatores devem ser avaliados, principalmente em relação a titanitas metamictizadas. No processo de resfriamento deste mineral, nas condições de tempo e temperatura de aquecimento, não pode ocorrer uma significativa reestruturação do mineral alterado (Cherniak, 1993). Isso é afirmado, pois em titanitas é comum a recristalização desses minerais em determinadas situações de aquecimento, em que, neste caso, o sistema será resetado e a perda de Pb será desconsiderada, comprometendo a análise da temperatura de fechamento.

Outras descobertas acerca do estudo da temperatura de fechamento foram apresentadas, relacionando diferentes sistemas geocronológicos que passaram por um mesmo histórico termal ou analisando distintos históricos termais em um determinado sistema. Em relação ao sistema isotópico de U-Pb em monazitas, esses estudos exibiram valores de Tc de 600°C (Köppel and Grünenfelder, 1975), 530°C (Wagner et al., 1977), e 720°-750°C (Copeland et al., 1988). Smith and Giletti (1997) determinaram um valor de 620°C de acordo com estudo feito anteriormente por Suziki et al., (1994), e um valor bem próximo de 680°C. Estudos mais recentes (Gardés et al., 2006; Cherniak et al., 2004) apresentaram uma alta temperatura de fechamento para monazitas em torno de 900°C, resultado de uma baixa taxa de perda de Pb devido à baixa difusão deste elemento. Isto pode ser explicado pelo fato do elemento Pb possuir um local específico na estrutura cristalina da monazita, o que dificulta a baixa tendência deste elemento ser removido e escapar pelo processo de perda de Pb (Nasdala et al., 2020).

Entretanto, na presença de um fluido aquoso ou *melt*, o sistema isotópico da monazita pode ser comprometido. Este mineral pode se recristalizar a partir de processos de dissolução e precipitação durante a interação com fluidos, o que pode originar uma monazita com características química e isotópicas distintas da fase relíctica. Esse processo pode afetar mais a sistemática U-(Th)-Pb em relação ao mecanismo de perda de

Pb por difusão e está associado com a composição do fluido e a temperatura (Seydoux-Guillaume et al., 2002).

2.2.7 Entrada de Pb comum no sistema U-Pb

O processo de incorporação de Pb comum no sistema se refere ao chumbo que é não radiogênico, ou seja, não provém do decaimento do urânio *in-situ*. Ele pode ter sido incorporado ao mineral por meio de impurezas de chumbo que entraram durante a sua cristalização, sendo considerado chumbo comum inicial (Poupeau and Rivera et al., 1985).

Para compreender melhor o processo de entrada de Pb_c nas titanitas, são destacadas as seguintes regras propostas por Goldschmidt: (1) Pb⁺² substitui facilmente o Ca⁺² presente na estrutura cristalina do mineral, mesmo que a difusão de Pb seja lenta, e (2) a maioria do Pb_c pode ter sido incorporado no momento de sua cristalização, embora também seja necessário considerar a existência de Pb⁴⁺ que é um elemento provável a ser agregado na estrutura do mineral devido ao seu raio atômico (Kramers et al., 2009).

Devido a essas características, as análises dos dados isotópicos das titanitas necessitam de uma maior cautela na avaliação do teor e proporção do Pb_c, com o intuito de realizar uma correção precisa ou utilizar método de regressão linear a partir da ancoragem no valor de Pb comum inicial (e.g. Stacey and Kramers, 1975; Gibson and Ireland, 1996).

2.3 O sistema isotópico Sm-Nd

2.3.1 Interpretação das razões Sm-Nd e os reservatórios terrestres

O Sm e o Nd são elementos terras raras muito utilizados na geoquímica isotópica. Esta utilização ocorre devido ao fato do ¹⁴⁷Sm ser radioativo e decair para ¹⁴³Nd a partir de emissão de partículas alfa ($\lambda = 6.54 \times 10^{-12} \text{anos}^{-1}$). Na natureza, o Sm apresenta sete isótopos de ocorrência natural, dos quais apenas o ¹⁴⁷Sm, ¹⁴⁸Sm e ¹⁴⁹Sm são radioativos. Entretanto, como o ¹⁴⁷Sm apresenta um tempo de meia-vida relativamente curto (106 Ga), é possível medir as pequenas diferenças na abundâncias de ¹⁴³Nd ao longo de milhões de anos. Por outro lado, o ¹⁴⁸Sm e o ¹⁴⁹Sm apresentam meia-vidas muito longas, não possibilitando a análise de variações nos isótopos-filho ¹⁴⁴Nd e ¹⁴⁵Nd, respectivamente, na escala de tempo geológico (Dickin 2005).

Os elementos Sm e Nd fazem parte dos lantanídeos. Como apresentam a mesma valência (carga +3) e raios iônico similares (0.96 a 1.00 Å), esses elementos podem ser considerados isoquímicos. Assim, a variação da razão Sm/Nd não é muito distinta e não

ultrapassa o limite de 0.1 a 0.54 nos minerais e nas rochas (Sato 1998). Nessas condições, o Sm e o Nd não se difundem com facilidade no estado sólido, ou seja, em um processo metamórfico, pode gerar uma redistribuição desses elementos em fases minerais neoformadas, porém o sistema de rocha total mantém fechado (sem migração dos ETR) (Sato, 1998).

Entretanto, em processos de fracionamento magmáticos, a concentração desses elementos tende a aumentar e a razão Sm/Nd tende a diminuir. Como o Nd possui uma concentração maior que o Sm em rochas crustais, a razão Sm/Nd é menor em relação as rochas do manto superior (Dickin, 2005).

Estudos realizados por DePaolo e Wasserburg (1976a) em rochas ígneas terrestres apontaram que a razão inicial de $^{143}\text{Nd}/^{144}\text{Nd}$ de plútons Arqueanos eram consistentes com a evolução do reservatório uniforme condrítico (CHUR) analisado a partir de meteoritos. Como o ^{147}Sm decai para ^{143}Nd , a razão $^{143}\text{Nd}/^{144}\text{Nd}$ tende a aumentar. Esse fato pode ser apresentado em um modelo de evolução da idade da Terra (4.6 Ga) associado ao estudo de rochas terrestres e desses meteoritos (Jacobsen and Wasserburg 1980; DePaolo and Wasserburg 1976a).

Os dados obtidos a partir desses meteoritos condríticos apresentam uma razão $^{143}\text{Nd}/^{144}\text{Nd}$ primordial de 0.50685 ± 0.00008 (Wasserburg et al., 1981). Essa razão pode ser compreendida como a razão obtida pela Terra durante sua origem e antes dos eventos de diferenciação de núcleo, manto e crosta. Assim, a Terra e os meteoritos condríticos caracterizam um modelo em que a evolução isotópica do Nd e a razão Sm/Nd são iguais (Hamilton et al., 1983).

Entretanto, analisando um processo de diferenciação entre o manto e a crosta, podemos considerar que existem reservatórios com razões Sm/Nd distintas. Ou seja, em ambientes crustais, os processos que envolveram a formação de magmas mantélicos para formação da crosta continental foram contemplados por eventos de fracionamento de Sm e Nd. Neste contexto, a concentração de Nd na crosta é maior do que o manto, em que este é empobrecido em Nd em comparação ao Sm. Assim, baseado neste modelo, os reservatórios mantélicos empobrecidos demonstram valores da razão $^{143}\text{Nd}/^{144}\text{Nd}$ maior que o reservatório condrítico (CHUR) (Dickin, 2005).

2.3.2 A sistemática de decaimento Sm-Nd

O processo de decaimento do ^{146}Sm e ^{147}Sm para os isótopos-filho ^{142}Nd e ^{143}Nd , respectivamente, ocorre a partir da liberação de uma partícula alfa retida no núcleo

atômico. Para calcular a idade a partir da razão $^{147}\text{Sm}/^{143}\text{Nd}$, é utilizada a equação de decaimento radioativo padrão (Equação E), no qual “p” remete ao tempo presente, λ a constante de decaimento para o ^{147}Sm , “0” o momento em que $t=0$ e “t” representa o tempo:

$$\left(^{143}\text{Nd}/^{144}\text{Nd} \right)_p = \left(^{143}\text{Nd}/^{144}\text{Nd} \right)_0 + \left(^{147}\text{Sm}/^{144}\text{Nd} \right)_p \times (e^{\lambda t} - 1) \quad (\text{E})$$

É importante ressaltar que, nesta equação, para dois ou mais materiais originados no mesmo tempo e com o mesmo teor isotópico de Nd, por exemplo, vários outros minerais se formam rapidamente a partir de uma lava uniforme, o que permite plotar as razões calculadas de $^{143}\text{Nd}/^{144}\text{Nd}$ e $^{147}\text{Sm}/^{144}\text{Nd}$. Consequentemente, é formada uma linha, chamada de isócrona, com a inclinação igual a $e^{\lambda t-1}$ e o intercepto no eixo y representando a razão $^{143}\text{Nd}/^{144}\text{Nd}$ no momento de cristalização dos minerais (Carlson, 2013).

2.3.3 O estudo da geoquímica e cosmoquímica do Sm-Nd

O termo elementos “refratários litófilos” é utilizado para descrever o Sm e o Nd, assim como todos os outros elementos terras raras. Como ambos os elementos apresentam alta temperatura de condensação (Nd=1,602 °C, Sm=1,590 °C; Lodders, 2003) de um gás de composição solar, eles são considerados elementos refratários. Após a formação do Sol, ocorreu o resfriamento da nébula solar gasosa e, consequentemente, o Sm e Nd se condensaram primeiramente em partículas sólidas, junto a outros elementos. Neste contexto, os processos de condensação ou evaporação não são capazes de fracionar o Sm e o Nd de um para o outro, pois esses elementos apresentam temperaturas de condensação aproximadas. Além disso, como o Sm e o Nd são menos solúveis em *melts*/sólidos de ferro (siderófilos) ou de sulfetos (calcófilos) comparados aos de silicatos, eles são caracterizados como elementos litófilos (Carlson, 2013).

Como os ETR são considerados “refratários litófilos”, é possível observar que em vários tipos de meteoritos primitivos, que possuem a química baseada na volatilidade e na separação de metal do silicato, esses elementos exibem um padrão com variação estreita associado à abundância relativa de ETR e uma pequena variação nas razões de Sm-Nd (Jacobsen and Wasserburg 1980; Boyet and Carlson 2007; Bouvier et al., 2008). Devido a essas características, é possível analisar a abundância dos elementos refratários litófilos das massas silicáticas da Terra a partir dos meteoritos primitivos (McDonoug and Sun 1995; Palm and O’Neil 2003). Para os meteoritos primitivos/sistema solar, é

apresentada a razão de $^{147}\text{Sm}/^{144}\text{Nd} = 0.1960 \pm 0.0004$ e $^{143}\text{Nd}/^{144}\text{Nd} = 0.512630 \pm 11$ (Bouvier et al., 2008).

Os eventos que demonstram um elevado potencial para separar o Sm do Nd são os de fusão parcial e cristalização fracionada. O que representa a capacidade de os minerais fracionar os elementos é o coeficiente de partição, em que é a razão da concentração de um elemento no mineral comparado a concentração do mesmo elemento no *melt* com o qual o mineral está em equilíbrio químico. De um modo geral, a tendência do coeficiente de partição é ser baixo para os ETR nos minerais silicáticos, ou seja, são considerados incompatíveis. Dessa forma, no processo de fusão parcial, esses elementos se deslocam para o *melt* e ficam retidos no líquido residual durante a cristalização fracionada (Carlson 2013).

2.3.4 Notação ϵNd

Uma outra ferramenta muito utilizada nos estudos geoquímicos e geocronológicos é a notação ϵNd (Dickin, 1995) (Equação F). Esse indicador petrogenético apresenta uma relação entre os valores das razões de $^{143}\text{Nd}/^{144}\text{Nd}$ da amostra analisada e do reservatório condritico, podendo ser definida da seguinte maneira:

$$\epsilon\text{Nd} = \left[\frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}} - (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}}{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}} \right] \times 10000 \quad (\text{F})$$

Para interpretar o significado dessa notação, podemos afirmar que o ϵNd é positivo se a razão de $^{143}\text{Nd}/^{144}\text{Nd}$ da rocha estudada for maior que os valores do reservatório condritico. Isso indica que a fonte deste magma é proveniente de um manto empobrecido e a razão Sm/Nd é maior que a do condrito. Se o valor de ϵNd for igual a zero, podemos concluir que a razão $^{143}\text{Nd}/^{144}\text{Nd}$ é igual a do condrito (Dickin, 2005). Em outro contexto, se o valor de ϵNd for negativo, isso indica que a rocha fonte que deu origem ao magma possuía uma razão $^{143}\text{Nd}/^{144}\text{Nd}$ inferior à do condrito, representando um magma de origem crustal (Bertotti, 2005).

CAPÍTULO 3

MATERIAIS E MÉTODOS

3.1 Revisão bibliográfica

Primeiramente, foram feitas várias pesquisas em artigos relacionados à geocronologia U-Pb, aos estudos dos traçadores isotópicos de Sm-Nd e às análises de elementos traços em titanitas e monazitas caracterizadas como materiais de referência para o método de LA-ICP-MS. Foram consultadas as melhores técnicas empregadas para se caracterizar um material de referência a partir de análises de alta resolução espacial (SHRIMP, LA-ICP-MS) e alta precisão (ID-TIMS). Além disso, a técnica de abrasão química e tratamento térmico realizada em zircões também foi realizada nesta pesquisa, com o objetivo de encontrar os valores adequados das concentrações químicas e temperatura para recuperar a estrutura cristalina dos grãos de titanita e desenvolver um material de referência mais translúcido/cristalino e homogêneo, a partir da remoção de áreas danificadas e imperfeitas. Por último, para realizar o estudo de caso feito durante o estágio internacional na Universidade de Stellenbosch, foram investigados vários artigos que analisaram a composição isotópica de U-Pb, Sm-Nd e Sr-Sr em minerais acessórios associados à sua composição química para interpretar processos metamórficos em rochas que experienciaram interação com fluidos.

3.2 Preparação das amostras e métodos analíticos

Para as análises das titanitas Khan River e Bear Lake, foram selecionados vários fragmentos, provenientes de megacristais, fraturados em tamanhos de 0.1 e 0.4 cm. Para a monazita Vermilion, os maiores grãos, com tamanho entre 0.05 e 0.1 cm, foram selecionados. Os fragmentos das titanitas e grãos das monazitas mais translúcidos e homogêneos (livre de fraturas e inclusões) foram separados cuidadosamente.

Para realizar uma caracterização ideal dos materiais de referência de titanita e monazita, foram utilizadas as seguintes técnicas analíticas em distintos laboratórios: ID-TIMS, SHRIMP, LA-ICP-MS (*quadrupole-Q*, *singlecollector-SF* e *multicollector-MC*), solução-MC-ICP-MS e microsonda eletrônica. As amostras de titanitas passaram por tratamentos térmicos e de abrasão química. Ambas as amostras de titanitas e monazitas foram preparadas em um *mount* acrílico com 2,5 cm de diâmetro preenchido por uma resina de baixo Pb com endurecedor (marca Specifix). Para a exposição dos fragmentos, a pastilha foi lixada suavemente e depois polida para adquirir uma superfície lisa e ideal para imageamento via *backscatter* (BSE) e para serem realizadas as análises químicas e isotópicas. O estudo de caso realizado em amostras de metapelitos do Cinturão Limpopo foi feito utilizando-se as técnicas analíticas empregadas na caracterização dos materiais

de referência desta tese, como forma de aplicar a metodologia desenvolvida em análises em lâmina delgada e nos minerais acessórios amostrados. As técnicas analíticas utilizadas neste trabalho e o local onde as análises foram realizadas estão resumidos na Tabela 3.1. Os detalhes e maiores informações sobre os procedimentos analíticos para a caracterização dos materiais de referência podem ser encontrados no item Metodologias no Capítulo 4 para as titanitas e no Capítulo 5 para as monazitas e, para o estudo de caso nos metapelitos do Cinturão Limpopo, no Capítulo 6.

Tabela 3.1: Resumo das técnicas analíticas utilizadas e do local das análises

	Tratamento químico	Imageamento	Composição química			Geocronologia U-Pb						Composição isotópica de Sm-Nd			
Técnica analítica	Abrasão química*	MEV - BSE	EPMA	LA-SF-ICP-MS	LA-Q-ICP-MS	ID-TIMS		SHRIMP	LA-SF-ICP-MS	LA-MC-ICP-MS	LA-Q-ICP-MS	ID-TIMS	Solução MC-ICP-MS	LA-MC-ICP-MS	
Local das análises	UFOP	UFOP/ SU	UFOP/ Minnesota	UnB/ UFOP	SKLLE/ SU	Oslo	Toronto	ANU	UnB/ UFOP	UFOP	SKLLE/ Portsmouth	UnB	UnB	UFOP	SKLLE

*O procedimento de abrasão química foi realizado somente nas titanitas

3.2.1 *Abrasão química*

Nesta etapa, foram realizados vários experimentos com o intuito de adquirir fragmentos mais homogêneos e translúcidos após o tratamento térmico e a abrasão química, a partir da remoção das áreas danificadas/fraturadas. Foram destacados os testes que apresentaram resultados mais satisfatórios para encontrar as concentrações adequadas dos ácidos utilizados. Após a quebra dos cristais das titanitas Khan River e Bear Lake, os fragmentos selecionados foram colocados em um cadinho de porcelana em uma mufla e, em seguida, submetidos a um tratamento térmico em uma temperatura de 850°C durante 60 h. As amostras foram armazenadas em tubos de Teflon, junto com os ácidos nítrico (HNO_3) e fluorídrico (HF), para serem digeridas no micro-ondas ETHOS 1 de 1500W a 120 bar. Para a obtenção de um bom resultado, foram realizados três experimentos:

Primeiramente, as amostras foram analisadas em um procedimento com dois estágios: (1) 10 minutos em 175 °C e (2) 10 minutos em 60 °C. As concentrações utilizadas foram de 0,1 ml de HF e 3,95ml 1:1 HNO_3 + água Milli-Q (H_2O). Após o fim da digestão das análises nestes parâmetros analíticos, todos os fragmentos foram dissolvidos.

Em seguida, no segundo experimento, os parâmetros analíticos e as condições de tempo e temperatura foram mantidos, porém utilizou-se uma concentração menor de HF (0,05 ml de HF e 3,975ml 1:1 HNO_3 + água Milli-Q (H_2O)). Após a abrasão química, os fragmentos foram limpos com ácido clorídrico (HCl) e água ultrapura Mili-Q e, em seguida, colocados em uma centrífuga. Neste teste, os fragmentos apresentaram uma borda amarelada de corrosão, porém o interior dos cristais permaneceu preservado. Esse procedimento de limpeza foi repetido por cinco etapas. Por último, utilizou-se água deionizada para lavar os cristais tratados. As amostras foram colocadas para secar em uma estufa a 60 °C por um dia.

No terceiro experimento, os parâmetros analíticos de tempo e temperatura foram alterados para (1) 10 minutos em 90 °C e (2) 25 minutos em 60 °C. Porém, manteve-se a mesma concentração de 0,05 ml de HF e 3,975ml 1:1 HNO_3 + água Milli-Q (H_2O). Por fim, os fragmentos permaneceram bem preservados e homogêneos e as porções mais danificadas, fraturadas e heterogêneas foram removidas, restando porções mais uniformes, com uma coloração amarelada e mais translúcida. Os cristais foram limpos em repetidas sessões com água Milli-Q, sem o uso de HCl, pois este ácido também causou

uma pequena corrosão nas titanitas. Estas ficaram em uma estufa a 60°C para secarem durante um dia.

3.2.2 *Imageamento de microscopia eletrônica e composição de elementos maiores*

Com o intuito de analisar e caracterizar a homogeneidade dos fragmentos dos potenciais materiais de referência de titanitas Khan River e Bear Lake e grãos da monazita Vermilion amostrados, foi realizado o imageamento por elétrons retroespalhados (BSE – *backscattered electrons*). Esse método permite a observação de fraturas, porções zoneadas e não uniformes que simbolizam as variações composicionais internas. A partir de uma emissão de feixe de elétrons com alta energia, é possível gerar imagens tridimensionais com elevada resolução da superfície. Quando este feixe principal incide na amostra, são gerados sinais distintos emitidos por elétrons secundários ou retroespalhados. Estes sinais são captados por detectores, permitindo a obtenção de imagens. Além disso, a emissão de raios-X medida permite a aquisição de dados de microanálise elementar (EDS) (e.g. Goldstein et al., 1992). O uso desta técnica é essencial para interpretar a homogeneidade isotópica e composicional das amostras em estudo, no qual as variações internas dos minerais podem ser investigadas a partir de diferentes tons em escala de cinza nas imagens obtidas.

As imagens de *backscatter* (BSE) das titanitas (Khan River e Bear Lake) e monazitas (Vermilion) foram adquiridas no Laboratório de Microanálises da Universidade Federal de Ouro Preto (UFOP). O equipamento utilizado foi o microscópio *scanner* de elétrons JSM-6510 JEOL, operando a uma voltagem de 15 kV e corrente de 20nA.

Para o estudo petrográfico em lâmina delgada dos metapelitos do Cinturão Limpopo, o imageamento no microcópio eletrônico e a composição de elementos maiores foram realizadas na *Electron Microscopy Unit* da *Central Analytical Facility* na Universidade de Stellenbosch. As imagens de BSE e a composição de elementos maiores foram realizadas no microscópio eletrônico de varredura Zeiss EVO SEM equipado com o detector *Oxford Instruments* × Max 20 mm², que é um espectrômetro dispersivo de raio-X. Os dados foram adquiridos por meio do *software* Oxford INCA. As imagens de catodoluminescência em apatitas catadas e montadas no *mount* foi adquirida no Zeiss Merlin FE-SEM. A imagens de BSE nas monazitas catadas e montadas no *mount* foram obtidas no Laboratório de Microanálises da Universidade Federal de Ouro Preto (UFOP). O microscópio eletrônico de varredura utilizado foi o JSM-6510 JEOL.

3.2.3 *Microsonda Eletrônica*

A microsonda eletrônica é um instrumento analítico não-destrutivo que permite analisar a composição química de pequenas quantidades do material em estudo. A partir da emissão de um feixe de elétrons na amostra, esta emite raios-x com comprimentos de onda específicos de cada elemento, tornando possível obter a concentração do elemento medido (e.g., Goldstein, 2003; Merlet and Llovet, 2012). Esse método permitiu avaliar a composição química dos elementos maiores, a homogeneidade dos minerais de titanita e monazita caracterizados como materiais de referência e investigar as heterogeneidades nas concentrações encontradas em algumas porções das amostras analisadas.

As análises de elementos maiores nas titanitas Khan River e Bear Lake foram obtidas no Laboratório de Microanálises e Microscopia (UFOP), utilizando a microsonda eletrônica JEOL JXA-8230 equipado com cinco sistemas de espectrometria por dispersão de comprimento de onda (WDS). Os parâmetros analíticos empregados na microsonda eletrônica foram configurados em uma voltagem de aceleração 15 kV, intensidade da corrente do feixe de 20 nA e diâmetro do feixe de 10 µm. O pacote de redução dos dados JEOL/EPMA foi utilizado para calibração, correção e quantificação das análises seguindo a metodologia proposta por Carvalho et al., (2022).

As análises de monazita Vermilion foram realizadas em uma microsonda eletrônica JEOL JXA-82000 no laboratório McSwiggen & Associates, Minnessota, EUA. As configurações analíticas empregaram uma voltagem de aceleração 15 kV, intensidade da corrente do feixe de 20 nA e diâmetro do feixe de 10 µm. Os materiais utilizados para analisar os elementos terras raras eram fosfatos de elementos terras raras livres de Pb fornecidos por Astimex (www.astimex.com). O material de referência empregado para medir o Pb foi o NIST SRM-1412 e para analisar o U e o Th foram dois materiais de referência de vidro providenciados por Micro-Analysis Consultants Ltd. (www.macstandards.co.uk).

3.2.4 *Composição de Elementos Traços*

A técnica de aquisição de elementos traços por *Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry* (LA-ICP-MS) tem sido utilizada há mais de trinta anos para analisar materiais naturais e sintéticos. Esta técnica consiste na ablação de uma pequena porção material em estudo por meio de um feixe de *laser*, produzindo um aerossol. Este é transportado por um gás carregador (geralmente He) até o plasma de argônio indutivamente acoplado, no qual o material é excitado e transformado em íons.

Essas partículas são direcionadas para um pequeno feixe dentro do instrumento, no qual cada elemento é separado de acordo com a razão massa/carga pelo espectrômetro de massa e quantificados por um detector (Günther and Hattendorf, 2005; Sylvester and Jackson, 2016).

Para verificar a composição química e interpretar a homogeneidade dos potenciais materiais de referência em estudo, foram utilizados os espectrômetros de massa do tipo monoleitor (LA-SF-ICP-MS) para analisar as titanitas (Khan River e Bear Lake) e monazitas (Vermilion), e do tipo quadrupolo (LA-Q-ICP-MS), para analisar novamente as monazitas. O uso de mais de uma técnica é importante para observar a homogeneidade do mineral e o comportamento das concentrações obtidas a partir de técnicas com diferentes precisões analíticas na caracterização de materiais de referência naturais. Para as amostras de metapelitos do Cinturão Limpopo analisados, os minerais de apatita e granada foram analisados *in situ* via monoleitor setor magnético (SF) ICP-MS e as apatitas e monazitas catadas e montadas no *mount* foram analisadas via setor magnético (SF) ICP-MS e via quadrupolo (Q) ICP-MS, respectivamente.

3.2.4.1 LA-SF-ICP-MS

As análises de composições de elementos traços nas monazitas Vermilion para serem caracterizadas com potenciais materiais de referência foi feita no Laboratório de Estudos Geodinâmicos, Geocronológicos e Ambientais da Universidade de Brasília, Brasil, usando um campo de setor de coletor único de alta resolução Thermo Finnigan Element XR acoplado a um Excimer Iridia de 193 nm (ArF) sistema de ablação a laser. Os resultados foram processados em Iolite 4.0 (Paton et al., 2011) como sinal resolvido no tempo usando o esquema de redução de dados de elementos traços (DRS). A inspeção de sinal individual foi determinada com auxílio do VizualAge (Petrus and Kamber 2012).

As análises de elementos traços da monazita (Vermilion) e das titanitas (Khan River e Bear Lake) e as análises das granadas e apatitas (estudo de caso no Cinturão Limpopo) foram obtidas por meio do equipamento Element II SC-ICP-MS acoplado no sistema a 213 Nd:YAG (CETAC UP-213 nm) de ablação a laser no Laboratório de Geocronologia na Universidade Federal de Ouro Preto (UFOP). A redução dos dados foi processada pelo *software* Glitter (Van Achterbergh et al., 2001; Griffin et al., 2008) e Saturn – Trace Elements (Figueiredo, 2022).

3.2.4.2 LA-Q-ICP-MS

As análises de elementos traços em monazitas (Vermilion) também foram realizadas no *State Key Laboratory of Lithospheric Evolution (SKLLE)*, Instituto de Geologia e Geofísica, Academia de Ciência Chinesa. Os dados foram obtidos usando um Agilent 7500a Q-ICP-MS acoplado a um sistema a laser 193nm ArF excimer (Geolas HD, Lambda Physik, Göttingen, Germany). O *software* interno ICPMSDataCal (Liu et al., 2010) foi utilizado para reduzir os dados.

Os dados de composição química de elementos traços de monazita (metapelitos do Cinturão Limpopo) também foram adquiridos utilizando-se o *laser* Resolution 193nm Excimer da Applied Spectra conectado a um Agilent 8800 QQQ ICP-MS na Central Analytical Facility na Universidade de Stellenbosch. O pacote de *software* de redução de dados LADR da Norris Scientific (Norris et al., 2021) foi utilizado para processamento de dados.

3.2.5 Geocronologia U-Pb por ID-TIMS

Os fragmentos mais translúcidos e livre de inclusões de titanita e monazita foram selecionados e separados para serem datados pela técnica de ID-TIMS, que apresenta elevada precisão analítica. Esse método fornece os valores recomendados de U-Pb para os materiais de referência em estudo. De um modo geral, esta técnica consiste na dissolução das amostras (rocha total ou minerais) dissolvidos em recipientes de Teflon utilizando-se HF ou HCl, no qual as amostras selecionadas são dopadas com uma solução traçadora, em que os elementos U e Pb são separados dos outros elementos usando química de troca iônica (Schoene, 2014). Este processo de separação dos elementos de U e Pb a partir da química de troca iônica tem como objetivo reduzir potenciais interferências de massa antes de iniciar as análises, assim como remover outros elementos que podem comprometer a ionização do U e do Pb nos filamentos. Isso evita que a aquisição do sinal seja afetada e a precisão seja comprometida. O método ID-TIMS, portanto, apresenta resultados com elevada precisão nas razões isotópicas de U-Pb em torno de 0.05% rotineiramente adquiridas nos laboratórios (Schoene, 2014).

Neste estudo, as análises de titanita (Khan River e Bear Lake) e monazita (Vermilion) foram realizadas nos laboratórios da Universidade de Oslo (Noruega) e no Jack Satterly Geochronology Laboratory na Universidade de Toronto (Canadá). Para ambos os potenciais materiais de referência caracterizados, as análises foram feitas nos dois laboratórios para avaliar a homogeneidade e reprodutibilidade dos razões isotópicas de U-Pb adquiridas.

3.2.6 Geocronologia U-Pb por SHRIMP

Outra técnica analítica que possui elevada precisão é a de microsonda iônica. Esse método conhecido como SHRIMP (*Sensitive High-Resolution Ion Microprobe*) forma a base da geocronologia U-Th-Pb SIMS (*Secondary Ionization Mass Spectrometry*) (Compston et al., 1984). Esta técnica permite analisar pequenas porções (<100 μm) de uma amostra para medir composições isotópicas e abundâncias elementares (Andersen and Hinthorne, 1972a, b; Shimizu et al., 1978). Esta técnica possibilita interpretar o contexto petrográfico do mineral em estudo e observar as feições das amostras a partir de técnicas de imageamento. A tecnologia de SIMS é amplamente utilizada e recomendada devido à habilidade em ablar as amostras em um diâmetro de furo pequeno (10 - 40 μm) em profundidades bem rasas (< 4 μm) atingindo a superfície analisada com alta energia no feixe iônico (geralmente O^+ ou O^{2+}) em vácuo (Schoene et al., 2014).

Alíquotas selecionadas criteriosamente das titanitas Khan River e Bear Lake, juntamente com BLR1 e MKCO1, foram moldadas em discos de epóxi, moídas e polidas para expor a seção média dos grãos. O imageamento de elétrons retroespalhados (BSE) foi conduzida usando um SEM Analítico JEOL JSM6610A (microscópio eletrônico de varredura) na Research School of Earth Sciences (RSES), Universidade Nacional Australiana (ANU), Canberra, equipado com um detector de catodoluminescência Robinson (CL). Fotomicrografias de luz refletida e transmitida juntamente com imagens BSE foram preparadas para análise de domínios livres de inclusões ou trincas. As análises isotópicas U-Th-Pb das titanitas Khan River e Bear Lake foram realizadas em uma microsonda de íons de alta resolução sensível (SHRIMP II), um espectrômetro de massa de íons secundários de alta precisão (SIMS), na RSES, ANU. Os procedimentos analíticos são semelhantes aos descritos em Williams (1998 e suas referências) e Ireland e Williams (2003). Cada análise representa seis varreduras através das diferentes massas. Os dados SIMS U-Pb para todos os materiais de referência de titanita (Ling et al., 2022) foram reunidos para verificar os efeitos da matriz na determinação da idade das amostras.

Análises isotópicas U-Th-Pb da monazita Vermilion também foram realizadas na RSES, ANU. Os procedimentos analíticos são semelhantes aos descritos em Williams (1998 e suas referências) e Ireland e Williams (2003). Vários grãos da monazita Vermilion foram selecionados e preparados em um disco de epóxi junto com o material de referência 44069 (Aleinikoff et al., 2006). A imagem de elétrons retroespalhados (BSE) foi conduzida usando um SEM Analítico JEOL JSM6610A (microscópio

eletrônico de varredura; RSES), equipado com um detector Robinson CL (catodoluminescência). Fotomicrografias de luz refletida e transmitida juntamente com imagens BSE foram feitas para investigar porções livres de inclusões ou fraturas. Cada análise representa seis varreduras através das diferentes estações de massa. Os dados foram reduzidos usando a Macro SQUID Excel de Ludwig (2001a) e a Macro ISOPLOT/EX Excel de Ludwig (2001b).

3.2.7 Geocronologia U-Pb por LA-ICP-MS

A geocronologia via LA-ICP-MS vem se tornando uma técnica muito utilizada para aquisição de dados U-Pb em titanita (Kohr 2013). Com o intuito de analisar e caracterizar a homogeneidade dos elementos isotópicos dos potenciais materiais de referência de titanita (Khan River e Bear Lake) e monazita (Vermilion) e das amostras de metapelitos (Cinturão Limpopo) estudados, foram realizadas análises via LA-ICP-MS nos equipamentos quadrupolo (Q), monocolletor (single collector – SC) e multicoletor (multi collector - MC).

Análises geocronológicas de minerais acessórios por meio do LA-ICP-MS fornecem diversas vantagens em relação a outras técnicas de datação, como: baixo custo para realizar as análises U-Pb, alta resolução espacial no diâmetro do furo (20-100µm), rápido processo de aquisição de dados, simples processo de preparação das amostras (Simonetti et al., 2006) e análise de um grande volume de amostras simultaneamente.

O método consiste na emissão de laser na superfície da amostra em estudo, onde o material ablado, formado por aerossóis (vapor, partículas e aglomerados), é transportado para um espectrômetro de massa. Na geocronologia U-Pb, podem ser utilizados laser de comprimento de onda curto no estado sólido (como Nd-YAG) ou de fonte gasosa (ArF ou BrF₅ Excimer). As partículas abladadas são removidas da cela de ablação e então direcionadas para a tocha de plasma por meio de um gás carregador (geralmente são utilizados He e Ar) (Schoene, 2014). Nos estudos de geocronologia U-Pb, são utilizados os equipamentos com analisadores de massa do tipo quadrupolo (Q), e instrumentos com setor magnético mono (SF)- ou multicoletor (MC). Dentre esses métodos, é importante destacar que os equipamentos que contém setor magnético são mais sensíveis e com isso permitem com diâmetros do furo menor comparados com equipamentos do tipo quadrupolo (Schoene, 2014).

Os procedimentos analíticos de ablação a laser ICP-MS e a aquisição de dados de U-Pb geram incertezas associadas aos processos de ablação, transporte e ionização no

plasma. O fracionamento de U e Pb pode ser observado no local de ablação e pode estar vinculado à profundidade do furo (Hergenroder, 2006; Horn et al., 2000; Kosler et al., 2005; Paton et al., 2010), à forma com o laser forma os aerossóis e distribui as partículas (Guillong et al., 2003; Günther and Heinrich, 1999; Günther et al., 1997), e a ionização do plasma associada ao tipo de gás carregador (Guillong and Heinrich, 2007; Günther and Heinrich, 1999; Horn and Günther, 2003). É importante citar que a ablação em materiais com matriz distintas e/ou composições podem comprometer a obtenção de um dado acurado e preciso por afetar a sistemática do fracionamento de U e Pb (Black et al., 2004; Kosler et al., 2005). Considerando esses fatores, a precisão analítica do LA-ICP-MS é em torno de 1 a 2% (Horstwood, 2008; Sylvester, 2008).

3.2.7.1 Geocronologia U-Pb via LA-SF-ICP-MS

As amostras da monazita Vermilion foram investigadas no Laboratório de Estudos Geodinâmicos, Geocronológicos e Ambientais da Universidade de Brasília (UnB). Os fragmentos mais translúcidos e livre de inclusões foram selecionados. O equipamento monoleitor setor magnético de alta resolução ICP-MS Thermo Finnigan Element XR acoplado a um sistema de ablação a laser 193 nm Iridia Excimer (BrF_5) foi utilizado para medir as massas de interesse. O sistema de ablação a laser é equipado com uma câmara de volume duplo Cobalt. O espectrômetro de massa foi ajustado para melhorar a sensibilidade de U e Pb, minimizando a produção de óxido antes de cada sessão analítica. A análise de cada ponto individual foi medida em 10 s de *background* seguido por 20 s de aquisição de amostra. As análises utilizaram um diâmetro de furo de 15 μm , com taxa de repetição de 20 Hz e fluência do laser de $2,0 \text{ J cm}^{-2}$. Os dados brutos foram processados no Iolite 4.0 (Paton et al., 2011) como *time-resolved signal* e a inspeção individual do sinal foi feita com auxílio do VizualAge (Petrus and Kamber 2012). A correção de dados incluiu subtração em branco, correção LIEF usando um modelo exponencial mais linear.

Amostras das titanitas Khan River e Bear Lake selecionadas neste estudo foram analisadas em um ICP-MS Thermo-Finnigan Element II acoplado em um sistema de laser ablation CETAC UV Nd:YAG-213 nm no Laboratório de Geoquímica Isotópica da Universidade Federal de Ouro Preto (UFOP). Os dados foram obtidos em *time-resolved*, *peak jumping* e contagem de pulsos superior a 810 varreduras em massa, com tempo de *background* de 25s e 30s de ablação da amostra. As análises apresentaram um *spot size* de 40 μm , frequência de 10 Hz e uma saída de energia nominal de 30%, correspondendo a uma fluência de laser de $\sim 3,5 \text{ J/cm}^2$. Os dados brutos foram corrigidos *off-line*,

incluindo o fracionamento elementar induzido por laser, discriminação de massa instrumental e fracionamento elementar de Pb/U dependente do tempo. A redução dos dados foi realizada utilizando o software Glitter (Van Achterbergh et al., 2001; Griffin et al., 2008) e uma planilha Excel (Gerdes and Zeh 2006, 2009). Todas as idades são relatadas como 2 sigma (2s).

3.2.7.2 Geocronologia U-Pb via LA-MC-ICP-MS

Investigações geocronológicas realizadas por meio da técnica ICP-MS do tipo multicoletor apresentam maior acurácia e precisão das análises (em torno de 1% da idade). O desenvolvimento do equipamento do tipo MC-ICP-MS permitiu uma melhoria nas pesquisas associadas às análises de isótopos estáveis e radiogênicos. Isso se deve ao fato de que esta técnica analítica possui uma alta eficiência de ionização advinda da fonte ICP, além da capacidade de medir todas as massas simultaneamente e de modo contínuo (Simonetti et al., 2005). Com o intuito de aprimorar essa técnica, foi elaborado um conjunto de capacitores com contadores de íon modificados adaptados para aquisição de dados U-Pb (Simonetti et al., 2005; Paul et al., 2005).

As análises de U-Pb das titanitas Khan River e Bear Lake, da monazita Vermilion e das amostras de monazita e apatita dos metapelitos (Cinturão Limpopo) foram realizadas no multicoletor setor magnético (MC) ICP-MS Thermo Scientific Neptune Plus, acoplado a um sistema de laser de 193 nm Photon-Machine com cela de ablação HelEx, no Laboratório de Geoquímica Isotópica da Universidade Federal de Ouro Preto. Todas as massas relevantes foram analisadas simultaneamente: ^{202}Hg , ^{204}Pb + ^{204}Hg , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th and ^{238}U . A composição de U-Pb de cada furo a laser foi medida durante 60s de ablação com diâmetro do furo de 40 μm , frequência de 5Hz e fluência de 6 J/cm^2 . Todas as idades foram reportadas com incertezas em 2-sigma (2s). Os dados brutos foram processados no *software* Saturn (Silva et al., 2023).

3.2.7.3 Datação U-Pb via LA-Q-ICP-MS

O equipamento Agilent 7500a Q-ICP-MS acoplado a um sistema de laser excimer ArF de 193 nm (Geolas HD, Lambda Physik, Göttingen, Alemanha) foi utilizado para determinar as idades U-Pb da monazita Vermilion no State Key Laboratory of Lithospheric Evolution (SKLLE), China. Os grãos de monazitas analisados neste estudo no SKLLE diferem dos cristais de monazita selecionados e analisados nos demais laboratórios. A densidade de energia (fluência) nos pontos de ablação foi de $\sim 2.5 \text{ J cm}^{-2}$

e os diâmetros do feixe de laser foram de 24 μm a uma taxa de repetição de 3 Hz. Todas as razões isotópicas $^{207}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{238}\text{U}$ e $^{207}\text{Pb}/^{235}\text{U}$ medidas foram processadas usando o software ICPMSDataCal (Liu et al., 2010). As idades U-Pb e Th-Pb de cada ponto analisado e as idades de médias ponderadas foram calculadas usando o pacote de software ISOPLLOT 3.0 (Ludwig, 2003).

As análises da U-Pb da monazita Vermilion também foram realizadas na Universidade de Portsmouth – Inglaterra, utilizando o equipamento Jena PlasmaQuant Elite ICP-MS acoplado em um *laser* ASI RESolution 193 nm ArF excimer. O diâmetro do spot utilizado foi de 5 μm , com uma fluência de 2.0 J cm^{-2} e uma frequência de 1 Hz.

3.2.8 Composição isotópica de Sm-Nd

As análises das concentrações isotópicas de Sm-Nd podem ser utilizadas para investigar o tipo de fluido formador do mineral, o *melt* ou as fontes dos magmas que originaram a rocha (Hammerli et al., 2014). A utilização de diversas técnicas para investigar o comportamento das razões Sm-Nd e Nd-Nd contribui na certificação dos dados analisados e na avaliação reprodutibilidade dos dados. Para análises de Sm-Nd, é necessária uma determinação precisa e acurada das razões $^{143}\text{Nd}/^{144}\text{Nd}$ e $^{147}\text{Sm}/^{144}\text{Nd}$ para determinar uma razão $^{143}\text{Nd}/^{144}\text{Nd}$ inicial precisa. Entretanto, existem alguns fatores que devem ser contornados para medir a razão $^{143}\text{Nd}/^{144}\text{Nd}$, no qual é preciso realizar a correção de interferência isobárica das massas ^{144}Sm em ^{144}Nd . E, para determinar a razão $^{147}\text{Sm}/^{144}\text{Nd}$ acurada, é preciso realizar a correção do fracionamento elementar (Liu et al., 2012). Neste estudo, empregamos as técnicas de solução e *laser ablation* ICP-MS. A descrição completa dos parâmetros analíticos utilizados para caracterização dos potenciais materiais de referência está apresentada no Capítulo 4 para as titanitas, no Capítulo 5 para as monazitas e, para as análises do metapelitos do Cinturão Limpopo, no Capítulo 6 no subitem Metodologias.

3.2.8.1 Solução isotópica de Nd e Sm-Nd em ICP-MS

Amostras de titanitas Khan River e Bear Lake foram analisadas no Centro de Pesquisas Geocronológicas, Universidade de São Paulo (CPGeo-USP). As razões isotópicas de Nd foram obtidas por um espectrômetro de massa Neptune Plus Thermo Scientific MC-ICP-MS. Os procedimentos químicos foram realizados em um laboratório limpo classe ISO-7, equipado com capelas de fluxo laminar classe ISO-5. Todos os reagentes utilizados foram purificados. Uma amostra de 10 mg de titanita foi pesada em

um béquer de PTFE previamente limpo. A dissolução das titanitas foi realizada utilizando $\text{HNO}_3 + \text{HF}$ e HCl em um béquer de PTFE, à temperatura de 100 °C em uma *clean box*. Após a reação, a amostra foi evaporada até a secura, e 2 mL de HNO_3 1M foram adicionados ao resíduo e a solução estava pronta para separação cromatográfica. As razões isotópicas de $^{143}\text{Nd}/^{144}\text{Nd}$ foram normalizadas com os valores de $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ (De Paolo, 1981). As incertezas são apresentadas em 2s.

Outro lote de amostras de titanita foi analisado por solução MC-ICP-MS em um equipamento Thermo Scientific Neptune MC-ICP-MS em SKLLE. Os procedimentos químicos foram realizados em bancadas especiais classe 100 dentro de um laboratório limpo classe 1000. Alíquotas de titanita foram pesadas e a digestão foi realizada com uma mistura de $\text{HF-HNO}_3\text{-HClO}_4$ concentrado (2ml – 1ml – 0,2 ml) à temperatura de 120 °C por 1 semana. Após a reação, a cápsula foi aberta para evaporar o HClO_4 . Adicionou-se 1 ml de 6M HCl ao resíduo e depois secou-se. Este passo foi repetido duas vezes. Após o resfriamento, o resíduo foi dissolvido em 5 ml de 3M HCl e então posicionado em uma placa quente a ~100 °C durante a noite antes da separação química. Os procedimentos cromatográficos para separar os ETR e concentrar Sm e Nd seguiram os procedimentos descritos em detalhes em Yang et al. (2011). A razão $^{146}\text{Nd}/^{144}\text{Nd}$ de 0,7219 (O'Nions et al., 1977) e a lei exponencial (Russel et al., 1978) foram aplicadas para corrigir o viés de massa.

Análises dos anfibólios provenientes das amostras dos metapelitos (Cinturão Limpopo) foram realizadas no Laboratório de Estudos Geodinâmicos, Geocronólogos e Ambientais, Universidade de Brasília – UnB. Os anfibólios foram separados em duas alíquotas distintas de acordo com cada amostra. Os processos de separação e métodos analíticos aplicados foram reportados por Gioia and Pimentel (2000). As amostras foram lavadas e as partes desgastadas foram removidas, depois trituradas e pulverizadas até obter um pó de tamanho fino. Aproximadamente 10 ng de pó de anfibólio foram misturados com solução rápida $^{149}\text{Sm}/^{150}\text{Nd}$ e dissolvidos em cápsulas Savillex. As amostras utilizadas para extração de Sm-Nd foram submetidas a técnicas convencionais de troca catiônica baseadas em colunas de Teflon® contendo resina LN-Spec (HDEHP - ácido di-(2-etilhexil) fosfórico suportado por pó de politetrafluoretileno). As amostras foram analisadas em solução em um Thermo-Fisher Neptune MC-ICP-MS.

3.2.8.2 Composição isotópica de Sm-Nd via LA-MC-ICP-MS

As composições isotópicas de Sm-Nd dos potenciais materiais de referência de titanita (Khan River e Bear Lake) e monazita (Vermilion) foram obtidas no equipamento Thermo Finnigan Neptune Plus LA-MC-ICP-MS, acoplado a um sistema de ablação a laser de 193nm HelEx Photon Machine no Laboratório de Geoquímica Isotópica na UFOP. As análises foram realizadas com diâmetro do furo de 60 μm , frequência de 5 Hz e fluência de 6J/cm². A redução dos dados foi processada *off-line* utilizando uma planilha Excel *in-house* seguindo os procedimentos definidos por Gonçalves et al. (2018). Os dados obtidos foram corrigidos para *background*, interferência isobárica e viés de massa.

As amostras de apatita e monazita dos metapelitos do Cinturão Limpopo foram também analisadas no Laboratório de Geoquímica Isotópica na UFOP. As condições analíticas seguiram os mesmos protocolos mencionadas acima.

Os mesmos fragmentos das titanitas Khan River e Bear Lake analisados anteriormente e grãos distintos de monazita Vermilion foram analisados em SKLLE. As composições isotópicas de Sm-Nd foram obtidas utilizando o equipamento Neptune Plus MC-ICP-MS acoplado a um sistema de ablação a laser 193 nm ArF excimer. Os dados foram obtidos com diâmetro do furo de 60 μm e frequência de 6Hz. O tempo de aquisição de dados foi de 60s.

3.3 Desenvolvimento da tese/artigo científico

Após a revisão bibliográfica, análise, coleta e interpretação dos dados, tornou-se possível o desenvolvimento da tese, estruturada nos capítulos introdutórios, seguido da apresentação e discussão dos resultados em formato de artigo científico e conclusão. Para a elaboração deste estudo, foram seguidas as normas do Programa de Pós-Graduação em Geologia da Universidade de Brasília.

CAPÍTULO 4

**KHAN RIVER AND BEAR LAKE: TWO
NATURAL TITANITE REFERENCE
MATERIALS FOR HIGH-SPATIAL
RESOLUTION U-Pb MICROANALYSIS**

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ABSTRACT

The Khan River (Namibia) and Bear Lake (Canada) titanites are investigated as potential reference materials (RM) for LA-ICP-MS applications. The Bear Lake titanite is texturally and compositionally homogeneous. The Khan River titanite is texturally heterogeneous and characterised by variable trace element compositions and total rare earth element (REE) contents. However, both titanites have consistent U-Pb and Nd-isotope ratios. U-Pb ID-TIMS analyses yielded Pb_c -uncorrected intercept ages of 516.3 ± 1.3 Ma (2s, $n = 5$, MSWD = 2.4) and 1067.81 ± 0.74 Ma (2s, $n = 4$, MSWD = 0.35) for Khan River and Bear Lake titanites, respectively. Multiple U-Pb LA-SF/MC-ICP-MS analyses gave consistent Pb_c -uncorrected intercept ages for both, Khan River ($517 \pm 1/5$ Ma, 2s, $n = 262$, MSWD = 1.5) and Bear Lake ($1070 \pm 1/11$ Ma, 2s, $n = 325$, MSWD = 0.88). U-Pb SHRIMP analyses on the same material returned identical (within uncertainty) ages. Khan River and Bear Lake gave internally consistent solution MC-ICP-MS $^{143}Nd/^{144}Nd$ ratios of 0.511587 ± 0.000027 (2s, $n = 2$) and 0.512321 ± 0.000004 (2s, $n = 2$), respectively. The $^{143}Nd/^{144}Nd$ ratios via solution-MC-ICP-MS and LA-ICP-MS all agree within uncertainty and suggest that both titanites can be used as RMs for Nd-isotope analyses.

Keywords: titanite, reference material, LA-ICP-MS, U-Pb, Sm-Nd

4.1 Introduction

Improvements in microanalytical high-spatial resolution techniques such as LA-ICP-MS have broadly expanded the use of accessory minerals to investigate complex geological processes. Titanite $\text{Ca}(\text{Ti}, \text{Al}, \text{Fe}^{3+})\text{SiO}_4(\text{O}, \text{OH}, \text{F})$, for example, is an accessory mineral phase that incorporates substantial amounts of trace elements, including rare earth elements (REE), Sr, U (10–1000 $\mu\text{g.g}^{-1}$), and proportionally smaller quantities of common (non-radiogenic) Pb (Pbc; 1–5 $\mu\text{g.g}^{-1}$). It occurs in a wide range of igneous and metamorphic rocks, and in hydrothermal ore deposits (Force, 1991, Frost *et al.* 2000, Harlov *et al.* 2006, Buick *et al.* 2007, Xiang *et al.* 2007). Its moderate to high closure temperature to Pb volume diffusion ($\sim 700^\circ\text{C}$ or higher; Cherniak 1993, Frost *et al.* 2000, Spencer *et al.* 2013, Stearns *et al.* 2015, Gao *et al.* 2012) is particularly useful for petrochronological investigations of heating/cooling mechanisms, in a wide range of geological settings such as mobile belts, cratonic regions and deeply buried basins (e.g., Aguilar *et al.* 2017, Hu *et al.* 2017, Corfu and Stone, 1998). Applications of titanite U-Pb geochronology include the timing of crystallization during prograde or peak metamorphic conditions, recrystallization produced by strain, and the age of inherited older pre-magmatic or pre-metamorphic constituents (e.g., Tucker *et al.* 1986, Getty and Gromet, 1992, Corfu *et al.* 1994, Krogh, 1994, Zhang and Schärer, 1996, Pidgeon *et al.* 1996, Corfu, 1996). In addition, titanite can be used to constrain resetting ages by hydrothermal and thermal events (generated by magmatism) and crystallization in retrogressive processes caused by moderate heating or increased fluid activity (Corfu and Stone, 1998). Titanite has been widely applied in regional tectono-metamorphic studies that combine U-Pb age information with other geochronometers such as zircon, monazite, apatite and rutile to define temperature–time histories (Schoene *et al.* 2008, Aguilar *et al.* 2017).

Relative to zircon, titanite is more reactive during metamorphism and fluid circulation, and it is more sensitive to multiple thermal events related to regional/contact metamorphism, shear zone development, and/or hydrothermal alteration (e.g., Kohn 2017). It also accommodates significant amounts of high field strength elements (HFSE), including Nb, Ta, Zr, Hf, U and Th (Tiepolo *et al.* 2002), which are essential for investigating the geochemistry of magmatic systems and fluid sources of hydrothermal events (Frost *et al.* 2000, Amelin 2009). Some titanite phases are also enriched in Sm and Nd (and other light REE) (Tiepolo *et al.* 2002, Prowatke and Klemme 2005, Xie *et al.* 2010) and are thus potentially suitable for *in situ* Sm-Nd LA-ICP-MS analyses. Given

that Nd closure temperatures for volume diffusion are well above 800°C (Cherniak 1995; effective diffusion radius of 100 μm and cooling rate of 10°C Ma⁻¹), the combination of textural information, trace elements and *in situ* Sm-Nd isotopes in titanite may provide valuable information related to magma sources, metamorphic history and/or fluid-induced processes.

Despite the advantages of high-spatial resolution analyses via LA-ICP-MS, the destructive nature of this technique demands a continuous supply of well-characterised natural reference materials. Currently, there are only a few natural titanite crystals available as reference materials for U-Pb SIMS/LA-ICP-MS geochronology (Table 4.1), including Khan (518 $\pm$ 2 Ma; Kinny *et al.* 1994, Heaman *et al.* 2009), BLR-1 (1047.1 $\pm$ 0.4 Ma; Aleinikoff *et al.* 2007), OLT1 (1015 $\pm$ 2 Ma; Kennedy *et al.* 2010) and MKED1 (1517.3 $\pm$ 0.3 Ma; Spandler *et al.* 2016). Ma *et al.* (2019) presented another eight potential titanite reference materials for Sm-Nd isotope geochemistry. However, evaluation of the U-Pb systematics of these materials remains to be done via bulk isotope dilution-thermal ionization mass spectrometry (ID-TIMS). Here, we characterise two new potential titanite reference materials for LA-ICP-MS applications: the Khan River and the Bear Lake titanite. These titanites come from the same region as the original Khan titanite (Kinny *et al.* 1994, Heaman 2009), and BLR-1 titanite (Aleinikoff *et al.* 2007). Since they were collected at different localities (Khan River titanite) or were purchased from a mineral dealer (Bear Lake titanite), a full chemical and isotopic characterisation is required to assess their potential as reference materials. Moreover, in the case of our Bear Lake crystal, the reference age is significantly older than that of BLR-1 (see below). In this study we provide new U-Pb ages, Sm-Nd isotope compositions and trace element concentrations for the Khan River and the Bear Lake titanites. Our data were acquired at independent laboratories and allowed testing the reproducibility of the isotope ratios and trace element compositions. We further compare the new results with the existing data for both the Khan and BLR-1 titanites.

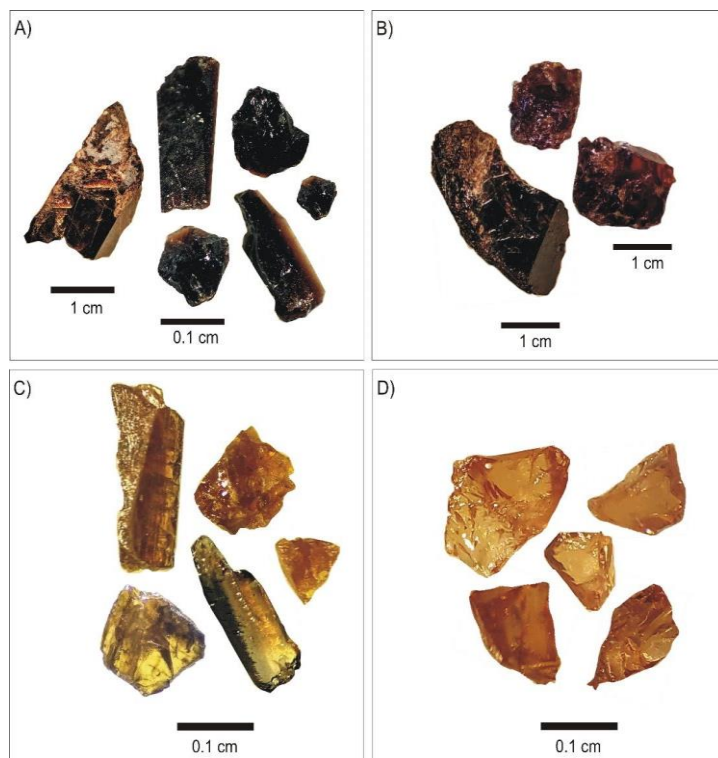


Figure 4.1: A-B) Crystal fragments of Khan River (A) and Bear Lake (B) titanite, showing a dark-brown color prior to thermal annealing and chemical abrasion. C-D) Khan River (C) and Bear Lake (D), after thermal annealing and chemical abrasion. Notice a clear change in color from dark-brown to light-honey in all fragments. The Khan River chips exhibit areas that remained unaltered by the abrasion, including corroded outline and some fractures. The Bear Lake fragments are all transparent and nearly devoid of fractures.

Table 4.1: Summary of natural titanite reference materials and potential titanite for LA-ICP-MS analyses and their U-Pb and Sm-Nd data

Reference material	Technique	$^{207}\text{Pb}/^{206}\text{Pb}$ (2s%)	$^{207}\text{Pb}/^{235}\text{U}$ (2s%)	$^{206}\text{Pb}/^{238}\text{U}$ (2s%)	Reference age	References	Technique	$^{147}\text{Sm}/^{144}\text{Nd}^*$	$^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 2s$)	References
MKED1	ID-TIMS	0.0947 ± 0.0190	3.4632 ± 0.0403	0.2654 ± 0.0244	1517.3 ± 0.3	1	ID-TIMS	0.1270	0.511630 ± 0.000003	1
OLT-1	ID-TIMS	-	1.7145 ± 0.5541	0.1701 ± 0.3527	1014.8 ± 2.0	2	LA-MC-ICP-MS	0.1313	0.512270 ± 0.000026	3
Mt. Painter	ID-TIMS	-	0.5521 ± 3.7200	0.7106 ± 1.5200	439 ± 1	4	ID-TIMS	0.1703	0.511851 ± 0.000006	4
Ontario	LA-ICP-MS	0.0892 ± 2.9148	2.21 ± 2.71	0.1796 ± 1.9488	1056 ± 5	5, 6	ID-MC-ICP-MS	0.1928	0.512833 ± 0.000008	6
T3	LA-ICP-MS	0.0772 ± 3.1088	2.06 ± 5.34	0.1938 ± 2.9928	1138 ± 6	6	ID-MC-ICP-MS	0.1958	0.512611 ± 0.000012	6
Tory Hill	ID-TIMS	0.1171 ± 0.2463	3.0368 ± 0.3063	0.1882 ± 0.0873	1039 ± 23	7	ID-TIMS	0.1314	0.512310 ± 0.000005	7
Chengchao (CC102)	LA-ICP-MS	0.0485 ± 3.3838	0.1376 ± 3.4957	0.0206 ± 1.2493	131.2 ± 0.2	8	-	-	-	-

References: 1 - Spandler *et al.* (2016); 2 - Kennedy *et al.* (2010); 3 - Xu *et al.* (2018); 4 - Elburg *et al.* (2013); 5 - Sun *et al.* (2012); 6 - Ma *et al.* (2019); 7 - Fischer *et al.* (2020); 8 - Hu *et al.* (2017)

4.2 Origin of the Khan River and Bear Lake titanite

4.2.1 Khan River titanite

The Khan River titanite was obtained from a pegmatite intruded in calc-silicate rocks of the Khan Formation (Nosib Group), in the Central Zone of the E-W trending Damara Belt, Namibia. The Central Zone underwent a protracted felsic magmatic history, from c. 565 Ma to 480 Ma (Jung *et al.* 2000, Milani *et al.* 2015). In the southern Central Zone low-pressure/high-temperature regional metamorphism (Masberg *et al.* 1992) locally reached peak-granulite-facies conditions (~5 kbar, ~800-835°C) at c. 520 Ma (Longridge *et al.* 2017, Jung *et al.* 2019). Voluminous leucogranites and pegmatites were emplaced between 520 Ma and 508 Ma (Longridge *et al.* 2011).

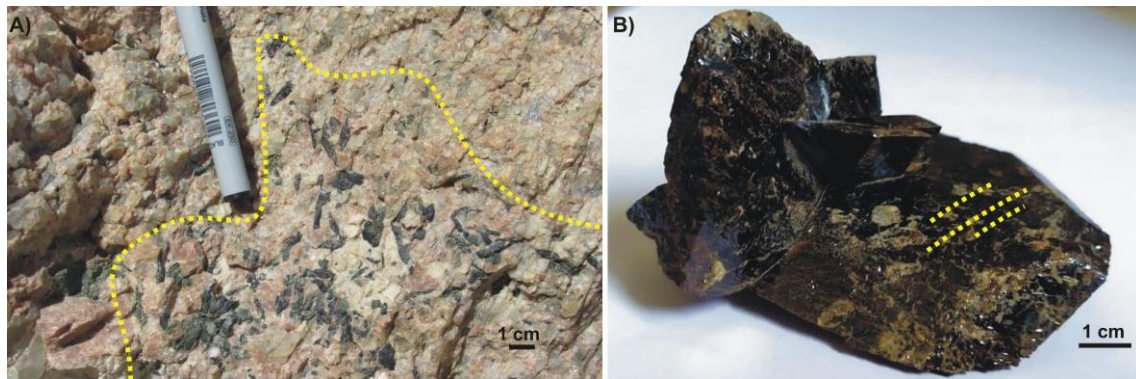


Figure 4.2: A) Khan River titanite (dark crystals in zone delimited by yellow dashed line) occurring within pegmatite composed mostly of quartz, microcline and plagioclase in contact with the Khan Formation. B) Bear Lake titanite specimen collected from the Bear Lake diggings. Dashed lines depict fracture direction.

The sampling site (22°31'57.02" S, 14°59'54.28" E) is approximately 2.5 km southeast of the entrance to the Khan Pegmatite mine, which was formerly mined for copper (Söhnge *et al.* 1939). Pegmatites intrusive into the Khan Formation typically contain quartz, microcline, clinopyroxene, hornblende, albite and minor titanite and apatite. Cu-bearing pegmatites may additionally contain pyrite, sphalerite, chalcopyrite, bornite and chalcocite (Söhnge *et al.* 1939). Titanite is particularly abundant close to the contact with Khan Formation country rocks (Fig. 4.2A). Samples of the Khan River titanite comprise 1-4 cm long, well-formed, dark brown crystals, which for most parts are free of inclusions (Fig. 4.1A). Most samples have fractures filled by quartz and/or feldspar, similar to the original Khan titanite (once widely distributed as reference material for SIMS U-Pb geochronology). Titanite from the Khan Pegmatite mine yielded an ID-TIMS U-Pb age of 518 ± 2 Ma (2s, Kinny *et al.* 1994).

4.2.2 *Bear Lake titanite*

The Bear Lake titanite comes from Bear Lake Diggings, near Tory Hill, Ontario, Canada. This region is located at the south-eastern edge of the amphibolite-facies Glamorgan Gneiss Complex, in the strongly deformed Central Metasedimentary Belt of the Grenville Province (Hewitt 1956). It is known for the occurrence of different types of coarse-grained world-class mineral specimens, such as biotite, apatite, amphibole, titanite, feldspar and uranothorite (Satterly 1943, Armstrong and Gittins 1968, Oberti *et al.* 2019). The titanite at this locality occurs in 1-2-meter-wide, E-W trending calcite veins or dykes (“vein-dykes”, Heinrich 1966); similar calcite vein-dykes are common throughout the Central Metasedimentary Belt Boundary Zone.

The origin of the calcite vein-dykes is contentious; they have been interpreted to represent primary carbonatitic melts (Heinrich 1966), metamorphosed and remobilized carbonatites (Moecher *et al.* 1997), or to reflect melting of carbonate rocks (Oberti *et al.* 2019). Moecher *et al.* (1997) obtained titanite U-Pb ID-TIMS ages in the range 1085-1035 Ma from different skarns. They linked these ages to multiple metasomatic reactions developed between calcite dykes and silicate wall rocks or to rock inclusions during the Late Ottawa stage of regional Grenville metamorphism. Moecher *et al.* (1997) also obtained older zircon U-Pb ages from the calcite vein-dykes, interpreted by them to date the emplacement of several generations of carbonatite precursors. The titanite U-Pb reference material BLR-1 (U-Pb ID-TIMS reference age of 1047.1 ± 0.4 Ma (2s), Aleinikoff *et al.* 2007) was obtained from Bear Lake Diggings (Mazdab 2009).

Our Bear Lake titanite sample comprises well-formed wedge-shaped crystals, purchased from a local mineral dealer. The crystals range from 1.0 to 5.5 cm across and about 1.0 to 2.0 cm thick (Fig. 4.2B). Each individual crystal contains large (0.1-0.5 cm²) domains that are homogeneous, free of fractures and inclusions: such domains can be easily extracted and mounted for use as reference material.

4.3 Analytical methods

Several crystals of the Khan River titanite (Fig. 4.1A) and one large crystal of the Bear Lake titanite (Fig. 4.1B) were investigated. We extracted one fragment from each of the Khan River crystals and labeled them FKR1 to FKR9. From the Bear Lake crystal, we extracted eight fragments that were labeled FBL1 to FBL8. The fragments range in size from 0.1 to 0.5 cm long and 0.1 to 0.4 cm wide, and are dominantly reddish-brown.

Prior to LA-ICP-MS analysis, we applied the chemical abrasion technique (Mattinson 2005) to remove fractured/damaged portions of the fragments. Although Pb loss in titanite is uncommon, fractured/damaged domains are likely to record isotopic disturbances/heterogeneities, and the removal of such domains via chemical abrasion (CA) aids in the acquisition of precise and accurate data from the reference materials. It is worth noting that the chemical treatment leaves behind only recovered/undamaged domains, which can be further scrutinized by backscattered electron imaging prior to LA-ICP-MS analyses. The chemical treatment also improves transparency, enabling a better selection of spot location when using the transmitted light of the laser ablation systems.

4.3.1 Chemical Abrasion

The chemical abrasion (Mattinson 2005) was performed at the Laboratório de Geoquímica at the Universidade Federal de Ouro Preto (UFOP). All fragments were first annealed at 850°C in a porcelain crucible for 60h. The annealed grains were ultrasonically cleaned and then acid attacked in a cleaned Teflon micro-centrifuge tube, in a solution of 0.05 ml 27.83M HF (Suprapur, Merck, Germany) and 3.975 ml 1:1 14.34M HNO₃ (Suprapur, Merck, Germany) + H₂O (ultrapure from Millipore Q-Pod Element System) in a microwave oven (Milestone Ethos1) at 1500W. The samples were heated for 10 minutes at 90 °C and 120 bar and, subsequently, heated for 25 minutes at 60°C and 120 bar. The chemically abraded grains were cleaned and separated in ultrapure water for 10 min at 3000 rpm using a centrifuge (Fanem Excelsa 2206) and then washed with ultrapure water. The crystals were then dried in an oven at 60°C for one day.

4.3.2 Backscatter electron (BSE) imaging and Electron Microprobe analysis

Backscattered electron (BSE) images were acquired using a JSM-6510 JEOL scanning electron microscope operating at 15kV and 20nA for energy and current, respectively.

Major element analyses were carried out at the UFOP Microscopy and Microanalysis Laboratory (LMic) using a JEOL JXA-8230 electron microprobe equipped with five wavelength-dispersive systems (WDS). The probe was set to an accelerating voltage of 15 kV, beam current of 20 nA, and spot size of 10 µm. Calibration used well-characterised mineral standards (wollastonite for Si and Ca, hematite for Fe, almandine for Al, rutile for Ti, tugtupite for Cl, strontiofluorite for F). Data collection employed 20 s counting times for both peak and background for all elements except F, for which

counting times were 150 s for both on peak and background. The data reduction package JEOL/EPMA was used to perform the calibration, overlap correction and quantification (see Carvalho *et al.* 2022 for more details on analytical conditions).

4.3.3 Chemical composition via LA-ICP-MS

Minor and trace element analyses of the samples were obtained at UFOP using a Thermo Scientific Element II SF-ICP-MS coupled to a CETAC UV Nd:YAG-213 nm laser ablation system. Samples were ablated and carried by helium gas (0.3 L/min), flushed to minimize aerosol deposition, and mixed with argon gas (0.95 L/min) prior to introduction in the ablation cell. For spot analyses, the laser repetition rate was set to 10 Hz, with beam diameter and laser fluence set to 30 μm and 6 J/cm², respectively. The following masses were analysed: ⁴⁵Sc, ⁸⁸Sr, ⁸⁹Y, ⁹¹Zr, ⁹³Nb, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ²⁰⁸Pb, ²³²Th and ²³⁸U. The background and sample ablation were acquired for 20s and 60s, respectively. Data reduction was performed offline using Glitter software (Van Achterbergh *et al.* 2001, Griffin *et al.* 2008). Stoichiometric CaO (27.0 m/m %) was used as the internal standard element for quantification. The main calibrant was the NIST-612 glass and, for quality-control, the BCR and BHVO glasses were used (values from Jochum *et al.* 2016). For each cycle of sample analyses, the glasses were ablated at the beginning and at the end. The accuracy and precision of the measurements were based on the specific element concentrations of the external reference materials. The accuracy of the data for the reference materials (BCR and BHVO glasses) were within 5-10% of the accepted values. The data for samples are consistent with titanite stoichiometry.

4.3.4 U-Pb ID-TIMS

U-Pb ID-TIMS analyses were carried out at the University of Oslo (Norway) and the Jack Satterly Geochronology Laboratory (JSL), University of Toronto (Canada). At Oslo the titanites were cleaned in hot HNO₃, water and acetone. The fragments were dried and then weighted, moved to a Savillex vial with the addition of ²⁰²Pb-²⁰⁵Pb-²³⁵U spike. The dissolution process was undertaken on a hotplate with HF (+HNO₃) for 6 days, and then, after evaporation of the solution, re-dissolved overnight in 3N HCl. To separate U and Pb, the solutions were treated with a single-stage HCl-HBr mini-column method, and then loaded on Re-filaments with Si-gel and H₃PO₄ and analysed on a MAT262 mass spectrometer. The Pb and U ratios were measured in static mode on Faraday cups, except

for $^{207}\text{Pb}/^{204}\text{Pb}$ ratios which were acquired with a secondary electron multiplier. The $^{205}\text{Pb}/^{202}\text{Pb}$ ratio was applied to correct the Pb fractionation while U was corrected with a value of 0.12 ± 0.06 ‰/amu based on long-term U500 reference material measurements. The analyses were also corrected for blanks of 2 pg for Pb and 0.1 pg for U, applying a composition derived from the model of Stacey and Kramers (1975) to correct the initial Pb_c . The decay constants used in the calculation are those of Jaffey *et al.* (1971) and $^{238}\text{U}/^{235}\text{U} = 137.818$ (Hiess *et al.*, 2012).

At JSL the titanites were cleaned in 8N HNO_3 at room temperature and loaded with 0.010 μL 8N HNO_3 into Teflon dissolution capsules with ~ 120 μL 50% HF and a mixed ^{205}Pb - ^{235}U isotopic tracer solution. Dissolution was at 195°C for 3 days. Samples were dried to a precipitate and re-dissolved in 3.1N HCl prior to loading into anion exchange columns. An HBr chemical separation procedure was performed to isolate Pb and U, which was dried in H_3PO_4 and loaded onto outgassed rhenium filaments with silica gel. U and Pb were analysed with a VG354 mass spectrometer using either 3 Faraday collectors (^{205}Pb - ^{206}Pb - ^{207}Pb) and a Daly detector in pulse counting mode (^{204}Pb) to measure the Pb isotopes simultaneously, or a Daly detector in dynamic pulse counting mode. U was measured in 3 Faraday cups in static collection mode or by using a single Daly detector. VG Sector software was used for data acquisition. Corrections to the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ dates for initial ^{230}Th disequilibrium have been made assuming a Th/U ratio in the magma of 4.2. Initial common Pb (Pb_c) was corrected using the Pb evolution model of Stacey and Kramers (1975) and assuming a Pb procedural blank of 1 pg Pb, 0.1 pg U. Fractionation correction for Pb and U was 0.1‰ per atomic mass unit. The mass discrimination correction for the Daly detector is constant at 0.05‰ per atomic mass unit. Amplifier gains and Daly characteristics were monitored using the SRM 982 Pb reference material. Decay constants used were those of Jaffey *et al.* (1971): ^{238}U and ^{235}U are $1.55125 \times 10^{-10}/\text{yr}$ and $9.8485 \times 10^{-10}/\text{yr}$, respectively. A $^{238}\text{U}/^{235}\text{U}$ ratio of 137.818 (Hiess *et al.*, 2012) was used for the $^{207}\text{Pb}/^{206}\text{Pb}$ model age calculation. U–Pb data reduction and age calculations were performed using in-house Visual Basic programs written by D.W. Davis. All age uncertainties quoted in the text and table, and uncertainty ellipses in the concordia diagrams are given at the 95% confidence interval. Plotting and age calculations were done using Isoplot 3.00 (Ludwig 2003).

4.3.5 U-Pb SHRIMP

Hand-picked aliquots of Bear Lake (BL) and Khan River (KR) titanites together with BLR1 and MKCO1 were cast into epoxy disks, ground, and polished to expose the midsection of the grains. Backscattered electron (BSE) imaging was conducted using a JEOL JSM6610A Analytical SEM (scanning electron microscope) in Research School of Earth Sciences (RSES), The Australian National University (ANU), Canberra, equipped with a Robinson cathodoluminescence (CL) detector. Reflected and transmitted light photomicrographs together with BSE images were prepared for analysis of domains free of inclusions or cracks.

U-Th-Pb isotopic analyses of Khan River and Bear Lake titanites were carried out on a sensitive high-resolution ion microprobe (SHRIMP II), a high precision secondary ion mass spectrometer (SIMS), at RSES, ANU. Analytical procedures are similar to those described in Williams (1998 and references therein) and Ireland and Williams (2003). Each analysis represents six scans through the different masses. The following masses were measured: $^{56}\text{Fe}^{16}\text{O}$, $^{40}\text{Ca}^{48}\text{Ti}_2^{16}\text{O}_4$, ^{204}Pb , 204.1 (background), ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{238}U , $^{232}\text{Th}^{16}\text{O}$, $^{238}\text{U}^{16}\text{O}$, $^{238}\text{U}^{16}\text{O}_2$. Counting time varies from 2 seconds to 30 seconds. Note that O_2^- rather than O^- or total oxygen primary beam was used. Uranium and Th abundances were calculated with reference to BLR1 (260 $\mu\text{g g}^{-1}\text{U}$), and the Pb/U ratios were normalized relative to a value of 0.17635 for the $^{206}\text{Pb}/^{238}\text{U}$ ratio of BLR1, equivalent to an age of 1047.1 Ma (Aleinikoff *et al.* 2007). The ratios were calculated from an empirical linear power law relationship defined between Pb^+/U^+ and UO^+/U^+ , from all the measurements performed on the reference material BLR1. Data were reduced using the SQUID Excel Macro of Ludwig (2001a) and the ISOPLOT/EX Excel Macro of Ludwig (2001b) and are tabulated in the Electronic Supplement – 1. MKED1, YQ82 and MTPHR titanites from two separate mounts were also analysed in the same session to check matrix effect in age determination (c.f. Ling *et al.* 2022). The SIMS U-Pb data for all the titanite reference materials (this study; Ling *et al.* 2022) were taken together to check for matrix effects in the age determination of the samples (see details in Supporting Information).

4.3.6 U-Pb LA-SF-ICP-MS

U-Pb data were acquired using a Thermo Scientific Element II, single collector (SF) ICP-MS coupled to a CETAC UV Nd:YAG-213 nm laser ablation system at the

Laboratório de Geoquímica Isotópica at UFOP. The data were acquired in time-resolved, peak-jumping, pulse-counting mode, producing over 810 mass scans during 25 s of background acquisition and 30 s of sample ablation. Each analysis used a spot size of 40 μm with a repetition rate of 10 Hz, and a laser fluence of $\sim 3.5 \text{ J/cm}^2$. With an approximate depth penetration of $\sim 0.6 \mu\text{m s}^{-1}$ and a 0.9 s integration time (=15 mass scans = 1 ratio), any relevant alteration of the Pb/Pb and U/Pb ratios on the μm scale can be detected. Raw counts were corrected offline for background signal, instrumental mass bias, and time-dependent elemental fractionation. The data reduction was performed using the Glitter software (Van Achterbergh *et al.* 2001, Griffin *et al.* 2008) and an in-house spreadsheet (Gerdes and Zeh 2006, 2009). Because of the variable initial Pb ratios of the titanite samples, and the technical difficulties in measuring ^{204}Pb via LA-ICP-MS (e.g., Chew *et al.* 2014, Lana *et al.* 2017), none of the U-Pb analyses from UFOP were corrected for Pb_c . Dates are therefore reported here, and elsewhere, as lower intercepts on the Tera-Wasserburg Concordia diagram. All dates/ages are reported at 2 sigma (2s).

The Blue Berry zircon (Lana *et al.* 2017, Santos *et al.* 2017) was used as the primary reference material to correct for mass bias and instrumental drift on the relevant ratios. GJ-1 zircon was used as quality control ($602 \pm 5 \text{ Ma}$, Jackson *et al.* 2004, Horstwood *et al.* 2016). Titanite reference materials included the titanites MKED1 (Spandler *et al.* 2016), OLT1 (Kennedy *et al.* 2010), BLR-1 (Aleinikoff *et al.* 2007), and Mt Painter (ME99DI2) (Elburg *et al.* 2003) (Electronic Supplement - 1). MKED1 titanite reference material was used to calculate the matrix-related offset (0-1%) between titanite and zircon. The offset correction was applied to titanite reference materials and samples. Uncertainties (2s) were propagated by quadratic addition of the external reproducibility of the primary reference material during the analytical session and the within-run precision of each analysis. Systematic uncertainties were quadratically added on each final date and are reported as $\pm \alpha/\beta$ (without/with systematic uncertainties; Horstwood *et al.* 2016).

The U-Pb data obtained for the reference materials during the analytical sessions were compiled and checked for consistency with the published ages. (Electronic Supplement - 1). The obtained intercept age of $1518 \pm 2/15 \text{ Ma}$ (2s, $n = 101$, MSWD = 0.35) for the MKED1 titanite is consistent, within uncertainty, with the ID-TIMS data of Spandler *et al.* (2016, $1517.3 \pm 0.3 \text{ Ma}$, 2s, weighted mean $^{206}\text{Pb}/^{238}\text{U}$). The intercept age of $1013 \pm 8/13 \text{ Ma}$ (2s, $n = 14$, MSWD = 0.028) for the OLT1 titanite agrees, within

uncertainty, with the age proposed by Kennedy *et al.* (2010, 1015 ± 2 Ma, 2s, concordia). Results of the intercept age for the BLR-1 titanite ($1050 \pm 2/11$ Ma, 2s, $n = 51$, MSWD = 0.57) are similar to published data by Aleinikoff *et al.* (2007, 1047.1 ± 0.4 Ma, weighted mean $^{206}\text{Pb}/^{238}\text{U}$). The obtained intercept age of $440 \pm 4/6$ Ma (2s, $n = 33$, MSWD = 0.035) for the Mt Painter titanite agrees, within uncertainty, with the published ID-TIMS concordia age reported by Elburg *et al.* (2003, 439 ± 1 Ma). The calculated concordia age of $606 \pm 2/6$ Ma (2s, $n = 44$, MSWD = 0.47, no offset applied) for GJ-1 zircon is also consistent, within uncertainty, with the previous published results (602 ± 5 Ma, 2s, weighted mean $^{206}\text{Pb}/^{238}\text{U}$, e.g., Horstwood *et al.* 2016).

4.3.7 U-Pb LA-MC-ICP-MS

High spatial resolution titanite U-Pb ages were also obtained on a Thermo Scientific Neptune Plus Multi-collector ICP-MS coupled to a 193 nm HeEX Photon Machine Laser ablation system at the Laboratório de Geoquímica Isotópica at UFOP. The signal was collected on the following ion-counters (ICs): ^{208}Pb on IC6, ^{207}Pb on IC1B, ^{206}Pb on IC2, $^{204}\text{Hg} + \text{Pb}$ on IC5, and ^{202}Hg on IC4. ^{232}Th and ^{238}U were acquired on Faraday cups H2 and H4, respectively. All relevant masses were measured simultaneously. The U-Pb data of individual spots were measured during 60 s of ablation (20 s of background + 40 s of sample) with a 40 μm spot size, 5 Hz repetition rate and 6 J/cm^2 fluence.

The raw titanite U-Pb data were corrected offline for background, laser-induced element fractionation and instrument mass bias, using the Saturn software (Silva *et al.* 2020). GJ-1 zircon (Jackson *et al.* 2004) was used as the primary reference material while Mt Painter (Elburg *et al.* 2003), Khan (Kinny *et al.* 1994), BLR-1 (Aleinikoff *et al.* 2007), OLT1 (Kennedy *et al.* 2010) titanites and Plešovice zircon (Sláma *et al.* 2008) were used as quality control (Electronic Supplement - 1). The matrix related offset (0-1%) between titanite and zircon reference materials was calculated using the MKED1 titanite reference material. This offset was applied to the titanite references materials and samples. Uncertainty propagation followed Horstwood *et al.* (2016) and are reported as $\pm \alpha/\beta$ (without/with systematic uncertainties) at 2s confidence interval.

MKED1 titanite yielded a lower intercept age of $1516 \pm 1/15$ Ma (2s, MSWD = 0.24, $n = 59$) consistent, within uncertainty, with the reference age of 1517.3 ± 0.3 Ma (Spandler *et al.* 2016). Mt Painter titanite pooled a lower intercept age of $441 \pm 1/5$ Ma

(2s, MSWD = 5.3, n = 58), consistent with the published value of 439 ± 1 Ma (Elburg *et al.* 2003). Khan titanite presented a lower intercept age of $519 \pm 3/6$ Ma (2s, MSWD = 0.3, n = 14) which is consistent, within uncertainties, with the reported ID-TIMS age of 518 ± 2 Ma (Kinny *et al.* 1994). The BLR-1 titanite yielded a lower intercept age at $1049 \pm 2/11$ Ma (2s, n = 16, MSWD = 1.5) and agrees, within uncertainty, with the reference age of 1047.1 ± 0.3 Ma (Aleinikoff *et al.* 2007). Data from OLT1 resulted in a lower intercept age of $1015 \pm 2/10$ Ma (2s, n = 39, MSWD = 2.8) and correspond, within uncertainty, with the age of 1015 ± 2.0 Ma (Kennedy *et al.* 2010). Data from the Plešovice zircon produced a concordia age of $337 \pm 1/4$ Ma (2s, n = 8, MSWD = 1.7, no offset applied), in agreement with the reference $^{206}\text{Pb}/^{238}\text{U}$ age of 337 ± 0.4 Ma (Sláma *et al.* 2008).

4.3.8 Nd and Sm-Nd isotopes solution mode MC-ICP-MS

Solution ICP-MS analyses were obtained at the Centro de Pesquisas Geocronológicas, Universidade de São Paulo (CPGeo-USP), and at the State Key Laboratory of Lithospheric Evolution (SKLLE), Institute of Geology and Geophysics, Chinese Academy of Sciences.

At CPGeo-USP, all chemical procedures were performed in a class ISO-7 clean laboratory, provided with class ISO-5 laminar flow hoods. All reagents used were purified. A 10 mg titanite sample was weighed in a previously cleaned PTFE beaker. Titanite dissolution was carried out using $\text{HNO}_3 + \text{HF}$ and HCl in a PTFE beaker, at a temperature of 100°C in a "clean box". After the reaction, the sample was evaporated to dryness, and 2 ml of 1M HNO_3 was added to the residue and the solution was ready for chromatographic separation. RE Spec 100-150 μm resin (Eichrom Industries Inc.) was used to separate the rare earth element group. The column was assembled with 70 mg of previously decontaminated RE Spec resin. After washing with 1M HNO_3 , the REE group was eluted with 0.05M HNO_3 . The solution was loaded into a new column for Nd separation using Ln Spec100-150 μm resin (Eichrom Industries Inc.). Nd was eluted with 0.26M HCl . The Nd isotope ratios were obtained by mass spectrometry using a Neptune Plus Thermo Scientific MC-ICP-MS. $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios were normalised to the value of $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ (De Paolo, 1981) and uncertainties are given at 2s. The complete dataset for samples and reference material applied (JNdi) are in Electronic Supplement – 2.

Another batch of Sm-Nd isotope compositions were obtained by solution-mode MC-ICP-MS using a Thermo Scientific Neptune MC-ICP-MS, at SKLLE. The chemical procedures were performed on special class 100 work benches inside a class 1000 clean laboratory. Titanite aliquots were weighted and the digestion was carried out with a mix of concentrated HF-HNO₃-HClO₄ (2ml – 1ml – 0.2 ml) at a temperature of 120 °C for 1 week. After the reaction, the capsule was opened to evaporate the HClO₄. One ml of 6M HCl was added to the residue and then dried down. This step was repeated twice. After cooling, the residue was dissolved in 5 ml of 3M HCl and then positioned on a hot plate at ~100 °C overnight prior to chemical separation. The chromatography procedures to separate the REE and concentrate Sm and Nd followed the procedures described in detail in Yang *et al.* (2011). The ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219 (O’Nions *et al.* 1977) and the exponential law (Russel *et al.* 1978) were applied to correct for mass bias. The JNdi-1 isotope reference solution was used for the analytical session. The Alfa Sm standard solution was measured after each cycle of five samples (¹⁴⁷Sm/¹⁴⁹Sm = 1.08680, Dubois *et al.* 1992, Isnard *et al.* 2005) and was employed to externally correct the ¹⁴⁷Sm/¹⁴⁹Sm ratio of the spiked samples for mass bias. The Sm concentration of the actual sample is calculated from the corrected ¹⁴⁷Sm/¹⁴⁹Sm ratio, applying the isotope dilution equation.

4.3.9 Sm-Nd isotope composition via LA-ICP-MS

Sm-Nd isotope compositions were determined by multi-collector (MC) LA-ICP-MS at the Departamento de Geologia, UFOP and at SKLLE, Institute of Geology and Geophysics, Chinese Academy of Sciences.

At UFOP, the Sm-Nd isotope determination was carried out using a Thermo Scientific Neptune Plus LA-MC-ICP-MS coupled to a 193 nm HeEX Photon Machine laser ablation system. Full instrumentation and protocols are described in Gonçalves *et al.* (2018). Helium (0.3 L/min) was used as the carrier gas for ablation, mixed with argon (0.95 L/min) and nitrogen (0.03 L/min) prior to introduction to the ICP. Data were obtained with a spot size of 60 µm, 5 Hz repetition rate and 6 J/cm² fluence. Typical beam intensities for MKED1 were ca. 6V for Nd. The data were processed offline using an in-house Excel spreadsheet following Gonçalves *et al.* (2018). The obtained data were corrected for background, mass interference and mass bias. MKED1 titanite (Spandler *et al.* 2016) and NIST612 glass (Hollocher *et al.* 1995) were used as primary reference materials for different runs to calibrate the Nd ratios. The Sm-Nd ratios were calibrated

using MKED1 titanite. BLR-1, OLT1 and Khan titanites (Aleinikoff *et al.* 2007, Kennedy *et al.* 2010 and Kinny *et al.* 1994, respectively), Madagascar apatite (Yang *et al.* 2014) and Sumé apatite (an in-house reference material - Lana *et al.* 2022), were used for quality control (Electronic Supplement – 2). BLR-1 titanite yielded an average $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.1912 ± 0.0005 (2s, n = 24) and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.51279 ± 0.00004 (2s, n = 24), both within uncertainty of the values reported by Ma *et al.* (2019, 0.1939 ± 0.0045 and 0.51283 ± 0.00005 , respectively). OLT1 titanite produced an average $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.1312 ± 0.0003 (2s, n = 25) and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.51230 ± 0.00004 (2s, n = 25), consistent with the reference values of 0.1313 ± 0.0019 and 0.51227 ± 0.00003 (Xu *et al.* 2018). Khan titanite pooled an average $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.1191 ± 0.0003 (2s, n = 24) and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.51161 ± 0.00003 (2s, n = 24), within uncertainty of the values published by Ma *et al.* (2019, 0.1188 ± 0.0050 and 0.51164 ± 0.00004 , respectively). Madagascar apatite ($^{147}\text{Sm}/^{144}\text{Nd} = 0.0818 \pm 0.0005$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.51135 \pm 0.00002$, Yang *et al.* 2014), produced an average $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.0814 ± 0.0002 (2s, n = 6) and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.51132 ± 0.00005 (2s, n = 6). Sumé apatite ($^{147}\text{Sm}/^{144}\text{Nd} = 0.0766 \pm 0.0002$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.51075 \pm 0.00004$, Lana *et al.* 2022), yielded an average $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.0766 ± 0.0002 (2s, n = 33) and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.51075 ± 0.00004 (2s, n = 33).

At SKLLE, the Sm-Nd isotope compositions were obtained using a Neptune Plus MC-ICP-MS coupled to a 193 nm ArF excimer laser ablation system. The Neptune Plus MC-ICP-MS was tuned and optimized for maximum sensitivity using a JNdi-1 isotope reference solution prior to laser analysis. For spot analyses, the laser repetition rate was set to 6 Hz, with laser spot size set to 60 μm . Each spot analysis consisted of approximately 60 s data acquisition with the laser turned on. Total voltage obtained for the conditions for OLT1 was ca. 1.5 V for Nd. In order to obtain accurate $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ data by LA-MC-ICP-MS, we have adopted the recently revised natural Sm isotopic abundances ($^{147}\text{Sm}/^{149}\text{Sm} = 1.08680$ and $^{144}\text{Sm}/^{149}\text{Sm} = 0.22332$) (Yang *et al.* 2014). First, the measured $^{147}\text{Sm}/^{149}\text{Sm}$ ratio was used to calculate the Sm mass bias and then divided the ^{147}Sm intensity by the natural $^{147}\text{Sm}/^{144}\text{Sm}$ ratio of 4.866559 to estimate the Sm interference on mass 144. Then the interference-corrected $^{146}\text{Nd}/^{144}\text{Nd}$ ratio was used to calculate the Nd mass bias. Finally, the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{145}\text{Nd}/^{144}\text{Nd}$ ratios were normalised using the exponential law. The $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of unknown samples can also be calculated using the exponential law after correcting for isobaric interference of ^{144}Sm on ^{144}Nd as described above. Titanite reference material OLT1 (n =

17), measured as an unknown sample, gave a mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512230 ± 0.000024 (2s) and $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.1247 ± 0.0009 (2s), which are consistent with the recommended value reported by Ma *et al.* (2019) (Table 4.1).

4.4 Results

4.4.1 Chemical Abrasion

The procedures involving thermal annealing (850 °C, 60h) and chemical abrasion (90 °C, 10 min and 60 °C, 20 min) yielded positive results for both the Khan River and Bear Lake titanites: (1) the crystal fragments became more translucent, (2) the color changed from brown to light-honey and (3) the most fractured and altered areas were removed by the acid, concentrating the best portions of the grains (areas less fractured and uniform). These features are best exemplified by the Kahn River titanite sample (Fig. 4.1C, D).

4.4.2 Chemical characterisation

BSE images show different textures for the titanite fragments (Fig. 4.3). The Khan River titanite is marked by fractures separating unzoned from sector-zoned domains (Fig. 4.3). Some fragments only presented sector zoning textures, whereas others were predominantly unzoned. The BSE images for the Bear Lake titanite are internally homogeneous at a scale of 200 μm to 500 μm (Fig. 4.4).

EMPA analysis of a number of fragments reveal that the Khan River and Bear Lake titanite are both homogeneous in terms of major element composition (Table 4.2). The Khan River titanite has Al_2O_3 of 1.3 to 2.1 % m/m and Fe_2O_3 of 2.0 to 3.6 % m/m. The Nb_2O_5 contents vary from 1.2 to 2.0 % m/m. Bear Lake titanite has Al_2O_3 and Fe_2O_3 around 1.3 % m/m and 2.1 % m/m, respectively. The Nb_2O_5 contents are approximately 1.1 % m/m. Aluminium and Fe are likely to substitute for Ti on the Ti octahedral site (Frost *et al.* 2000). More details can be found in the online supporting information (Electronic Supplement – 2).

In terms of trace element concentrations, the individual fragments of the Khan River and Bear Lake titanites have significant amounts of Zr, Hf, Nb, Ta, Nd, Th, U, Pb, Y and REE, as expected (e.g. Frost *et al.* 2000, Tiepolo *et al.* 2002). The Khan River titanite crystals have high concentrations of U ($\sim 500 \mu\text{g.g}^{-1}$), Th ($\sim 300 \mu\text{g.g}^{-1}$), Y ($\sim 4100 \mu\text{g.g}^{-1}$), Nb ($\sim 10000 \mu\text{g.g}^{-1}$) and Ta ($\sim 2700 \mu\text{g.g}^{-1}$). The Nd content is also high, but variable from ~ 1600 to $3800 \mu\text{g.g}^{-1}$ (between fragments) and from 1 to 16 %RSD (within

fragments) (Table 4.3). Khan River titanite shows similar REE patterns on a chondrite-normalised diagram, exhibiting a lower relative enrichment of the LREE over the MREE ($\text{La/Gd}_N = 3.31$), a significant negative Eu anomaly ($\text{Eu/Eu}^* = 0.32$), a flat M-HREE pattern ($\text{Gd/Lu}_N = 0.91$) and enrichment from Ho to Lu (Fig. 4.5A). Fragments FKR4 and FKR7 are enriched in HREE relative to the other fragments. Total REE contents vary by as much as 49% between the fragments, but individual fragments (e.g., FKR1, FKR2, FKR7 and FKR8) show rather small variations, with reproducibility better than 5% (RSD).

The Bear Lake titanite contains abundant Nb ($\sim 5900 \mu\text{g.g}^{-1}$), Zr ($\sim 1100 \mu\text{g.g}^{-1}$), Ta ($\sim 209 \mu\text{g.g}^{-1}$) and moderate to low contents of U ($\sim 140 \mu\text{g.g}^{-1}$), Th ($\sim 260 \mu\text{g.g}^{-1}$), Y ($\sim 500 \mu\text{g.g}^{-1}$). In addition, the Nd content is also high and homogeneous, showing a slightly variation from ~ 1100 to $1200 \mu\text{g.g}^{-1}$ (between fragments) and from 0.4 to 1.5 %RSD (within fragments) (Table 4.4). It has moderate Th/U (~ 1.8) and Nd/Y (~ 2.3) and high Nb/Ta (~ 28.4) compared to others titanite reference materials (e.g., MKED1, Khan, BLR-1 and OLT1). The chondrite-normalised REE pattern is completely different from the Khan River titanite, showing a smaller relative enrichment in the LREE, a negligible Eu/Eu* and a steeper HREE pattern (Fig. 4.5B). The analysed crystal fragments show more homogeneous REE contents relative to the Khan River titanite fragments (Fig. 4.5). Our REE data for the Bear Lake titanite show a hump-shaped pattern from Er to Lu and subchondritic Y/Ho (~ 21). These features (described as the lanthanide tetrad effect, Horie *et al.* 2008, Xie *et al.* 2010) are observed in other titanites (BLR-1, OLT1 and MKED1, Aleinikoff *et al.* 2007, Kennedy *et al.* 2010, Spandler *et al.* 2016), and seem to indicate crystallization from highly differentiated fluids (e.g., Irber *et al.* 1999).

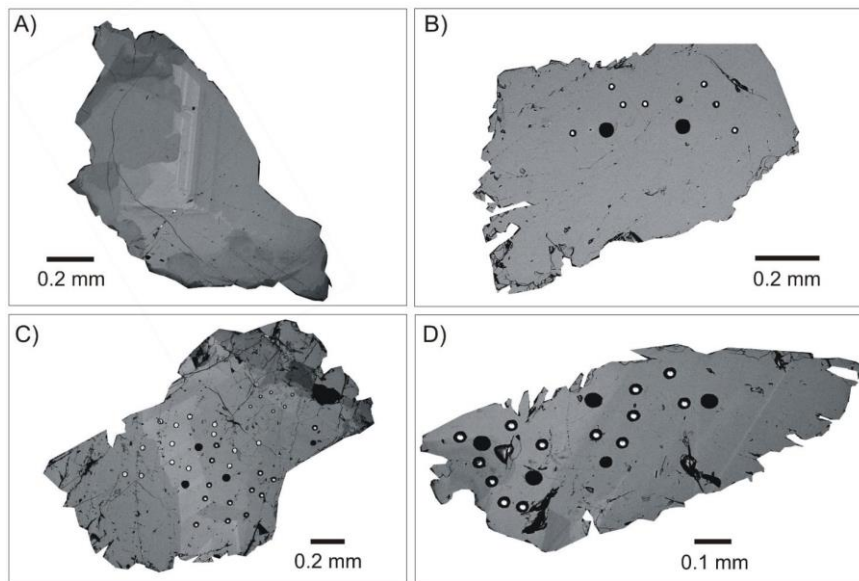


Figure 4.3: Backscatter (BSE) images of fragments of the Khan River titanite megacrysts: A) grain without thermal annealing and chemical abrasion, showing sector zoning. B-C-D) chips that were thermally annealed and chemically abraded presenting rather homogeneous domains, sector zoning and some fractures. The black/white circular holes are the laser ablation pits.

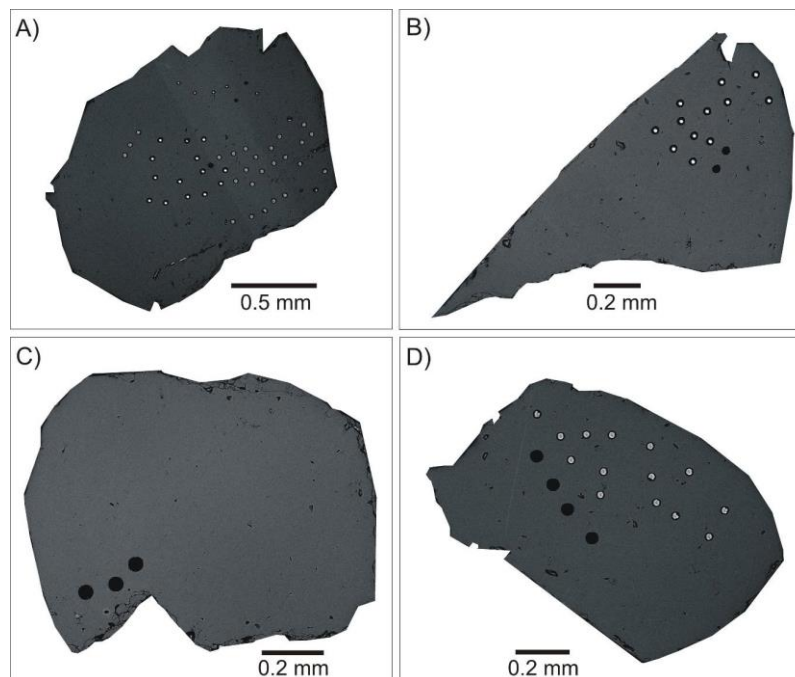


Figure 4.4: Backscatter (BSE) images of fragments of the Bear Lake titanite megacrysts after thermal annealing and chemical abrasion. A) Fragment showing both faint sector zoning and uniform areas. B-C-D) Chips showing homogeneous domains. The black/white circular holes are the laser ablation pits.

Table 4.2: Major element composition (% m/m) of Khan River and Bear Lake titanite

	FKR1 (n = 10)		FKR2 (n = 8)		FKR3 (n = 10)		FKR4 (n = 10)		FKR5 (n = 6)		FKR6 (n = 5)		FBL1 (n = 6)		FBL2 (n = 6)		FBL3 (n = 6)	
	Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD
SiO ₂	29.65	0.61	29.70	0.35	29.59	0.40	29.96	0.58	30.16	0.56	29.82	0.56	30.35	0.31	30.43	0.12	30.38	0.49
TiO ₂	31.98	1.25	32.96	2.30	32.60	0.84	33.17	0.88	32.91	1.64	32.27	0.58	36.51	0.45	36.78	0.27	36.20	0.46
Al ₂ O ₃	1.67	6.77	1.34	7.78	1.37	10.11	1.79	8.38	2.14	12.07	1.95	1.47	1.25	6.29	1.25	2.47	1.25	2.04
FeO	2.62	3.45	2.03	14.09	2.07	17.71	3.14	3.00	3.22	4.69	3.56	1.36	2.08	6.28	2.19	2.73	2.12	1.56
CaO	26.44	0.83	26.42	1.28	26.22	1.66	27.33	0.60	27.15	0.87	26.80	0.28	27.21	0.99	27.65	0.72	27.45	0.66
Nb ₂ O ₅	2.01	11.31	1.74	15.79	1.75	12.81	1.25	6.95	1.27	10.34	1.20	3.84	1.14	8.46	1.08	2.02	1.13	3.30
Na ₂ O	0.04	61.35	0.07	32.75	0.06	35.58	0.05	118.70	0.06	48.45	0.03	70.80	0.32	10.20	0.32	8.59	0.31	8.15
ZrO ₂	0.16	25.96	0.09	98.77	0.07	72.92	0.19	29.76	0.11	53.10	0.22	10.77	0.22	6.02	0.23	12.85	0.24	22.09
Cr ₂ O ₃	0.05	34.29	0.07	50.62	0.08	22.97	0.02	61.17	0.03	55.50	0.02	40.55	0.01	57.94	0.01	81.95	0.01	111.07
V ₂ O ₃	1.65	12.86	2.13	31.27	2.37	17.76	0.67	2.78	0.60	10.79	0.73	2.96	0.08	13.69	0.08	27.17	0.12	11.62
MnO	0.04	30.72	0.13	57.62	0.15	46.95	0.03	43.90	0.04	30.54	0.03	22.98	0.09	6.97	0.09	12.54	0.09	10.57
Ta ₂ O ₅	0.40	37.26	0.38	39.32	0.36	32.94	0.13	51.99	0.14	46.75	0.12	34.29	-	-	-	-	-	-
Total	96.72	0.39	97.07	0.41	96.72	0.48	97.74	0.19	97.83	0.37	96.77	0.22	99.28	0.33	100.10	0.27	99.31	0.42

n = number of data

Major elements reported in % m/m oxide normalized to 100%

Table 4.3: Trace element compositions for the Khan River and Khan titanite

(μg.g-1)	Khan River																	
	FKR1		FKR2		FKR3		FKR4		FKR5		FKR6		FKR7		FKR8		FKR9	
	Average (n=3)	% RSD	Average (n=5)	% RSD	Average (n=3)	% RSD	Average (n=3)	% RSD	Average (n=2)	% RSD	Average (n=3)	% RSD	Average (n=3)	% RSD	Average (n=3)	% RSD	Average (n=3)	% RSD
Sc	38	2.4	13	24.6	12	2.0	35	3.7	32	15.8	13	34.5	10	0.3	51	13.3	19	11.5
Sr	22	2.9	20	4.6	16	1.7	20	5.6	19	2.6	17	7.2	21	4.3	16	0.9	22	8.4
Y	5629	1.5	3048	19.8	2654	0.7	5105	3.8	5169	12.8	2354	10.8	2457	1.7	6979	1.4	3643	6.4
Zr	334	2.0	504	23.2	143	1.1	414	11.7	469	29.6	496	34.7	720	3.8	302	1.0	409	4.8
Nb	12249	1.3	10629	31.1	8471	2.5	11284	11.3	9251	3.8	8307	8.1	6599	11.2	9092	26.8	13951	12.5
La	2988	0.2	2019	27.7	419	1.6	2319	9.4	2238	2.9	1717	44.0	2696	10.8	1594	3.2	1331	8.1
Ce	9534	2.8	6282	20.4	2591	1.0	7654	6.2	7264	6.5	5325	33.1	7560	8.0	5842	2.9	4456	6.7
Pr	1107	0.6	672	14.5	405	0.6	904	5.9	866	10.2	603	22.4	793	5.6	842	3.7	532	5.3
Nd	3810	1.3	2206	14.6	1640	1.2	3149	6.1	3068	9.2	2143	15.6	2657	3.7	3416	2.9	1820	5.0
Sm	810	1.9	404	10.8	382	2.6	686	3.5	685	7.0	408	3.6	461	2.4	887	4.4	363	2.8
Eu	78	2.0	46	14.4	47	1.4	70	4.9	70	6.3	47	3.6	51	1.9	82	8.6	37	2.7
Gd	718	1.6	376	9.7	331	0.8	613	3.5	620	9.1	368	4.0	418	1.5	794	4.1	344	3.1
Tb	119	1.1	60	7.6	59	2.1	106	2.0	107	10.1	57	3.4	61	0.5	146	4.4	59	2.5
Dy	804	1.7	428	8.3	406	1.2	717	2.0	745	9.6	383	6.9	408	1.6	974	2.6	436	5.9
Ho	159	2.7	91	11.2	83	1.3	145	2.5	149	11.0	76	4.2	83	1.3	187	2.3	97	9.7
Er	531	1.7	314	17.4	274	0.9	478	3.1	490	10.2	245	6.4	270	2.6	618	1.6	366	11.9
Tm	103	1.9	59	25.4	50	1.6	91	3.7	93	14.3	41	9.6	45	3.1	116	1.6	75	10.9
Yb	866	1.1	489	31.5	411	1.5	775	7.2	767	15.9	319	16.1	336	3.8	997	1.0	672	6.9
Lu	100	0.5	55	35.7	47	1.5	88	7.7	89	20.1	35	15.5	38	4.9	120	1.7	81	5.6
Hf	26	3.0	36	9.2	20	3.3	29	13.4	31	23.4	36	22.3	46	6.0	22	0.8	31	9.9
Ta	3726	0.7	2816	28.4	2311	2.6	3092	22.6	2133	3.8	1839	10.2	1563	24.3	2490	35.8	3875	18.6
Pb	21	2.7	20	44.3	6	1.8	21	12.5	19	2.9	16	52.5	33	14.6	13	2.5	13	12.1
Th	358	3.0	337	45.2	98	1.8	339	11.3	322	0.9	284	51.7	613	14.0	230	2.0	233	14.5
U	492	1.8	478	22.8	182	2.0	554	9.0	576	0.8	381	47.2	613	1.8	499	4.6	395	5.1

*Compiled from Heaman 2009; **Compiled from Ma et al., 2019

Table 4.3: Continued...

Khan				
(µg.g-1)	Average* (n=21)	SD	Average** (n=21)	2s
Sc	2.2	0.4	-	-
Sr	22	1	23	3.7
Y	3156	111	3404	333
Zr	475	26	306	30
Nb	4340	285	4563	630
La	2265	124	2457	251
Ce	6169	310	6972	650
Pr	797	41	845	69
Nd	3084	141	3252	240
Sm	615	28	636	43
Eu	68	3	71.2	4.9
Gd	514	24	436	33
Tb	90	4	95.1	7.3
Dy	552	24	585	49
Ho	113	5	118	11
Er	325	13	340	34
Tm	52	2	53.7	6.2
Yb	382	15	395	52
Lu	48	2	50.1	7.1
Hf	38	3	39	3.2
Ta	779	89	765	310
Pb	30	10	<5.35	-
Th	565	31	595	83
U	741	25	754	56

Table 4.4: Trace element compositions for the Bear Lake and BLR-1 titanite

Bear Lake									BLR-1		
	FBL1		FBL2		FBL3		FBL4				
($\mu\text{g.g}^{-1}$)	Average (n=3)	% RSD	Average (n=3)	% RSD	Average (n=3)	% RSD	Average (n=4)	% RSD	($\mu\text{g.g}^{-1}$)	Average* (n=20)	2s
Sc	4	2.4	5	3.2	4	0.6	4	4.2	Sc	-	-
Sr	305	1.3	312	1.5	301	0.7	302	0.7	Sr	54.2	20
Y	509	1.3	524	1.7	504	1.2	490	0.6	Y	3652	96
Zr	1194	3.6	1250	1.6	1093	2.7	1060	1.2	Zr	830	36
Nb	5874	2.2	6835	1.8	5615	0.6	5428	1.9	Nb	3797	120
La	384	0.5	408	1.0	372	0.4	360	1.2	La	403	16
Ce	1772	1.2	1881	2.4	1717	0.5	1664	1.5	Ce	1799	70
Pr	275	1.0	287	1.0	262	1.4	255	0.7	Pr	321	8
Nd	1183	0.4	1249	1.3	1164	1.5	1139	1.1	Nd	1646	35
Sm	259	0.6	267	1.4	251	1.2	245	1.6	Sm	527	14
Eu	64	0.8	67	0.2	62	1.8	61	1.2	Eu	86	3.3
Gd	188	0.9	194	0.7	182	0.9	178	0.8	Gd	473	14
Tb	26	1.5	27	1.2	26	0.9	25	1.6	Tb	125	4
Dy	145	0.3	151	0.4	143	1.1	139	1.0	Dy	873	24
Ho	24	1.2	25	1.7	24	1.0	23	1.4	Ho	186	6
Er	63	0.3	66	1.2	62	1.1	60	1.1	Er	516	16
Tm	8	2.1	9	0.3	8	1.3	8	1.7	Tm	69.6	2.4
Yb	50	0.6	52	1.7	48	0.6	48	1.1	Yb	379	11
Lu	4	1.4	5	2.0	4	1.0	4	2.1	Lu	30.9	1.1
Hf	28	4.1	28	2.2	25	1.3	24	1.6	Hf	57.2	3
Ta	212	2.8	252	1.3	187	1.9	187	2.0	Ta	174	7
Pb	36	1.7	40	1.9	33	1.6	32	1.1	Pb	<5.59	-
Th	257	1.2	291	1.2	241	0.6	232	1.2	Th	219	15
U	144	1.2	159	2.5	135	0.6	129	0.7	U	334	20

*Compiled from Ma et al., 2019

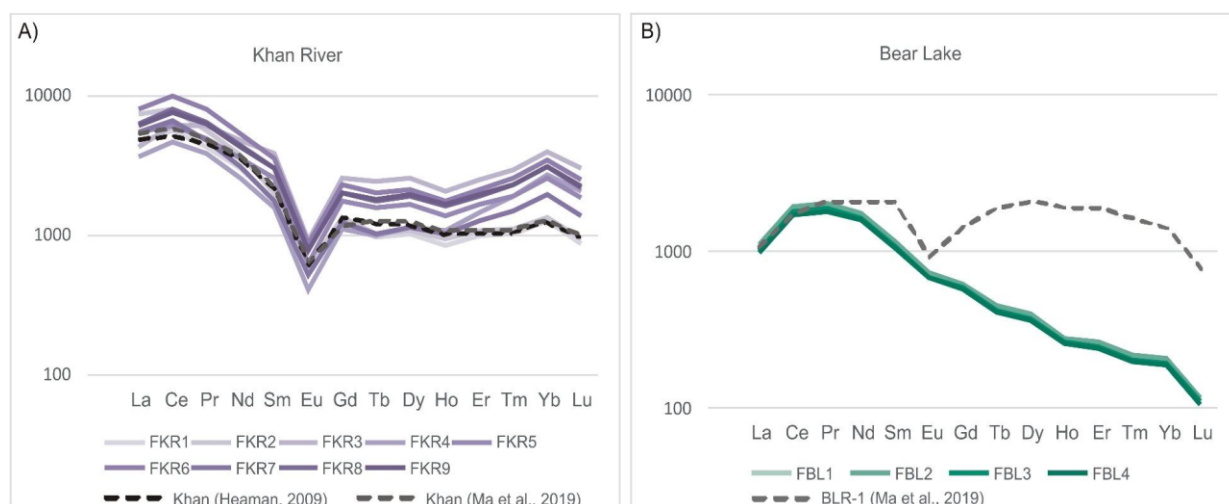


Figure 4.5: Chondrite-normalised (Taylor and McLennan, 1985) trace element composition of A) nine fragments of the Khan River titanite in comparison with previous data of Khan titanite and B) four fragments of the Bear Lake titanite in comparison with previous data of BLR-1 titanite (see discussion).

4.4.3 ID-TIMS U-Pb dates

Table 4.5 presents high-precision U-Pb data obtained from the two independent analytical facilities, University of Oslo and University of Toronto. Five fragments of the Khan River titanite show relatively low (but variable) levels of Pb_c (0.5 to 0.9 $\mu\text{g.g}^{-1}$), and high $^{206}\text{Pb}/^{204}\text{Pb}$ (2637 to 4650). They record consistent $^{206}\text{Pb}/^{238}\text{U}$ ratios, which gave a precise Pb_c -uncorrected weighted mean of 0.08381 ± 0.00027 (2s, MSWD = 3.8) and a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 518.8 ± 1.6 Ma (2s, MSWD = 3.8) (Fig. 4.6A). The $^{207}\text{Pb}/^{206}\text{Pb}$ ratios vary considerably from 0.0603 ± 0.0003 to 0.0624 ± 0.0001 (2s), and the $^{207}\text{Pb}/^{206}\text{Pb}$ ages vary from 614.9 ± 11.8 Ma (2s) to 688.2 ± 1.7 Ma (2s) reflecting variable intake of Pb_c . The estimated initial Pb_c ratio was acquired from the ID-TIMS Pb_c -uncorrected intercept age, plotted on a TW diagram, and calculated using the Stacey & Kramers Pb evolution curve (Stacey & Kramers 1975, $Pb_c = 0.870$). The Pb_c -uncorrected ratios yielded a Tera-Wasserburg lower intercept age of 516.3 ± 1.3 Ma (2s, MSWD = 2.4, anchored at the initial $Pb_c = 0.870$) (Fig. 4.6B). The Pb_c -corrected data produced individual $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios that are internally consistent within uncertainty (Table 4.5) and give weighted mean ratios of 0.08328 ± 0.00026 (2s, MSWD = 4.8) and 0.05760 ± 0.00007 (2s, MSWD = 1.6), respectively, and a concordia age of 515.6 ± 1.3 Ma (2s, MSWD = 2.8) (Fig. 4.6D). The $^{206}\text{Pb}/^{238}\text{U}$ Pb_c -corrected weighted mean age of 515.7 ± 1.6 Ma (2s, MSWD = 4.8) differs by <1% from the uncorrected age (Fig. 4.6C). The Pb_c -corrected $^{207}\text{Pb}/^{206}\text{Pb}$ dates differ by up to 20% from the uncorrected data (Table 4.5).

ID-TIMS U-Pb data for five fragments of the Bear Lake titanite exhibit high levels of Pb_c (2.8 - 3.5 $\mu\text{g.g}^{-1}$) and, consequently, low $^{206}\text{Pb}/^{204}\text{Pb}$ (323 to 354) (Table 4.5). The analyses gave a $^{206}\text{Pb}/^{238}\text{U}$ Pb_c -uncorrected weighted mean ratio of 0.18774 ± 0.00012 (2s, MSWD = 1.07) and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 1109.10 ± 0.66 Ma (2s, MSWD = 1.07) (Fig. 4.7A). The $^{207}\text{Pb}/^{206}\text{Pb}$ ratios varied from 0.1144 ± 0.0002 (2s) to 0.1182 ± 0.0002 (2s) and gave $^{207}\text{Pb}/^{206}\text{Pb}$ dates that range from 1870.6 ± 3.9 (2s) to 1929.3 ± 2.9 (2s) (Table 4.5). The estimated initial Pb_c value for the Bear Lake titanite ($Pb_c = 0.914$) was obtained as described above for Khan River. Pooling the Pb_c -uncorrected analyses together results in a Tera-Wasserburg lower intercept age of 1067.81 ± 0.74 Ma (2s, MSWD = 0.35; anchored at 0.914) (Fig. 4.7B). The Pb_c -corrected $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios overlap within uncertainty of each other (Table 4.5, Fig. 4.7D), giving weighted mean ratios of 0.17867 ± 0.00054 (2s, MSWD = 2.5) and 0.07433 ± 0.00029

(2s, MSWD = 0.03), respectively. The Pb_c-corrected $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios are consistent within uncertainty (Table 4.5), giving a concordia age of 1059.2 ± 1.7 Ma (2s, MSWD = 1.5) (Fig. 4.7D). The $^{206}\text{Pb}/^{238}\text{U}$ Pb_c-corrected weighted mean age of 1059.7 ± 3.0 Ma (2s, MSWD = 2.4) differs by <5% from the uncorrected age (Fig. 4.7C). The Pb_c-corrected $^{207}\text{Pb}/^{206}\text{Pb}$ dates differ by up to 40% from the uncorrected data (Table 4.5).

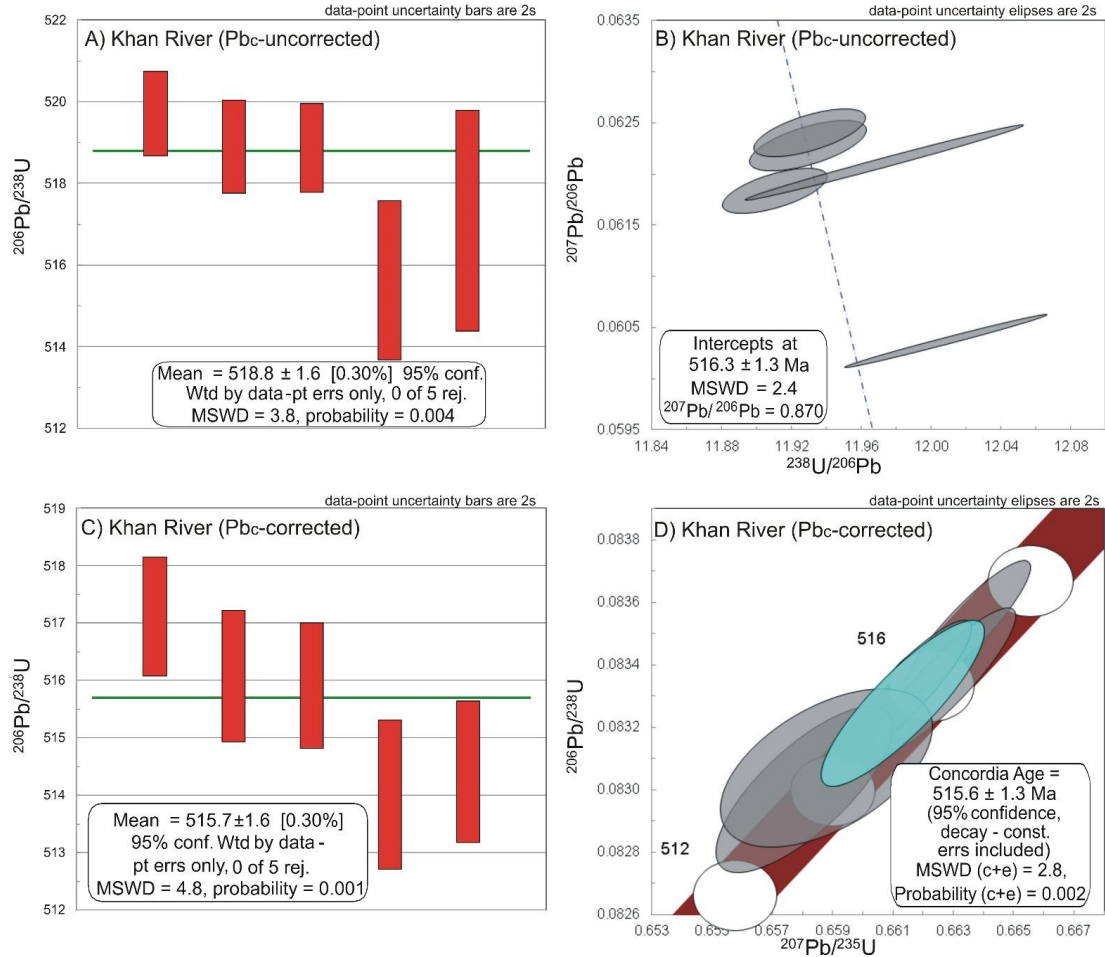


Figure 4.6: Pbc-uncorrected ages (A and B) and -corrected ages (C and D), weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages (A and C) and U-Pb TIMS concordia plots (B and D) for Khan River titanite.

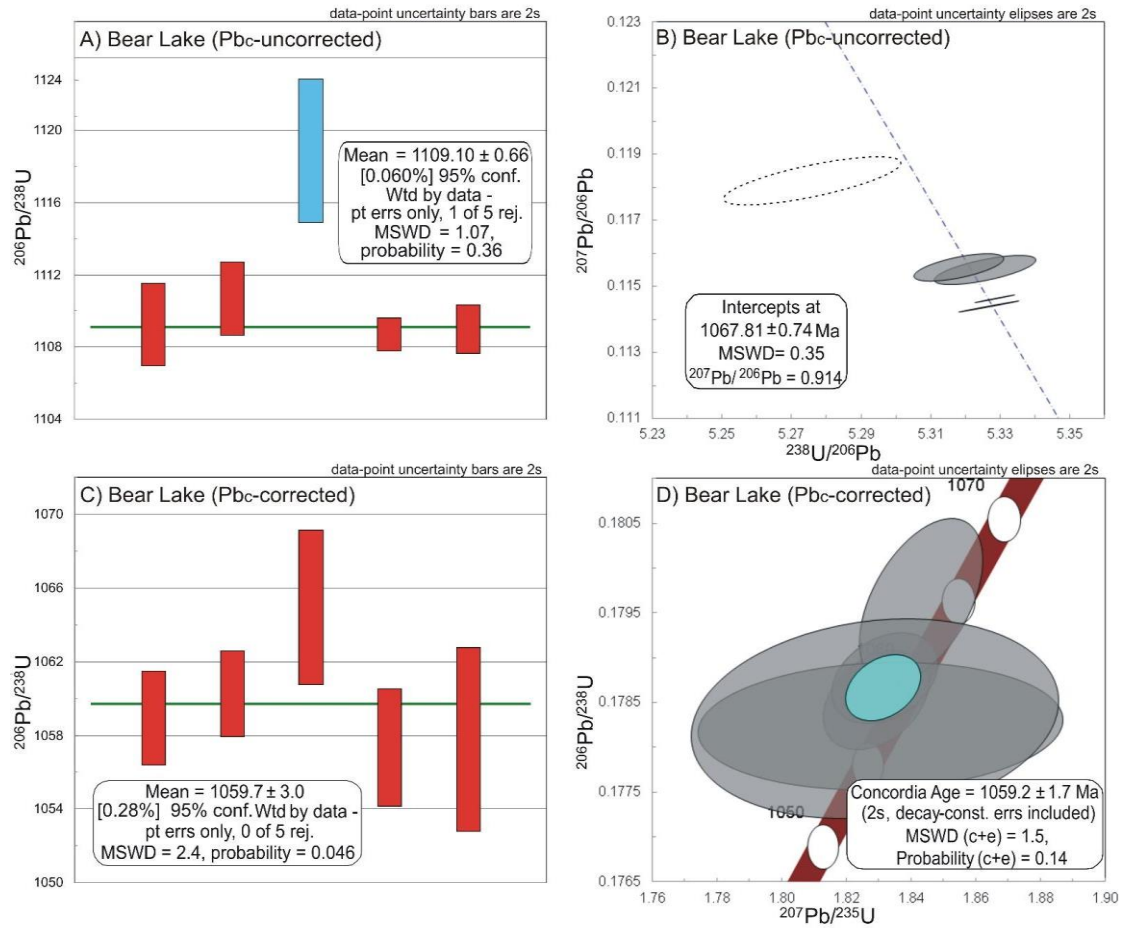


Figure 4.7: Pbc-uncorrected ages (A and B) and -corrected ages (C and D), weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages (A and C) and U-Pb TIMS concordia plots (B and D) for Bear Lake titanite. (A and B) The rejected point and the dashed ellipse were not included in the age calculation.

Table 4.5: ID-TIMS U-Pb results for the Khan River and Bear Lake titanite reference materials

						corrected for common Pb														
Fraction Analyzed	Weight	U	Th/U	Pbc	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²³⁵ U	± 2s	²⁰⁶ Pb/ ²³⁸ U	± 2s	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb	± 2s	²⁰⁶ Pb/ ²³⁸ U	± 2s	²⁰⁷ Pb/ ²³⁵ U	± 2s	²⁰⁷ Pb/ ²⁰⁶ Pb	± 2s	Disc. (%)	
	(ug) (1)	(µg.g-1) (2)	(3)	(pg) (4)	measured (5)	(6)	(abs) (6)	(6)	(abs) (6)	(6)	(6)	(abs) (6)	(6)	(abs) (6)	(6)	(abs) (6)	(abs) (6)	(abs) (6)		
Khan River																				
Oslo																				
FKR1	84	349	0.42	51	3056	0.6635	0.0017	0.0835	0.0002	0.90	0.0576	0.0001	517.1	1.0	516.7	1.0	515.0	2.5	-0.4	
FKR2	49	351	0.44	34	2637	0.6627	0.0019	0.0834	0.0002	0.89	0.0577	0.0001	516.1	1.1	516.3	1.2	517.1	2.9	0.2	
FKR3	87	508	0.51	83	2803	0.6614	0.0018	0.0833	0.0002	0.89	0.0576	0.0001	515.9	1.1	515.5	1.1	513.4	2.7	-0.5	
Toronto																				
FKR4	10	860	0.80	10	4650	0.6580	0.0024	0.0830	0.0002	0.75	0.0575	0.0001	514.0	1.3	513.4	1.5	510.6	5.3	-0.7	
FKR5	12	516	0.61	11	2920	0.6588	0.0029	0.0831	0.0002	0.52	0.0575	0.0002	514.4	1.2	513.9	1.8	511.3	8.2	-0.6	
Recommended values								0.08328	0.00026		0.05757	0.00022	515.7	1.6						
Bear Lake																				
Oslo																				
FBL1	80	86	2.16	239	338	1.8288	0.0133	0.1785	0.0005	0.35	0.0743	0.0005	1059.0	2.5	1055.9	4.8	1049.4	13.7	-1.0	
FBL2	93	91	2.18	296	339	1.8316	0.0134	0.1788	0.0004	0.33	0.0743	0.0005	1060.3	2.3	1056.8	4.8	1049.7	13.8	-1.1	
FBL3	244	99	2.29	892	323	1.8427	0.0156	0.1796	0.0008	0.50	0.0744	0.0005	1065.0	4.2	1060.8	5.6	1052.2	14.7	-1.3	
Toronto																				
FBL4	11	783	2.22	272	353	1.8302	0.0460	0.1782	0.0006	0.10	0.0745	0.0019	1057.4	3.2	1056.4	16.6	1054.3	50.8	-0.3	
FBL5	10	530	2.23	175	354	1.8286	0.0464	0.1783	0.0009	0.18	0.0744	0.0019	1057.8	5.0	1055.8	16.7	1051.5	50.7	-0.7	
Recommended values								0.17867	0.00054		0.07437	0.00023	1059.7	3.0						

Table 4.5: Continued.

not corrected for common Pb												
$^{207}\text{Pb}/^{235}\text{U}$	$\pm 2s$	$^{206}\text{Pb}/^{238}\text{U}$	$\pm 2s$	Rho	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2s$	$^{206}\text{Pb}/^{238}\text{U}$	$\pm 2s$	$^{207}\text{Pb}/^{235}\text{U}$	$\pm 2s$	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2s$
(7)	(abs) (7)	(7)	(abs) (7)	(7)	(7)	(abs) (7)	(7)	(abs) (7)	(7)	(abs) (7)	(7)	(abs) (7)
0.7160	0.0016	0.0840	0.0002	0.11	0.0618	0.0001	519.7	1.0	548.3	1.0	668.7	1.7
0.7199	0.0018	0.0838	0.0002	0.10	0.0623	0.0001	518.9	1.1	550.6	1.1	683.9	2.0
0.7213	0.0017	0.0838	0.0002	0.11	0.0624	0.0001	518.9	1.1	551.4	1.0	688.2	1.7
0.6933	0.0005	0.0833	0.0003	0.71	0.0603	0.0003	515.7	2.0	534.8	0.3	614.9	11.8
0.7154	0.0006	0.0835	0.0005	0.71	0.0621	0.0005	517.1	2.7	547.9	0.4	676.3	15.6
		0.08381	0.00027				518.8	1.6				
2.9908	0.0067	0.1878	0.0004	0.06	0.1155	0.0002	1109.3	2.3	1405.3	1.7	1888.0	2.6
2.9969	0.0068	0.1880	0.0004	0.06	0.1156	0.0002	1110.7	2.0	1406.8	1.7	1889.1	2.9
3.0892	0.0096	0.1895	0.0007	0.08	0.1182	0.0002	1118.9	4.0	1430.0	2.4	1929.3	2.9
2.9669	0.0002	0.1877	0.0002	0.71	0.1147	0.0002	1108.8	0.9	1399.2	0.1	1874.4	2.6
2.9616	0.0004	0.1877	0.0002	0.71	0.1144	0.0002	1109.1	1.4	1397.8	0.1	1870.6	3.9
		0.18774	0.00012				1109.1	0.7				

4.4.4 U-Pb SHRIMP dates

Khan River titanite is zoned as shown by BSE imaging (e.g., Fig. 4.3). The U-Pb analyses obtained from two fragments (FKR1 and FKR2) are within uncertainties of the ID-TIMS results. The spots returned consistent U content but relatively higher Th/U ratios (~ 1.2) compared to the ID-TIMS (~ 0.8) and LA-ICP-MS (~ 0.8) measurements (Table 4.6). Results from the Pb_c -uncorrected Khan River titanite fragments gave a lower intercept age of 521.4 ± 3.6 Ma (2s, $n = 21$, MSWD = 0.69) and a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 524.2 ± 3.3 Ma (2s, $n = 21$, MSWD = 0.80) (Figure 4.8). The ^{207}Pb -corrected $^{206}\text{Pb}/^{238}\text{U}$ ratios gave a small range of dates from 502 to 529 Ma. Several spots on compositionally homogeneous domains gave a weighted mean value of 520.9 ± 3.4 Ma (2s, $n = 21$, MSWD = 0.83) and a concordia age of 519.9 ± 3.3 Ma (2s, $n = 21$, MSWD = 1.03) (see Electronic Supplement - 1).

The results acquired from two fragments (FBL1 and FBL2) of the Bear Lake titanite gave U content and Th/U ratios which are within the same range to those obtained by ID-TIMS (Table 4.6). The obtained Pb_c -uncorrected data for Bear Lake titanite fragments yielded a lower intercept age of 1076.5 ± 8.1 Ma (2s, $n = 24$, MSWD = 0.45) and a weighted mean $^{206}Pb/^{238}U$ age of 1117.3 ± 7.1 Ma (2s, $n = 24$, MSWD = 0.68) (Figure 4.8). Results from the ^{207}Pb -corrected $^{206}Pb/^{238}U$ age exhibited a narrow range from 1045 to 1094 Ma, with weighted mean value of 1068.5 ± 7.2 Ma (2s, $n = 24$, MSWD = 0.55). The analyses provided a concordia age of 1072.2 ± 7.1 Ma (2s, $n = 24$, MSWD = 1.06) (see Electronic Supplement 1).

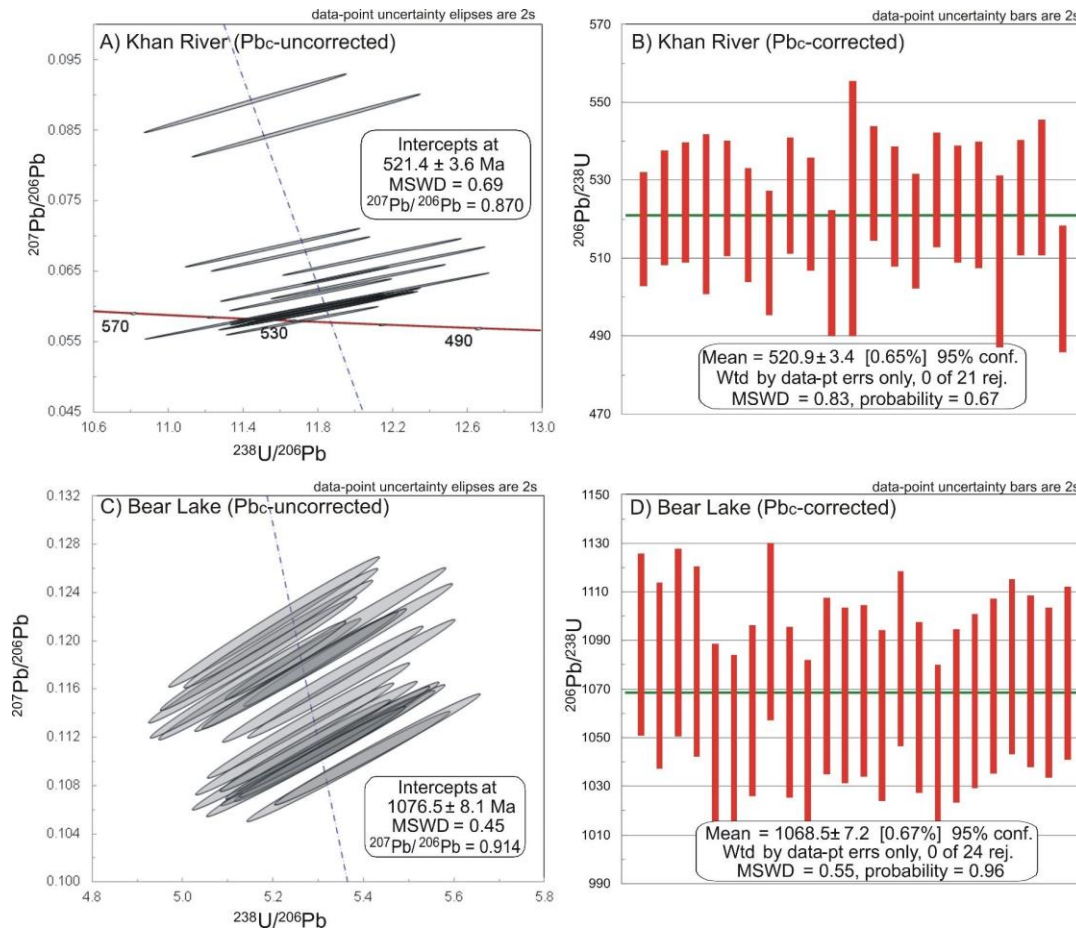


Figure 4.8: Summary of the U-Pb ages obtained via SHRIMP from Khan River and Bear Lake titanite on a Tera-Wasserburg diagram (A and C) and weighted mean $^{206}Pb/^{238}U$ ages (B and D).

Table 4.6: SHRIMP U-Pb data for the Khan River and Bear Lake titanite reference materials

Concentrations			Ratios							Ages						Weighted Average	Intercept date	207corr Weighted Average
Sample	U (µg.g-1)	Th/U	²⁰⁷ Pb/ ²⁰⁶ Pb	2s%	²⁰⁷ Pb/ ²³⁵ U	2s%	²⁰⁶ Pb/ ²³⁸ U	2s%	RHO	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁶ Pb/ ²³⁸ U		²⁰⁶ Pb/ ²³⁸ U
Khan River																		
FKR1	418	1.2	0.0646	2.3	0.7558	0.2	0.0847	3.0	0.07	741	48	570	1	524	8	524 ± 5	520 ± 5	520 ± 5
FKR2	393	1.3	0.0638	3.2	0.7463	0.2	0.0849	3.4	0.07	717	67	565	1	525	9	525 ± 5	523 ± 5	522 ± 5
Bear Lake																		
FBL1	110	3.1	0.1178	2.2	3.0903	0.4	0.1902	3.5	0.13	1922	40	1430	3	1123	37	1122 ± 10	1078 ± 12	1075 ± 9
FBL2	122	3.0	0.1121	2.1	2.9136	0.4	0.1885	3.4	0.13	1832	37	1385	3	1113	35	1113 ± 10	1075 ± 11	1069 ± 10

4.4.5 LA-ICP-MS U-Pb geochronology

LA-(MC/SF)-ICP-MS results for individual grains of the Khan River and Bear Lake titanites are presented in Tables 4.7 and 4.8 and illustrated in Figure 4.9. The full dataset can be found in the online supporting information (Electronic Supplement - 1, Figure S1). No Pb_c correction was applied. The Pb_c -uncorrected ratios are plotted on a Tera-Wasserburg diagram anchored through Pb_c (obtained by Stacey and Kramers, 1975), using a two-stage terrestrial Pb evolution model for the approximate age of the titanite.

Reproducibility tests via LA-SF/MC-ICP-MS from nine fragments of the Khan River titanite are within uncertainty of the ID-TIMS values (Table 4.7). The U content and the Th/U ratio are in agreement with the ID-TIMS values. LA-SF-ICP-MS analyses from the fragments yielded a lower intercept age of $519 \pm 1/5$ Ma (2s, MSWD = 1.3, n = 175) and a weighted mean $^{206}Pb/^{238}U$ age of $521 \pm 1/5$ Ma (2s, MSWD = 1.07) (see Supporting Information). LA-MC-ICP-MS data points returned a lower intercept age of $516 \pm 1/5$ Ma (2s, MSWD = 1.09, n = 87) and a weighted mean $^{206}Pb/^{238}U$ age of $518 \pm 1/5$ Ma (2s, MSWD = 1.04) (see Supporting Information). Combining all U-Pb LA-SF/MC-ICP-MS analyses gave an intercept age of $517 \pm 1/5$ Ma (2s, n = 262, MSWD = 1.5) and a weighted mean $^{206}Pb/^{238}U$ age of $518 \pm 1/5$ Ma (2s, n = 262, MSWD = 0.56) (Fig. 4.8A and B). One fragment (FKR1) from the batch gave a rather old date and was not considered further. This fragment was slightly different from the other in terms of color (dark brown) and with respect to the older dates, might indicate inheritance.

Reproducibility tests via LA-SF/MC-ICP-MS from eight fragments of the Bear Lake titanite resulted in dates within uncertainty of the Pb_c -uncorrected ID-TIMS data (Table 4.8). U and Th/U of individual spot analyses vary slightly within and between the grains, but are all in good agreement with the ID-TIMS data. LA-SF-ICP-MS analyses from the eight fragments yielded a lower intercept age of $1072 \pm 2/11$ Ma (2s, MSWD = 0.57, n = 154), and a Pb_c -uncorrected $^{206}Pb/^{238}U$ weighted mean age of $1113 \pm 1/11$ Ma (2s, MSWD = 0.72) (see Supporting Information). LA-MC-ICP-MS analyses returned a lower intercept age of $1070 \pm 1/11$ Ma (2s, MSWD = 1.14, n = 171) and a Pb_c -uncorrected $^{206}Pb/^{238}U$ weighted mean age of $1112 \pm 1/11$ Ma (2s, MSWD = 1.17) (see Supporting Information). The total of U-Pb LA-SF/MC-ICP-MS analyses gave an intercept age of $1070 \pm 1/11$ Ma (2s, n = 325, MSWD = 0.88) and a - Pb_c uncorrected - weighted mean $^{206}Pb/^{238}U$ age of $1112 \pm 1/11$ Ma (2s, n = 325, MSWD = 0.96) (Fig. 4.8C and D).

4.4.6 Use as secondary reference materials for LA-ICP-MS U-Pb dating

The Khan River and Bear Lake titanite were tested as reference materials to correct the matrix-related offset on the $^{206}\text{Pb}/^{238}\text{U}$ ratios. Zircon (GJ-1) was used as the main calibrant to correct for mass bias and instrument drift. Known titanite reference materials (MKED1, Spandler *et al.* 2016; OLT1, Kennedy *et al.* 2010; Mount Painter titanite, Elburg *et al.* 2003) were used and treated as unknowns (Table 4.9, Figure 4.10). More detailed results can be found in the online supporting information (Electronic Supplement – 1, Figure S2 and S3). The chemically abraded grains (this study) were also used as unknowns to verify the reproducibility of the analysis between treated and untreated fragments. The analytical procedures were identical to the previous LA-SF-ICP-MS data reported above at UFOP. The $^{206}\text{Pb}/^{238}\text{U}$ values used for normalisation were the averaged ID-TIMS Pb_c -uncorrected $^{206}\text{Pb}/^{238}\text{U}$ data (Table 4.5). The tests were done in two separate runs.

The first run used the untreated Khan River titanite, from which nineteen self-normalised spots gave an intercept age of $517 \pm 5/7$ Ma (2s, MSWD = 0.51) and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $518 \pm 5/7$ Ma (2s, MSWD = 0.53). The same normalising factor (1%) as used for untreated Khan River was applied to Bear Lake (without chemical abrasion), Khan River (chemically abraded), MKED1, OLT1 and Mount Painter titanite as unknowns (Table 4.9 and Figure 4.10). The untreated Bear Lake titanite produced a weighted mean Pb_c -uncorrected $^{206}\text{Pb}/^{238}\text{U}$ age of $1111 \pm 7/13$ Ma (2s, MSWD = 0.75, $n = 12$) and an intercept age of $1068 \pm 7/13$ Ma (2s, MSWD = 0.87, $n = 12$) in agreement with our previous ID-TIMS (Pb_c -uncorrected) and LA-ICP-MS data. The chemically abraded Khan River gave a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $518 \pm 9/10$ Ma (2s, $n = 11$, MSWD = 0.21) and an intercept age of $517 \pm 9/10$ Ma (2s, $n = 11$, MSWD = 0.24), consistent with our reported ID-TIMS and LA-ICP-MS data (chemically abraded fragments). MKED1 titanite (1517.3 ± 0.3 Ma, Spandler *et al.* 2016) gave a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $1516 \pm 11/19$ Ma (2s, MSWD = 0.47, $n = 10$) and a concordia age of $1517 \pm 13/20$ Ma (2s, MSWD = 2.1, $n = 10$). OLT1 titanite (1015 ± 2 Ma, Kennedy *et al.* 2010) yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $1024 \pm 7/12$ Ma (2s, MSWD = 0.63, $n = 11$) and an intercept age of $1014 \pm 7/12$ Ma (2s, MSWD = 0.64, $n = 11$). Finally, Mount Painter titanite (439 ± 1 Ma, Elburg *et al.* 2003) yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $448 \pm 4/6$ Ma (2s, MSWD = 1.07, $n = 10$) and an intercept age of $440 \pm 4/6$ Ma (2s, MSWD = 0.73, $n = 10$).

The second run used the untreated Bear Lake titanite, from which twenty self-normalised analyses produced an intercept age of $1069 \pm 5/12$ Ma (2s, MSWD = 1.09) and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $1111 \pm 6/13$ Ma (2s, MSWD = 1.16). The same normalising factor (1%) as used for untreated Bear Lake was applied to Khan River (without chemical abrasion), Bear Lake (chemically abraded), MKED1, OLT1 and Mount Painter titanite as unknowns (Table 4.9 and Figure 4.10). The untreated Khan River titanite produced a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $517 \pm 7/9$ Ma (2s, MSWD = 0.56, n = 11) and an intercept age of $516 \pm 7/9$ Ma (2s, MSWD = 0.60, n = 11). The chemically abraded Bear Lake titanite was analysed to verify the homogeneity related to the untreated fragments and produced a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $1113 \pm 6/13$ Ma (2s, n = 12, MSWD = 0.43) and an intercept age of $1072 \pm 6/12$ Ma (2s, n = 12, MSWD = 0.45). MKED1 titanite produced a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $1516 \pm 11/19$ Ma (2s, MSWD = 0.37, n = 11) and concordia age of $1515 \pm 8/17$ Ma (2s, MSWD = 1.14, n = 11). The data acquired from OLT1 titanite gave a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $1024 \pm 7/12$ Ma (2s, n = 11, MSWD = 0.79) and an intercept age of $1013 \pm 8/13$ Ma (2s, n = 11, MSWD = 0.90). Lastly, the Mount Painter titanite showed a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $446 \pm 10/11$ Ma (2s, n = 12, MSWD = 0.071) and intercept age of $441 \pm 10/11$ Ma (2s, n = 12, MSWD = 0.16).

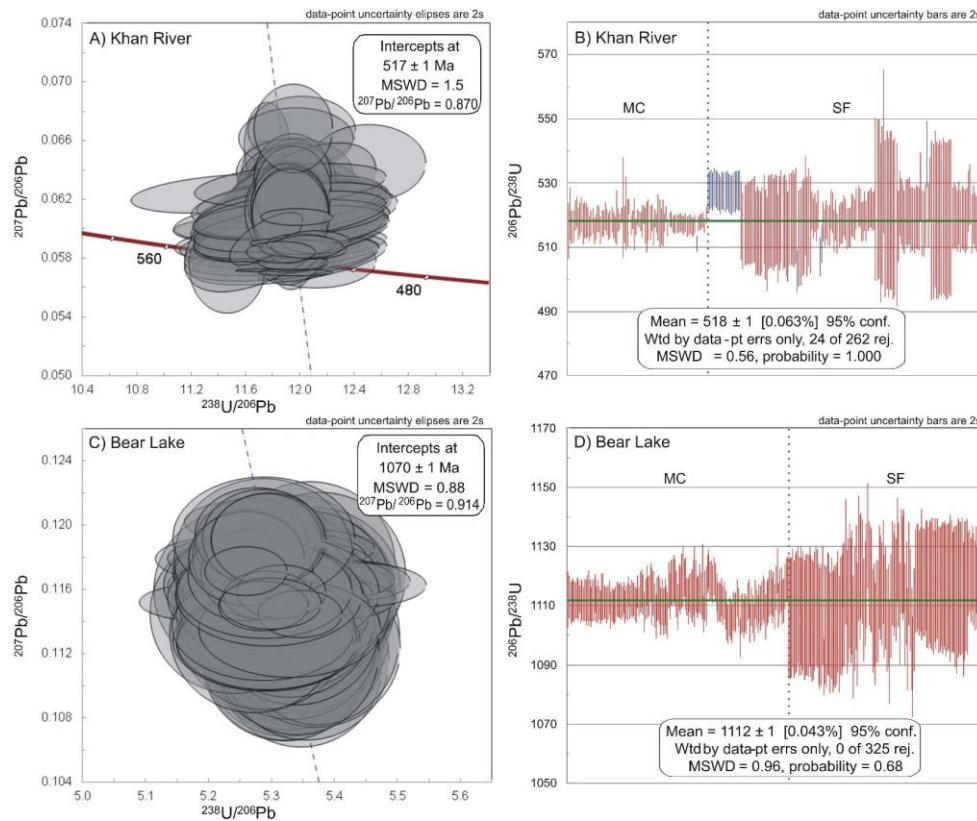


Figure 4.9: Compilation of the U-Pb ages obtained via LA-SF/MC-ICP-MS from the studied titanites on a Tera-Wasserburg diagram (A and C) and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages (B and D). The regression was anchored on the initial common lead determined using the Stacey and Kramers (1975) evolution model.

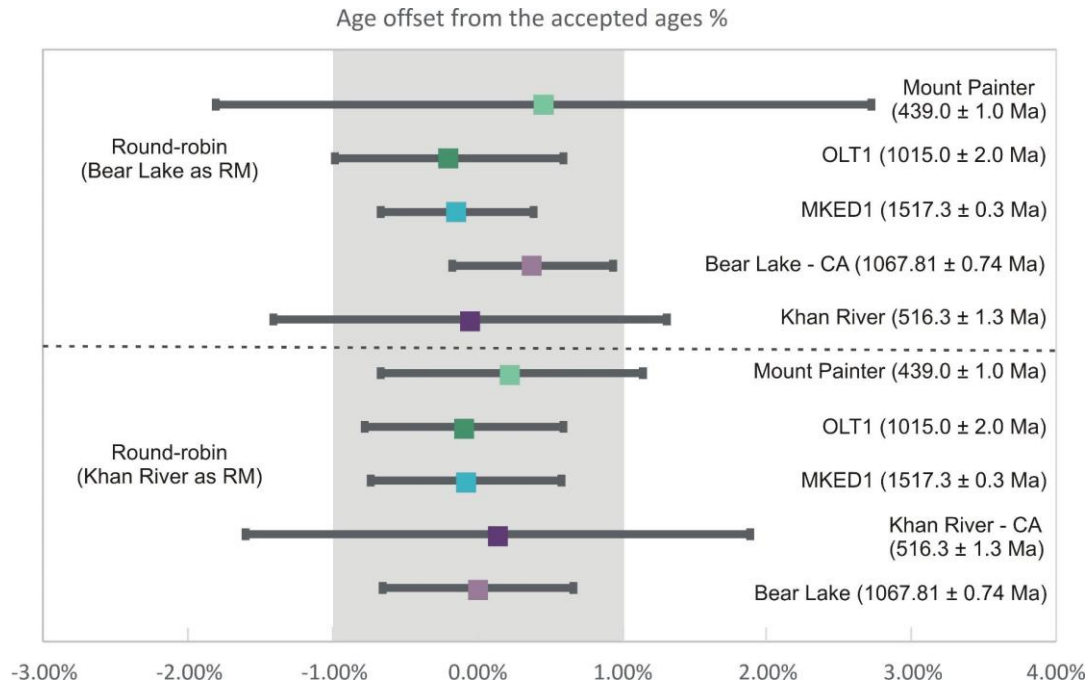


Figure 4.10: Offset from the accepted U-Pb ages from the reference materials tested in the round-robin analysis treated as unknowns. The ages are reported as concordia age (Mount Painter, OLT1), $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age (MKED1) and intercept age (Khan River and Bear Lake). For more details, see Table 4.1.

Table 4.7: Summary of U-Pb LA-ICP-MS analyses for the Khan River titanite

Concentrations				Ratios*							max/min dates
Sample	²⁰⁷ Pb CPS	U (µg.g-1)	Th/U	²⁰⁷ Pb/ ²⁰⁶ Pb	2s%	²⁰⁷ Pb/ ²³⁵ U	2s%	²⁰⁶ Pb/ ²³⁸ U	2s%	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb
<i>LA-SF-ICP-MS</i>											
FKR1 (n=21)	1110769	505	0.70	0.0622	4.0	0.7179	4.0	0.0853	1.2	0.30	830-627
FKR2 (n=36)	1333775	505	0.69	0.0615	4.0	0.7073	4.0	0.0834	2.8	0.69	828-522
FKR3 (n=8)	722279	446	0.75	0.0608	4.0	0.7000	4.0	0.0835	3.1	0.76	659-617
FKR4 (n=40)	840981	484	0.70	0.0602	4.0	0.6956	4.0	0.0838	1.2	0.31	695-551
FKR5 (n=14)	385367	433	0.77	0.0597	4.5	0.6944	4.5	0.0844	4.9	0.91	688-528
FKR6 (n=21)	361930	408	0.92	0.0609	4.4	0.7066	4.4	0.0842	2.0	0.47	717-510
FKR7 (n=13)	450274	379	0.88	0.0608	4.4	0.7033	4.4	0.0838	4.9	0.82	708-588
FKR8 (n=10)	462620	389	0.85	0.0622	4.4	0.7187	4.4	0.0838	1.9	0.44	832-634
FKR9 (n=12)	579012	424	0.79	0.0586	1.9	0.6764	1.9	0.0837	1.8	0.84	633-493
<i>LA-MC-ICP-MS</i>											
FKR1 (n=15)	16244	562	0.84	0.0617	1.1	0.7120	1.7	0.0837	1.1	0.66	772-602
FKR2 (n=16)	16096	566	0.82	0.0608	0.9	0.7010	1.3	0.0836	0.9	0.67	758-586
FKR3 (n=17)	24651	559	0.62	0.0636	0.6	0.7087	1.3	0.0838	1.0	0.80	731-569
FKR4 (n=18)	25183	576	0.72	0.0625	0.5	0.7147	1.0	0.0836	0.9	0.86	744-570
FKR5 (n=13)	21448	548	0.75	0.0593	0.5	0.6829	0.8	0.0835	0.6	0.78	647-538
FKR6 (n=8)	24960	587	0.75	0.0592	0.5	0.6812	0.7	0.0835	0.6	0.76	611-549

*ratios, dates and uncertainties are arithmetic average of the spots from individual fragments

**anchored at Pb_c = 0.870

Table 4.7: Continued.

Dates*						Weighted Average	Intercept age**
²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁶ Pb/ ²³⁸ U	
<i>LA-SF-ICP-MS</i>							
680	85	549	17	527	6	527 ± 1	526 ± 1
656	86	543	17	516	14	516 ± 2	514 ± 2
633	87	539	17	517	15	517 ± 5	515 ± 5
611	87	536	17	519	6	519 ± 1	517 ± 1
591	98	535	19	522	25	522 ± 7	521 ± 7
634	94	543	19	521	10	521 ± 2	520 ± 2
634	94	541	18	519	24	519 ± 7	517 ± 7
679	95	550	19	519	10	519 ± 3	516 ± 3
553	42	525	8	518	9	518 ± 3	517 ± 3
<i>LA-MC-ICP-MS</i>							
669	9	545	7	518	5	518 ± 1	516 ± 1
638	7	539	6	517	4	517 ± 1	516 ± 1
655	8	543	6	519	5	519 ± 4	517 ± 1
678	6	547	4	518	5	518 ± 1	516 ± 1
578	10	529	3	517	3	517 ± 1	516 ± 1
572	10	527	3	517	3	518 ± 1	517 ± 2

Table 4.8: Summary of U-Pb LA-ICP-MS analyses for the Bear Lake titanite

Concentrations				Ratios*							max/min dates
Sample	²⁰⁷ Pb CPS	U (µg·g ⁻¹)	Th/U	²⁰⁷ Pb/ ²⁰⁶ Pb	2s%	²⁰⁷ Pb/ ²³⁵ U	2s%	²⁰⁶ Pb/ ²³⁸ U	2s%	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb
<i>LA-SF-ICP-MS</i>											
FBL1 (n=28)	224208	147	1.74	0.1131	4.2	2.9199	4.2	0.1872	2.0	0.48	1908-1722
FBL2 (n=14)	208661	137	1.86	0.1142	4.2	2.9422	4.2	0.1868	2.0	0.49	1920-1827
FBL3 (n=14)	163891	147	1.74	0.1151	4.1	2.9918	4.1	0.1885	2.1	0.50	1909-1852
FBL4 (n=21)	260088	137	1.60	0.1159	1.9	3.0151	1.9	0.1888	1.7	0.89	1960-1853
FBL5 (n=21)	202433	125	1.72	0.1166	2.0	3.0282	2.0	0.1883	1.7	0.87	1934-1883
FBL6 (n=11)	16843	120	1.74	0.1149	2.0	3.0007	2.7	0.1895	1.8	0.68	1900-1857
FBL7 (n=20)	15604	140	1.73	0.1155	2.0	3.0115	2.9	0.1891	2.1	0.72	1925-1852
FBL8 (n=25)	21935	121	1.67	0.1162	1.9	3.0289	2.5	0.1890	1.7	0.66	1947-1841
<i>LA-MC-ICP-MS</i>											
FBL1 (n=28)	25167	149	1.70	0.1151	0.4	2.9882	0.6	0.1882	0.7	0.91	1904-1865
FBL2 (n=14)	23885	142	1.84	0.1154	0.4	2.9925	0.5	0.1881	0.6	0.93	1890-1882
FBL3 (n=14)	22478	132	1.86	0.1153	0.4	2.9922	0.5	0.1882	0.6	0.87	1892-1878
FBL4 (n=20)	21311	104	2.24	0.1158	0.4	3.0058	0.9	0.1883	0.7	0.85	1969-1875
FBL5 (n=25)	20318	116	2.23	0.1155	0.5	3.0064	1.0	0.1888	0.8	0.82	1916-1856
FBL6 (n=15)	17186	127	2.19	0.1157	0.7	3.0175	1.1	0.1891	0.7	0.69	1927-1873
FBL7 (n=33)	16536	101	2.19	0.1155	0.5	2.9876	0.8	0.1875	0.6	0.77	1929-1879
FBL8 (n=22)	25405	117	2.17	0.1152	0.3	2.9941	0.8	0.1885	0.7	0.92	1892-1865

*ratios, dates and uncertainties are arithmetic average of the spots from individual fragments

**anchored at Pb_c = 0.914

Table 4.8: Continued.

Dates*						Weighted Average	Intercept age**
²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁶ Pb/ ²³⁸ U	
<i>LA-SF-ICP-MS</i>							
1850	76	1387	32	1106	20	1106 ± 4	1067 ± 4
1867	76	1393	31	1104	20	1104 ± 5	1064 ± 6
1882	73	1406	32	1113	21	1113 ± 6	1072 ± 6
1893	35	1411	15	1115	18	1115 ± 4	1073 ± 4
1905	35	1415	15	1112	17	1113 ± 5	1069 ± 4
1878	35	1408	21	1119	19	1119 ± 6	1078 ± 6
1888	36	1410	22	1116	21	1116 ± 5	1075 ± 5
1898	34	1415	19	1116	17	1116 ± 3	1073 ± 3
<i>LA-MC-ICP-MS</i>							
1882	8	1405	5	1112	7	1112 ± 1	1070 ± 1
1886	7	1406	4	1111	6	1111 ± 2	1069 ± 2
1884	7	1406	4	1112	6	1112 ± 2	1070 ± 2
1892	8	1409	7	1112	7	1112 ± 2	1070 ± 2
1887	10	1409	7	1115	8	1115 ± 2	1073 ± 2
1891	13	1412	8	1116	7	1117 ± 2	1074 ± 2
1888	10	1404	6	1108	7	1108 ± 1	1066 ± 1
1883	6	1406	6	1113	8	1113 ± 2	1072 ± 2

Table 4.9: Summary of U-Pb analyses from the experiments involving Khan River and Bear Lake titanite as calibrant to correct the $^{206}\text{Pb}/^{238}\text{U}$ ratios

Concentrations				Ratios*						
Sample	^{207}Pb CPS	U ($\mu\text{g}\cdot\text{g}^{-1}$)	Th/U	$^{207}\text{Pb}/^{206}\text{Pb}$	2s%	$^{207}\text{Pb}/^{235}\text{U}$	2s%	$^{206}\text{Pb}/^{238}\text{U}$	2s%	RHO
<i>Khan River as secondary reference material</i>										
Bear Lake (n = 12)	11116	117	1.86	0.1170	1.6381	3.0356	2.8428	0.1881	2.3227	0.82
Khan River (CA) (n = 11)	15692	666	0.71	0.0604	3.1245	0.6962	7.1796	0.0836	6.4611	0.90
MKED1 (n = 12)	17249	155	2.25	0.0939	1.8357	3.4308	3.3551	0.2649	2.8053	0.83
OLT1 (n = 11)	21814	338	0.92	0.0842	1.6724	2.0026	2.9486	0.1725	2.4265	0.82
Mount Painter (n = 10)	2911	149	2.37	0.0717	4.8690	0.7121	5.8637	0.0720	3.0910	0.58
<i>Bear Lake as secondary reference material</i>										
Khan River (n = 11)	16386	558	0.71	0.0598	2.1820	0.6904	5.0613	0.0837	4.5659	0.90
Bear Lake (CA) (n = 12)	11869	102	2.33	0.1145	1.2410	2.9809	2.4810	0.1886	2.1486	0.88
MKED1 (n = 11)	20513	150	2.20	0.0947	1.7076	3.4642	3.3321	0.2652	2.8594	0.86
OLT1 (n = 11)	26772	344	0.86	0.0844	1.6583	2.0086	3.2902	0.1726	2.8397	0.86
Mount Painter (n = 12)	2926	122	2.39	0.0661	6.4820	0.6516	10.6126	0.0715	8.3090	0.79

*ratios, dates and uncertainties are arithmetic average of the spots from individual fragments

Table 4.9: Continued.

Dates*						Weighted Average	Intercept/ concordia age
²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁶ Pb/ ²³⁸ U	
1911	29	1417	22	1111	24	1111 ± 7	1068 ± 7
616	67	536	30	518	32	518 ± 9	517 ± 9
1506	35	1511	27	1515	38	1516 ± 11	1517 ± 13
1296	33	1116	20	1026	23	1024 ± 7	1014 ± 7
973	99	546	25	448	13	448 ± 4	440 ± 4
594	47	533	21	518	23	517 ± 7	516 ± 7
1874	22	1403	19	1114	22	1113 ± 6	1072 ± 6
1523	32	1519	27	1516	39	1516 ± 11	1515 ± 8
1302	32	1118	23	1027	27	1024 ± 7	1013 ± 8
791	135	508	44	445	36	446 ± 10	441 ± 10

4.4.7 Nd and Sm-Nd isotope solution MC-ICP-MS

The results of bulk Nd isotope measurements of Khan River and Bear Lake titanites obtained at the laboratory of CPGeo-USP and SKLLE are shown in Table 4.10 and Figure 4.11.

At CPGeo, the present-day $^{143}\text{Nd}/^{144}\text{Nd}$ of the Khan River titanite (FKR2 and FKR3) agree within uncertainty (2s, 0.511586 ± 0.000005 and 0.511590 ± 0.000005 , respectively), yielding a weighted mean of 0.511587 ± 0.000027 (2s, MSWD = 1.3) (Figure 4.11A). At SKLLE, the measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of Khan River titanite was higher, ranging from 0.511614 ± 0.000008 (2s) to 0.511679 ± 0.000009 (2s) (Figure 4.11A). The present-day $^{147}\text{Sm}/^{144}\text{Nd}$ ratio gave distinct values, ranging from 0.1053 to 0.1344 (uncertainties not calculated).

At CPGeo, the Nd isotope composition of two fragments of the Bear Lake titanite (FBL1 and FBL2) showed identical $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.512321 ± 0.000005 and 0.512321 ± 0.000006 , respectively (at 2s), with a weighted mean of 0.512321 ± 0.000004 (2s, MSWD = 0.001) (Figure 4.11B). The weighted mean of the $^{145}\text{Nd}/^{144}\text{Nd}$ ratio from all samples is 0.348419 ± 0.000002 , in agreement with the canonical value of 0.348415 ± 0.000005 (Wasserburg *et al.* 1981). At SKLLE, the measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratio showed homogenous results that agree within uncertainty, with a slightly variation from 0.512309 ± 0.000011 (2s) to 0.512323 ± 0.000010 (2s) and weighted mean of 0.512317 ± 0.000020 (2s, MSWD = 1.8) (Figure 4.11B). The $^{147}\text{Sm}/^{144}\text{Nd}$ ratios also showed similar values ranging from 0.1324 to 0.1329 (uncertainties not calculated).

4.4.8 In-situ Sm-Nd isotope measurements

The LA-MC-ICP-MS Sm-Nd isotope compositions from the Khan River and Bear Lake titanite samples, measured at two independent laboratories (UFOP and SKLLE), are presented in Table 4.10.

At UFOP, averaged $^{143}\text{Nd}/^{144}\text{Nd}$ ratios from FKR2, FKR3 FKR5, FKR6, FKR7 and FKR8 range from 0.51156 ± 0.00003 (2s) to 0.51163 ± 0.00003 (2s), agreeing well with $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the MC-ICP-MS solution data (Figure 4.11A). Fragment FKR4 gave a mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio that deviates from the solution data by <0.012%. The $^{147}\text{Sm}/^{144}\text{Nd}$ ratios show distinct isotope compositions between the chips. Fragments FKR2, FKR3, FKR6 and FKR7 gave more consistent mean values, varying from 0.0944 ± 0.0002 (2s) to 0.0995 ± 0.0002 (2s). FKR4 and FKR5 record slightly higher $^{147}\text{Sm}/^{144}\text{Nd}$

mean ratios of 0.1120 ± 0.0003 (2s) and 0.1047 ± 0.0003 (2s), respectively. FKR8 presented a higher value of 0.1317 ± 0.0003 (2s). At SKLLE, the mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of three fragments of the Khan River titanite (FKR5, FKR6 and FKR7) showed a small variation from 0.51158 ± 0.00003 (2s) to 0.51161 ± 0.00003 (2s) (Figure 4.11A). FKR6 and FKR7 fragments gave $^{147}\text{Sm}/^{144}\text{Nd}$ ratios which were the same within uncertainty of 0.0998 ± 0.0001 (2s) and 0.0999 ± 0.0002 (2s), respectively. FKR5 showed a slightly higher $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.1047 ± 0.0001 (2s). Initial epsilon Nd values (ϵNd_i) for the Khan River titanite range from -15.4 ± 0.7 (2s) to -13.7 ± 0.7 (2s) and are consistent with a crustal source (Table 4.10) for the host pegmatite. The averaged $^{143}\text{Nd}/^{144}\text{Nd}_i$ ratios for the different fragments (using as reference the U-Pb ID-TIMS age) overlap within uncertainty. The invariant $^{145}\text{Nd}/^{144}\text{Nd}$ is within uncertainty with the canonical value from Wasserburg *et al.* (1981).

The Sm-Nd LA-MC-ICP-MS isotope composition of four crystal fragments from Bear Lake titanite is relatively homogeneous (Table 4.10). At UFOP, the mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for individual fragments vary from 0.51227 ± 0.00004 (2s) to 0.51231 ± 0.00005 (2s), all consistent with the solution MC-ICP-MS data (Figure 4.11). The mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratios range from 0.1331 ± 0.0003 (2s) to 0.1325 ± 0.0003 (2s). At SKLLE, the averaged $^{147}\text{Sm}/^{144}\text{Nd}$ ratios for two of these fragments are 0.1334 ± 0.0001 (2s) and 0.1332 ± 0.0001 (2s). The mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are 0.51234 ± 0.00003 (2s) and 0.51233 ± 0.00003 (2s) and are all within uncertainty of the solution MC-ICP-MS results (Figure 4.11). The pooled $^{145}\text{Nd}/^{144}\text{Nd}$ ratio of 0.34839 ± 0.00002 is consistent with the canonical value of 0.348415 ± 0.000005 (Wasserburg *et al.* 1981). The ϵNd_i values of Bear Lake titanite vary from 1.5 ± 0.9 (2s) to 2.8 ± 0.7 (2s), revealing a juvenile source for the protolith. The weighted mean of the $^{145}\text{Nd}/^{144}\text{Nd}$ ratio of 0.34840 ± 0.00003 is again in agreement with the canonical value of 0.348415 ± 0.000005 (Wasserburg *et al.* 1981).

Table 4.10: Sm-Nd isotopic composition of the Khan River and Bear Lake titanites samples and reference materials by MC-ICP-MS

Sample	$\frac{^{147}\text{Sm}}{^{144}\text{Nd}}$	$\pm 2s$	$\frac{^{143}\text{Nd}}{^{144}\text{Nd}}$	$\pm 2s$	$\frac{^{143}\text{Nd}}{^{144}\text{Nd}_i}$	$\pm 2s$	$\frac{^{145}\text{Nd}}{^{144}\text{Nd}}$	$\pm 2s$	eNd _i	$\pm 2s$	Reference Age (Ma)
Khan River											
<i>Solution ICP-MS at CPGeo</i>											
FKR2	-	-	0.511586	0.000005	-	-	0.348419	0.000002	-	-	
FKR3	-	-	0.511590	0.000005	-	-	0.348420	0.000002	-	-	
<i>Solution ICP-MS at SKLLE</i>											
FKR1	0.1307	-	0.511664	0.000006	-	-	-	-	-	-	
FKR2	0.1344	-	0.511679	0.000009	-	-	-	-	-	-	
FKR3	0.1125	-	0.511628	0.000007	-	-	-	-	-	-	516
FKR4	0.1053	-	0.511614	0.000008	-	-	-	-	-	-	
<i>LA-ICP-MS at UFOP</i>											
FKR2 (n=15)	0.0980	0.0002	0.51158	0.00005	0.51125	0.00005	0.34840	0.00004	-14.2	0.8	
FKR3 (n=5)	0.0944	0.0002	0.51156	0.00003	0.51124	0.00003	0.34841	0.00003	-14.4	0.6	
FKR4 (n=5)	0.1120	0.0003	0.51165	0.00003	0.51127	0.00003	0.34841	0.00003	-13.7	0.7	
FKR5 (n=5)	0.1047	0.0003	0.51163	0.00003	0.51127	0.00003	0.34840	0.00003	-13.7	0.7	
FKR6 (n=5)	0.0992	0.0002	0.51160	0.00003	0.51127	0.00003	0.34840	0.00003	-13.8	0.7	
FKR7 (n=5)	0.0995	0.0002	0.51160	0.00003	0.51127	0.00003	0.34840	0.00003	-13.8	0.7	
FKR8 (n=15)	0.1317	0.0003	0.51163	0.00004	0.51118	0.00004	0.34841	0.00002	-15.4	0.7	
<i>LA-ICP-MS at SKLLE</i>											
FKR5 (n=20)	0.1047	0.0001	0.51161	0.00003	0.51125	0.00003	0.34839	0.00001	-14.1	0.6	
FKR6 (n=20)	0.0998	0.0001	0.51158	0.00002	0.51124	0.00002	0.34840	0.00001	-14.2	0.6	
FKR7 (n=5)	0.0999	0.0002	0.51158	0.00003	0.51124	0.00003	0.34839	0.00002	-14.2	0.6	
Bear Lake											
<i>Solution ICP-MS at CPGeo</i>											
FBL1	-	-	0.512321	0.000005	-	-	0.348421	0.000002	-	-	
FBL2	-	-	0.512321	0.000006	-	-	0.348417	0.000003	-	-	
<i>Solution ICP-MS at SKLLE</i>											
FBL1	0.1324	-	0.512318	0.000019	-	-	-	-	-	-	
FBL2	0.1329	-	0.512309	0.000011	-	-	-	-	-	-	1069
FBL3	0.1327	-	0.512323	0.000010	-	-	-	-	-	-	
<i>LA-ICP-MS at UFOP</i>											
FBL1 (n=8)	0.1329	0.0003	0.51231	0.00005	0.51140	0.00005	0.34840	0.00002	2.2	0.9	
FBL2 (n=5)	0.1331	0.0003	0.51228	0.00004	0.51136	0.00004	0.34840	0.00004	1.6	0.9	
FBL3 (n=10)	0.1327	0.0003	0.51228	0.00005	0.51136	0.00005	0.34839	0.00004	1.5	0.8	
FBL4 (n=13)	0.1325	0.0003	0.51227	0.00004	0.51136	0.00004	0.34839	0.00004	1.5	0.9	
<i>LA-ICP-MS at SKLLE</i>											
FBL1 (n=20)	0.1334	0.0001	0.51234	0.00003	0.51140	0.00003	0.34839	0.00002	2.8	0.7	
FBL2 (n=20)	0.1332	0.0001	0.51233	0.00003	0.51140	0.00003	0.34839	0.00002	2.7	0.7	

Notes: (i) = initial isotope ratio calculated

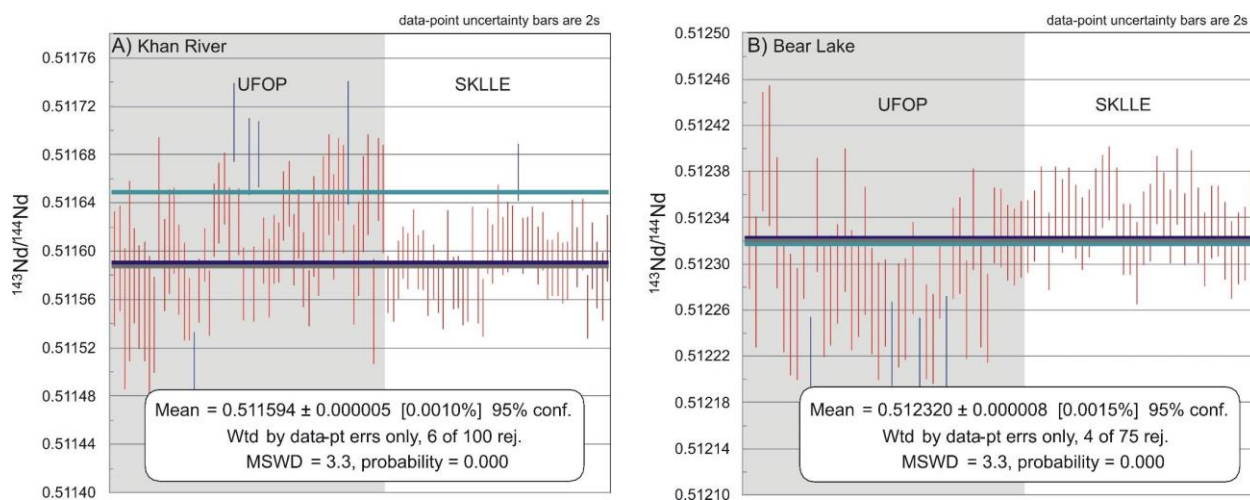


Figure 4.11: Comparison between the LA-ICP-MS and solution Nd isotope analyses obtained in different laboratories for Khan River (A) and Bear Lake (B) titanite. The weighted mean presented is from the LA-ICP-MS data (dark blue line). The weighted mean of the solution MC-ICP-MS is represented by the grey line (CPGeo – USP) and light blue line (SKLLE).

4.5 Discussion

4.5.1 Khan River as a potential reference material for LA-ICP-MS

All the crystal fragments from the Khan River titanite are relatively homogeneous in terms of major element concentrations. BSE imaging shows that the majority of the untreated fragments contain zoned portions, some fractures and imperfections (e.g. Fig. 4.3A); however, chemical abrasion removed most of these damaged areas (Fig. 4.3B, C and D). The improved transparency produced by the thermal annealing helps to select the best parts to be ablated, avoiding inclusions and the remaining imperfect domains.

Results of trace element analyses show that fragments FKR1, FKR3, FKR7 and FKR8 are compositionally homogeneous (Fig. 4.3A and 4.3C, Table 4.3) whereas fragments FKR2, FKR4, FKR5, FKR6 and FKR9 show small chemical variations, such as variable Sc, Sr, Y, Nb, La, Ce, Pr, Nd, Er, Tm, Yb, Hf, Ta, Pb, and Th (Table 4.3). The main explanation for these variations is that the fragments come from different crystals, but overall, all fragments have a chemical composition similar to the Khan titanite studied by Heaman (2009) and Ma *et al.* (2019) (discussed below).

The ID-TIMS U-Pb isotope data from the University of Oslo and University of Toronto for Khan River titanite show small amounts of Pb_c and high $^{206}Pb/^{204}Pb$ (2637 to 4650). The Pb_c -corrected and uncorrected U-Pb SHRIMP results are in agreement with the ID-TIMS reported data. The LA-ICP-MS Pb_c -uncorrected weighted mean $^{206}Pb/^{238}U$ ratios agree within uncertainty with those from ID-TIMS (Table 4.5). The $^{207}Pb/^{206}Pb$

ratios vary from 0.0603 ± 0.0003 (2s) to 0.0624 ± 0.0001 (2), clearly reflecting variable Pb_c in the samples. The Pb_c -uncorrected data obtained by the pooled results of LA-(MC+SF)-ICP-MS, which returned an intercept age of 517 ± 1 Ma (2s, MSWD = 1.5) and an average $^{206}Pb/^{238}U$ ratio of 0.08369 ± 0.00005 (2s, MSWD = 0.57), are consistent with the Pb_c -corrected ID-TIMS concordia age of 515.6 ± 1.3 Ma and the Pb_c -uncorrected intercept age of 516.3 ± 1.3 Ma acquired from both laboratories. The Pb_c -uncorrected $^{206}Pb/^{238}U$ dates obtained by LA-ICP-MS for the Khan River titanite fragments are identical within uncertainty (522 Ma to 516 Ma, LA-SF-ICP-MS; 519 Ma to 517 Ma, LA-MC-ICP-MS).

Given the average concentrations of U ($\sim 500 \mu g.g^{-1}$), the amount of radiogenic Pb is high compared to the Pb_c content, and the $^{206}Pb/^{238}U$ dates are only slightly influenced by the presence of initial common Pb. Also, the relatively low Pb_c content does not compromise the reproducibility of the $^{206}Pb/^{238}U$ dates, as observed in other existing reference materials (e.g. OLT1 titanite - Kennedy *et al.* 2010, Mt. Painter titanite - Elburg *et al.* 2003, Khan titanite - Kinny *et al.* 1994, Sumé apatite - Lana *et al.* 2022). Other titanite reference materials with small amounts of Pb_c show broad variations in the $^{206}Pb/^{204}Pb$ ratios (e.g., MKED1 – 117 %RSD, OLT1 – 18.9 %RSD, BLR-1 12.4 % RSD). The variations observed in the $^{206}Pb/^{204}Pb$ (25.4 %RSD) and $^{207}Pb/^{206}Pb$ (4.5%) ratios of Khan River are comparable to the above reference materials. Similar variations in the $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$ ratios are also observed in rutile (e.g., Sugluk-4 – 87.7 %RSD, Braccialli *et al.* 2013) and apatite (e.g., Durango - 23.4 %RSD, Paul *et al.* 2021) reference materials, yet they are used as reference materials to calibrate analyses. The Khan River titanite is thus a suitable secondary reference material for U-Pb LA-ICP-MS geochronology and can be used to correct the offset on the $^{206}Pb/^{238}U$ ratios in non-matrix matched runs as shown in the round robin results (Fig. 4.9 and Supporting Information).

Results for the $^{147}Sm/^{144}Nd$ ratios that were reported by LA-MC-ICP-MS at UFOP and SKLLE showed significant variations, ranging from 0.0944 ± 0.0002 (2s) to 0.1120 ± 0.0003 (2s), excluding the higher 0.1317 ± 0.0003 (2s) value from FKR8. The same fragments that were analysed in each laboratory showed consistent results within uncertainties. These values are similar and in the same range to those reported by solution MC-ICP-MS at SKLLE, which varied from 0.1053 to 0.1344 (Table 4.10). The $^{143}Nd/^{144}Nd$ ratios obtained for all the fragments by LA-MC-ICP-MS and solution ICP-MS (CPGeo/SKLLE) show a small variation from 0.51156 ± 0.00003 (2s) to $0.511679 \pm$

0.000009 (2s) (Fig. 4.10A). This variation is nevertheless not significant given the precision of the LA-ICP-MS data. Thus, this titanite can potentially be used as secondary reference material for Nd isotope analyses by LA-ICP-MS; however, more work still needs to be done to attest its suitability as calibrant for this isotopic system.

4.5.2 *Khan River versus Khan titanite*

The Khan River titanite and the original Khan titanite of Kinny *et al.* (1994) are similar in terms of major and trace element concentrations. They are both marked by some minor variability in trace element content, high Y (>3000 µg.g⁻¹), HFSE (e.g. Nb > 4000 µg.g⁻¹) and moderate LREE (over 3000 µg.g⁻¹ of Nd) concentrations. Their chondrite-normalised REE patterns are slightly fractionated in the LREE and show a smooth HREE pattern, with significant negative Eu anomalies (Eu/Eu* = 0.37 for Khan titanite, Heaman 2009) (Figure 4.5A). The Pb_c-corrected ID-TIMS weighted mean ²⁰⁶Pb/²³⁸U ages of 515.7 ± 1.6 Ma (MSWD = 4.8) obtained for the Khan River (this study) is in good agreement with the weighted mean ²⁰⁶Pb/²³⁸U age of 510.1 ± 4.9 Ma reported for the Khan titanite (see Heaman 2009, Table 4.11). Furthermore, our Pb_c-corrected concordia age of 515.6 ± 1.3 Ma agrees well with the 518 ± 2 Ma age reported for Khan (Kinny *et al.* 1994), and is only slightly younger than the intercept age of 522.2 ± 2.2 Ma (MSWD = 1.1) reported by Heaman (2009). Crystals analysed by Heaman (2009) showed higher Pb_c content and much higher ²⁰⁷Pb/²⁰⁶Pb ratios than Khan River titanite, but seem identical in origin.

In terms of the Nd isotope composition, the Khan River and Khan titanites are identical (this study, Ma *et al.* 2019, Xu *et al.* 2018). The data for Khan River titanite (all fragments) agree, within uncertainties, with the ¹⁴³Nd/¹⁴⁴Nd value obtained by Xu *et al.* (2018) (0.51163 ± 0.00003, 2s) and that reported by Ma *et al.* (2019) (0.51164 ± 0.00004, 2s) for Khan titanite. The ¹⁴⁷Sm/¹⁴⁴Nd obtained here for Khan River titanite is slightly different from the reported values of 0.1188 ± 0.0050 (2s, Ma *et al.* 2019) and 0.1217 ± 0.0002 (2s, Xu *et al.* 2018), but can be explained by the large variation in Sm and Nd content between different fragments (e.g., fragments FKR3, FKR5 and FKR8, Table 4.3). We noticed that both titanites (Khan River and Khan) are heterogeneous in trace elements compositions and this affects the ¹⁴⁷Sm/¹⁴⁴Nd ratios but not the ¹⁴³Nd/¹⁴⁴Nd ratios. In addition, the negative εNd_t values obtained in this study (-15.4 to -13.7) are consistent with the value of -14.3 ± 0.8 reported by Ma *et al.* (2019), indicating a similar crustal

source. Therefore, we suggest that Khan River and Khan originated from the same magma source but crystallized in different pegmatite bodies.

Table 4.11: Compilation of U-Pb ages and Sm-Nd isotopic data for the Khan titanite compared to Khan River titanite

	Method	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{235}\text{U}$	$^{206}\text{Pb}/^{238}\text{U}$	Intercept Age	Reference
Khan	ID-TIMS	522.3 ± 2.0 Ma	-	510.1 ± 4.9 Ma	522.2 ± 2.2 Ma	Heaman 2009
	ID-TIMS	518 ± 2 Ma	-	-	518 ± 2 Ma	Kinny et al., 1994
	LA-ICP-MS	-	-	-	520.9 ± 3.9 Ma	Chew et al., 2014
	LA-ICP-MS	-	-	521 ± 3 Ma	521 ± 3 Ma	Ma et al., 2019
	LA-ICP-MS	-	-	516.4 ± 3.5 Ma	517.5 ± 5.0 Ma	Spandler et al., 2016
	LA-ICP-MS	-	-	521 ± 3.3 Ma	515.5 ± 5.3 Ma	Spandler et al., 2016
	LA-ICP-MS	-	-	513.1 ± 5.3 Ma	516.9 ± 4.4 Ma	Simonetti et al., 2006
	LA-ICP-MS	-	539 ± 12 Ma*	518.5 ± 5.0 Ma*	-	Kohr 2013
	SHRIMP	524 ± 30 Ma	-	519 ± 11 Ma	522 ± 16 Ma	Sato et al., 2016
Khan River (recommended values)	ID-TIMS (Pbc-uncorrected)	-	-	518.8 ± 1.6 Ma	516.3 ± 1.3 Ma**	This study
	ID-TIMS (Pbc-corrected)	-	-	515.7 ± 1.6 Ma	515.6 ± 1.3 Ma***	This study
	Method	$^{147}\text{Sm}/^{144}\text{Nd}$ ($\pm 2\text{s}$)	$^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 2\text{s}$)	$^{143}\text{Nd}/^{144}\text{Nd}_i$ ($\pm 2\text{s}$)	eNd_i ($\pm 2\text{s}$)	Reference
Khan	LA-ICP-MS	0.1188 ± 0.0050	0.51164 ± 0.00004	0.51124 ± 0.00004	-14.3 ± 0.8	Ma et al., 2019
	LA-ICP-MS	0.1217 ± 0.0002	0.51163 ± 0.00003	-	-	Xu et al., 2018
Khan River (recommended values)	solution ICP-MS	-	0.511587 ± 0.000027	-	-	This study

*spot of 32 μm

**anchored at $\text{Pb}_c = 0.870$

***concordia age

4.5.3 Bear Lake as a potential reference material for LA-ICP-MS

Our analyses for the Bear Lake titanite fragments show a high level of homogeneity in the major and trace element contents (Table 4.2 and 4.4). BSE images show that the chemically-abraded crystal fragments are compositionally uniform and lack mineral inclusions (Fig. 4.4); the combination of chemical abrasion and thermal annealing resulted in a more transparent and crystalline fragment, further reflecting the homogeneity. Variability in the content of individual elements yielded values lower than 5 %RSD in all the fragments for element contents higher than $1 \mu\text{g.g}^{-1}$. The high content

of Sr and the absence of negative Eu anomalies are consistent with the composition of the carbonatites described by Moecher *et al.* (1997). These rocks had a depleted mantle source and were probably reworked to form the titanites, preserving the same REE pattern on a chondrite-normalised diagram.

The Pb_c-uncorrected ID-TIMS, SHRIMP and LA-ICP-MS U-Pb data from different laboratories gave the same results within uncertainty for the titanite fragments. All fragments have relatively high Pb_c (2.8 - 3.5 µg.g⁻¹) and relatively low ²⁰⁶Pb/²⁰⁴Pb ratios (323 to 354). The ID-TIMS Pb_c-uncorrected ²⁰⁷Pb/²⁰⁶Pb ratio varied from 0.1144 ± 0.0002 (2s) to 0.1182 ± 0.0002 (2s). Bear Lake titanite ID-TIMS data yielded a small variation in the ²⁰⁶Pb/²⁰⁴Pb (3.8 %RSD) and ²⁰⁷Pb/²⁰⁶Pb (1.2%), which is comparable to those for other primary reference materials (e.g., MKED1, OLT1, BLR-1). Small variations in the ²⁰⁷Pb/²⁰⁶Pb (~1 %RSD) of the Bear Lake are also seen in the LA-MC-ICP-MS data, suggesting that this titanite can possibly be used as a primary calibrant for U-Pb and Pb-Pb ratios. Thus, despite the high Pb_c amount in the samples, the ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁶Pb ratios are relatively homogeneous, which explains the good agreement between the TIMS, SHRIMP, and LA-ICP-MS results. The Pb_c-uncorrected data obtained by the pooled results of LA-(MC+SF)-ICP-MS, which gave an intercept age of 1070 ± 1 Ma (2s, MSWD = 0.88, n = 325) and a weighted mean ²⁰⁶Pb/²³⁸U ratio of 0.18826 ± 0.00009 (2s, MSWD = 0.93, n = 325), are both consistent with the ID-TIMS Pb_c-uncorrected intercept age, and the ID-TIMS ²⁰⁶Pb/²³⁸U weighted mean ratio (Table 4.5). The LA-(MC+SF)-ICP-MS ages are also in agreement with the ²⁰⁷Pb-based Pb_c corrected U-Pb SHRIMP age of 1068.5 ± 7.2 Ma (2s, n = 24, MSWD = 0.55) and the SHRIMP ²⁰⁴Pb-based Pb_c corrected concordia age of 1072.2 ± 7.1 Ma. The ID-TIMS Pb_c-corrected ratios gave a slightly younger age of 1059.2 ± 1.7 Ma, suggesting some overcorrection of the TIMS ratios (Table 4.5). Further investigations of the initial Pb are needed to explain the difference between the Pb_c-uncorrected intercept ages and the Pb_c-corrected TIMS ages.

The Sm-Nd isotopic composition for Bear Lake titanite from all the fragments that were acquired by LA-MC-ICP-MS shows relatively homogeneous ¹⁴⁷Sm/¹⁴⁴Nd ratios, which range from 0.1325 ± 0.0003 (2s) to 0.1334 ± 0.0001 (2s). The same fragments, FBL1 and FBL2, analysed in both laboratories show values in agreement within uncertainties. These results are in agreement with the values obtained by solution MC-ICP-MS at SKLLE, which ranged from 0.1324 to 0.1327. The ¹⁴³Nd/¹⁴⁴Nd ratio for all

fragments obtained by LA-MC-ICP-MS and solution ICP-MS (CPGeo/SKLLE) varied from 0.51227 ± 0.00004 (2s) to 0.51234 ± 0.00003 (2s), and agree within uncertainty within and between fragments (Fig. 4.10B).

The Bear Lake titanite is suitable as a reference material for U-Pb LA-ICP-MS geochronology. The LA-ICPMS experiments using Bear Lake titanite as reference material to correct the $^{206}\text{Pb}/^{238}\text{U}$ ratios (in non-matrix matched runs) returned fairly consistent ages for other reference materials treated as unknowns (Fig. 4.9). It is worth noting that the variable Pb_c content in the titanite can be corrected using different strategies (e.g., Storey *et al.* 2006, Chew *et al.* 2014, Thomson *et al.* 2012). Ideally the Pb_c should be corrected via the ^{204}Pb -based method (e.g., Storey *et al.* 2006), but this is only possible where accurate and precise measurements of ^{202}Hg and $^{204}(\text{Hg}+\text{Pb})$ can be obtained and the systematic uncertainties and artificial variations related to the ^{204}Pb calculations can be avoided (e.g., Bracciali *et al.* 2013). Considering the difficulty of some instruments in properly measuring ^{204}Pb , and given that there is no observable evidence for Pb loss events in the history of this titanite, the best option for Pb_c corrections would be via the ^{207}Pb method, which assumes an appropriate initial Pb composition.

4.5.4 *Bear Lake versus BLR-1 titanite*

Our Bear Lake titanite is markedly uniform in trace element contents and has no Eu anomaly, a feature clearly distinct to those reported for the BLR-1 reference material (Ma *et al.* 2019). BLR-1 titanite is characterised by chondrite-normalised REE patterns that peak in the middle to middle-heavy REE, show a large negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.40$, Ma *et al.* 2019) (e.g., Mazdab 2009) (Figure 4.5B). The Sm-Nd isotope data from our Bear Lake titanite are clearly different to the published values of BLR-1 reported by Xu *et al.* (2018, 0.1982 ± 0.0048 , 2s) and Ma *et al.* (2019, 0.1921 and 0.1939 ± 0.0045 , 2s) (Table 4.12). In terms of U-Pb geochronology, the Pb_c -corrected concordia age of 1059.2 ± 1.7 Ma (2s, MSWD = 1.5) obtained in this study for Bear Lake titanite is outside uncertainty of previously published intercept age of 1048 ± 7 Ma (2s, MSWD = 0.17) (Ma *et al.* 2009), and from the $^{206}\text{Pb}/^{238}\text{U}$ age of 1047.1 ± 0.4 Ma (2s, MSWD = 0.56) reported by Aleinikoff *et al.* (2007) for BLR-1 (Table 4.12). Thus, our results indicate that the Bear Lake and BLR-1 titanites come from different sources and crystallized at different times in the history of the Bear Lake Diggings. This interpretation is supported

by the difference in trace elements composition, Sm-Nd isotopic composition and U-Pb ages between Bear Lake and BLR-1 titanites.

Table 4.12: Compilation U-Pb ages and Sm-Nd isotopic data for the BLR-1 titanite compared to Bear Lake titanite

	Method	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{235}\text{U}$	$^{206}\text{Pb}/^{238}\text{U}$	Intercept Age	Reference
BLR-1	ID-TIMS	1049.9 ± 1.3 Ma	1048 ± 0.7 Ma	1047.1 ± 0.4 Ma	-	Aleinikoff et al., 2007
	LA-ICP-MS	-	-	1046 ± 5 Ma	1048 ± 6 Ma	Sun et al., 2012
	LA-ICP-MS	-	-	1048 ± 7 Ma	1048 ± 7 Ma	Ma et al., 2019
Bear Lake (recommended values)	ID-TIMS (Pbc-uncorrected)	-	-	1109.10 ± 0.66 Ma	1067.81 ± 0.74 Ma*	This study
	ID-TIMS (Pbc-corrected)	-	-	1059.7 ± 3.0 Ma	1059.2 ± 1.7 Ma**	This study
	Method	$^{147}\text{Sm}/^{144}\text{Nd}$ ($\pm 2s$)	$^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 2s$)	$^{143}\text{Nd}/^{144}\text{Nd}_i$ ($\pm 2s$)	ϵNd_i ($\pm 2s$)	Reference
BLR-1	LA-ICP-MS	0.1939 ± 0.0045	0.51283 ± 0.00005	0.51150 ± 0.00005	4.1 ± 1.0	Ma et al., 2019
	LA-ICP-MS	0.1982 ± 0.0048	0.51282 ± 0.00008	-	-	Xu et al., 2018
	ID-MC-ICP-MS	0.1921^{**}	0.512815 ± 0.000004	0.511496^{**}	4.1^{***}	Ma et al., 2019
Bear Lake (recommended values)	solution ICP-MS	0.1327 ± 0.0003	0.512321 ± 0.000004	-	-	This study

*anchored at $\text{Pb}_c = 0.914$

**concordia age

***uncertainty unpublished

4.6 Conclusions

Based on comprehensive bulk sample and high-spatial resolution microanalysis, we present two new potential titanite reference materials for high-spatial resolution analytical methods. The Khan River titanite shows consistent Nd isotopic homogeneity, but variable Sm-Nd ratios, has high contents of U, Th, radiogenic Pb and REE, and is relatively low and slightly variable in Pb_c . The chemical abrasion technique produced fragments that are free of damaged areas and the chemical treatment helps to identify the portions of the crystal that are suited for microanalysis. It is worth noting that the fragments and portions to be analysed must be carefully chosen, avoiding inclusions as well as areas that are highly heterogeneous (e.g., zoning, damaged portion) and fractured. The recommended values for this reference material are (1) Pb_c -uncorrected weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ratio of 0.08381 ± 0.00027 (2s); (2) Pb_c -corrected weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ratio of 0.08328 ± 0.00026 (2s), $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 0.05760 ± 0.00007 (2s), and (3) weighted mean

$^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.511587 ± 0.000027 (2s). We suggest that Khan River titanite is suitable as a secondary reference material for U-Pb geochronology and Nd-Nd isotope analyses.

The Bear Lake titanite is homogenous and more transparent than the Khan River titanite, and is free of mineral inclusions. It has a high degree of isotopic and chemical homogeneity, showing consistent Sm-Nd isotope ratios, high concentrations of REE, U, Th and radiogenic Pb, but contains relatively high levels of Pb_c . Pb_c is relatively homogeneous yielding minimal variations in the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. The recommended values for this reference material are (1) Pb_c -uncorrected weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ratio of 0.18774 ± 0.00012 (2s); (2) Pb_c -corrected weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ratio of 0.17867 ± 0.00054 (2s), $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 0.07433 ± 0.00029 (2s), and (3) weighted mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512321 ± 0.000004 (2s) and average $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of 0.1327 ± 0.0003 . The Bear Lake titanite can be used as a reference material for in situ trace element microanalysis and Sm-Nd isotope analysis, and U-Pb dating. The Bear Lake and the Khan River titanites are available in large quantities to be distributed to the scientific community upon request.

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CAPÍTULO 5

**THE VERMILION MONAZITE: A NEW
ARCHEAN MONAZITE REFERENCE
MATERIAL FOR U-Pb AND Sm-Nd
MICROANALYSIS BY LA-ICP-MS**

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ABSTRACT

Monazite (Vermilion) from the ~2.7 Ga Vermilion Granitic Complex (Minnesota, USA) was investigated as a potential reference material for U-Pb geochronology, using electron microprobe, high-precision ID-TIMS and high-spatial resolution techniques (LA-(Q/SF/MC)-ICP-MS and SHRIMP). Vermilion monazite is relatively homogeneous in BSE images. It is characterised as a monazite-(Ce) with uniform, relatively LREE-enriched chondrite-normalised REE patterns ($\text{Eu}/\text{Eu}^* = 0.074\text{--}0.085$). ID-TIMS U-Pb analyses yielded concordant to slightly (-0.6% to 1.8%) discordant isotope data with weighted mean $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ dates of 2668.6 ± 1.8 Ma (2σ , MSWD = 1.3, $n = 3$) and 2666.8 ± 1.8 Ma (2σ , MSWD = 4.0, $n = 4$). High-spatial resolution data from SHRIMP and LA-(Q/SF/MC)-ICP-MS agree with the ID-TIMS age. Using Vermilion monazite as primary reference material, LA-SF-ICP-MS analyses reproduced the age of several other reference monazites within -1.13% to +1.64% accuracy. Nd isotopes obtained via ID-TIMS and solution MC-ICP-MS returned consistent $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.510694 ± 0.000040 (2σ) and 0.510726 ± 0.000014 (2σ), respectively. The LA-MC-ICP-MS $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.51071 ± 0.00001 (2σ) and 0.51065 ± 0.00001 (2σ) are also in agreement within uncertainties. Results of Sm-Nd isotope analyses by LA-MC-ICP-MS from two laboratories yielded mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of 0.0869 ± 0.0002 (2.5 %RSD, 2σ , $n = 58$) and 0.0835 ± 0.0001 (2.2 %RSD, 2σ , $n = 50$), reflecting small variations in individual fragments. The initial epsilon Nd (ϵNdi) varies from -0.8 ± 0.5 to 0.6 ± 0.4 (2σ). The reproducibility of our results shows that Vermilion monazite can be used as a

primary reference material for U-Pb geochronology and is suitable as a secondary reference material for Sm-Nd isotopic tracing. The Archean age of Vermilion monazite, the oldest available as a reference material, will facilitate the investigation of Archean crustal evolution processes and broaden the prospect of studying ancient metamorphic events by combining matrix-matched U-Pb geochronology and Sm-Nd isotopic tracing.

Keywords: monazite, reference material, U-Pb geochronology, Sm-Nd isotope composition, trace element composition

5.1 Introduction

Monazite is ideal for U-Th-Pb geochronology because it incorporates high amounts of U and Th and little common Pb (Parrish, 1990). Its U-Th-Pb isotopic system is very robust to resetting by volume diffusion (under a range of crustal P-T conditions) and the very low Pb diffusivity in monazite results in high closure temperatures (ca. 900 °C for Pb; Cherniak et al. 2004; Gardés et al., 2006; Brady and Cherniak, 2010). Despite the high concentrations of radioactive Th and U, which are responsible for large irradiation doses throughout geologic time (usually on the order of 10¹⁹–10²⁰ α/g; Ruschel et al., 2012; Nasdala et al., 2020), monazite does not become metamict, and anneals at low T (ca. 150 °C), showing only modest levels of radiation damage (Meldrum et al., 1998; Nasdala et al., 2020). Solid-state recrystallisation is not common (Harlov et al., 2011) and may be restricted to localized deformation that leads to mechanical twinning and resetting of monazite U-Pb dates (Buick et al., 2010; Erickson et al., 2017; Fougereuse et al., 2020).

Experiments with monazite of a range of grain sizes show that coupled dissolution-precipitation processes resulting in reaction fronts are a common process (Teufel and Heinrich, 1997), especially in the presence of alkali-bearing fluids acting as catalysts. Seydoux-Guillaume et al., (2002) concluded that monazite U-Pb systematics are affected by dissolution/precipitation processes and that dissolution of monazite is directly linked to fluid composition and temperature. Ca-rich fluids are particularly efficient at dissolving monazite and disturbing their U-Pb system. In addition, fluid circulation in Ca-rich rocks containing monazite can cause mobilization of Ca from the host phase, resulting in the partial or total resetting of monazite U-Pb isotope systematics (De Wolf et al., 1993; Braun et al., 1998; Montel et al., 2000). Thus, monazite U-Pb geochronology may be useful for (a) tracking fluid sources, (b) dating fluid mobilisation

and ore precipitation, (c) dating solid-state deformation, (d) constraining the igneous crystallisation age of S-type felsic magmatic rocks, and (e) determining the timing and conditions of certain metamorphic processes. Monazite is also used to estimate the age and duration of hydrothermal circulation (Williams et al., 1996; Rasmussen et al., 2006; Williams et al., 2011; Gauthiez-Putallaz et al., 2016; Grand’Homme et al., 2016; Gonçalves et al., 2018).

Because monazite growth is highly sensitive to fluid/melt circulation, it can be widely used to investigate the evolution of the crust based on petrogenetic studies that use a combination of mineral chemistry, isotope composition and textural features that indicate dissolution-precipitation processes (e.g., McFarlane and McCulloch, 2007; Grand’Homme et al., 2016). Studies of Köppel and Grünenfelder (1975) revealed that monazite found in different samples that experienced the same P-T path have different U-Pb dates, indicating that some of the primary crystallisation ages were preserved without resetting during younger metamorphic events. Thus, monazite textures and composition may record the timing of mineral growth and are used together with major silicate mineral assemblages to interpret petrogenetic processes (Pyle and Spear, 2003; Vance et al., 2003; Foster et al., 2004; Schulz et al., 2021; Budzyń et al., 2017). Furthermore, the combination of monazite major and trace element compositions and U-Pb dates with the trace element compositions of major silicate minerals makes it a powerful tool for investigating pressure-temperature-time (P-T-t) paths (Pyle and Spear, 2003; Vance et al., 2003; Foster et al., 2004; Rubatto et al., 2006) and consequently helps to reconstruct the tectonic history of polymetamorphic terranes. As a detrital mineral, monazite – combined with zircon - is highly useful for tracking the evolution of the crust through comparison of age and tracer isotopes (Liu et al., 2017).

U-Th-Pb monazite geochronology is commonly undertaken via high-spatial resolution dating techniques such as ion microprobe (SIMS) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) (Suzuki and Adachi, 1991a; Montel et al., 1996; Scott and Gauthier, 1996; Catlos et al., 2000; Stern and Berman, 2000; Cocherie and Albarède, 2001; Budzyń et al., 2017; Schulz et al., 2021). These techniques provide the ability to date different textures and growth zones within crystals if they have enough radiogenic lead. Recent advances in the LA-ICP-MS U-Th-Pb dating technique allow fast acquisition of U-Pb data at high-spatial resolution (<10 µm), with precisions around 3% on individual $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ ratios/dates.

LA-ICP-MS geochronology demands large quantities of reference materials for matrix-matched calibration and quality control due to the destructive nature of this technique. Despite the availability of large quantities of some well-characterised monazite reference materials, such as Itambé (Gonçalves et al., 2016), Diamantina (Gonçalves et al., 2018), TS-Monazite (Budzýn et al., 2021), USGS 44069 (Aleinikoff et al., 2006), Iceland (Peterman, 2005; Alagna et al., 2008), RP-1 and FC-1 (Horstwood et al., 2003), Trebilcock (Tomascak et al., 1996), Steenkampskraal (Namaqualand; Knoper et al., 2000; Fisher et al., 2020), others are difficult to obtain, or are available in only small aliquots, e.g. Thompson Mine (Williams et al., 1996), Manangotry (Paquette et al., 1994, Horstwood et al., 2003) (Table 5.1). Other potential monazite reference materials may contain an excess of common Pb components related to mineral inclusions, as shown for example for Steenkampskraal (Namaqualand; Knoper et al., 2000) in recent work from Fisher et al., (2020; Table 5.1). Additionally, no Archean homogeneous monazite reference material is widely available (e.g., Table 5.1). Some reference materials (e.g., the 1766 Ma Thompson Mine monazite; Williams et al., 1996) do not have published recommended U/Pb (TIMS) ratios or may be too rich in Th leading to matrix effects (e.g. Stern and Berman, 2000; Fletcher et al., 2010; Ling et al., 2017). In general, there is a lack of monazite reference materials well-characterised by high-precision techniques for both U-Pb and Sm-Nd isotopes analyses (e.g. ID-TIMS, solution MC-ICP-MS) (Table 5.1).

Table 5.1: Compilation of U-Pb and Sm-Nd data from monazite reference materials

Sample	Technique	Ages (Ma)				Technique	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	Reference Sm-Nd data
		$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{235}\text{U}$	$^{206}\text{Pb}/^{238}\text{U}$	Reference age				
Thompson Mine	ID-TIMS	-	-	-	1766 Ma (1)	-	-	-	-
Steenkampskraal (Namaqualand)	ID-TIMS	-	-	1026 ± 1.5 and 1038 ± 0.6 (3)	1027 ± 1 Ma (2)	ID-TIMS	0.0940 ± 4	0.511893 ± 12	3
TS-monazite	ID-TIMS	905.26 ± 0.24/2.5	910.42 ± 0.34	912.54 ± 0.45	910.42 ± 0.34 Ma (4)	-	-	-	-
Iveland	LA-Q-ICP-MS	956 ± 26	941 ± 11	934 ± 7	870 - 1043 Ma (5)	LA-MC-ICP-MS	0.2708 ± 161	0.512963 ± 93	5
Manangotry	ID-TIMS	554.0 ± 4.1	553.1 ± 1.6	552.9 ± 1.9	555 ± 1 Ma (6)	ID-TIMS	0.0711 ± 5	0.511044 ± 22	5
Itambé	ID-TIMS	481.82 ± 0.91	506.44 ± 0.73	511.79 ± 0.52	506.44 ± 0.73 Ma (7)	LA-MC-ICP-MS	0.1955 ± 41	0.512424 ± 24	7
Diamantina	ID-TIMS	496.6 ± 1.1	495.53 ± 0.53	495.26 ± 0.54	495.26 ± 0.54 Ma (8)	LA-MC-ICP-MS	0.1177 ± 2	0.511427 ± 3	8
USGS 44069	ID-TIMS	425.3 ± 1.1	424.89 ± 0.35	424.86 ± 0.36	424.9 ± 0.4 Ma (9)	LA-MC-ICP-MS	0.1159 ± 64	0.512175 ± 40	5
Trebilcock	ID-TIMS	210	272	279	271.5 ± 2.0 Ma (10)	ID-TIMS	0.2167 ± 125	0.512616 ± 11	11
RP-1	ID-TIMS	24.9 ± 6.5	63.4 ± 0.3	64.4 ± 0.3	64.4 ± 0.3 Ma (6)	-	-	-	-
FC-1	ID-TIMS	-	53.2 ± 0.6	55.7 ± 0.6	55.7 ± 0.6 Ma (6)	-	-	-	-

References: 1 - Williams et al., (1996); 2 - Kaur et al., (2016); 3 - Fisher et al., (2020); 4 - Budzyń et al., (2021); 5 - Liu et al., (2012); 6 - Horstwood et al., (2003); 7 - Gonçalves et al., (2016); 8 - Gonçalves et al., (2018); 9 - Aleinikoff et al., (2006); 10 - Tomascak et al., (1996); 11 - Fisher et al., (2011).

Note: mean dates uncertainties given at 2σ

The importance of using an Archean reference material is due to the necessity of precisely determining the isotope ratios and dates in old monazite samples, which have distinctive Pb-Pb/U-Pb isotope ratios relative to most currently used monazite reference materials. The contrasting U content and the U/Pb ratios observed between older and younger samples are prone to laser-induced matrix effects and thus it is recommended to use older (preferably Archean) reference materials for Archean samples since these have dates/ratios similar to the unknowns for calibration/normalisation (Paton et al., 2010).

This study aims to investigate the suitability of Archean monazite from the Vermilion Granitic Complex (northern Minnesota - USA) as a matrix-compatible reference material for U-Pb LA-ICP-MS geochronology and Sm-Nd isotope analyses by means of solution mode and LA-MC-ICP-MS (laser ablation-(multi-collector)-inductively coupled plasma-mass spectrometry) analyses. We investigate the chemical homogeneity of the Vermilion monazite by means of electron probe micro-analyser (EPMA) and LA-ICP-MS, and its suitability for U-Pb dating using different high-spatial resolution techniques (LA-ICP-MS, SHRIMP (Sensitive High Resolution Ion MicroProbe)) and high-precision technique (ID-TIMS; isotope dilution-thermal ionisation mass spectrometry).

5.2 Geological setting

The Neoarchean Vermilion Granitic Complex (VGC), northeastern Minnesota, represents a granite-gneiss-migmatite terrane consisting of metasedimentary, mafic, tonalitic, granodioritic, and granitic rocks. The 2700 Ma VGC is located in the western portion of the Quetico gneiss belt in the Superior Province of the Canadian Shield (Day and Weiblen, 1986). Rocks of the VGC were metamorphosed at amphibolite-facies conditions (McCall et al., 1990). The supracrustal rocks are represented by biotite schists (which have greywacke precursors) and amphibolites, and are locally intruded by granites (Windley, 1977). The Archean granitoid rocks have been classified into an early sodium-rich, pre- to syn-kinematic, tonalite, trondhjemite, and granodiorite suite, and a late potassium-rich granite suite (Windley, 1977). The potassium-rich granites were emplaced as syn- to post-kinematic plutons and batholiths into foliated country rocks (Schwerdtner et al., 1979). The metasedimentary rocks underwent ca. 2675 Ma (Salerno, 2017) amphibolite-facies regional metamorphism at peak pressure-temperature conditions of 0.3 - 0.5 GPa and 600 °C (Salerno, 2017). The schists typically contain garnet-sillimanite-

muscovite-biotite-plagioclase-quartz mineral assemblages (Day and Weiblen, 1986; Salerno, 2017).

The bulk rock chondrite-normalised REE patterns of the biotite-schist samples are typical of Archean metagreywacke (Williams, 1978; Taylor and McLennan, 1981; McLennan et al., 1984). Salerno (2017) reported that zircon LA-ICP-MS U-Pb data obtained from biotite schists defined slightly discordant results with upper intercept ages from 2725 ± 14 Ma (1σ) to 2721 ± 10 Ma (1σ). These zircons show igneous growth zoning in cathodoluminescence images, suggesting that they are detrital grains of originally magmatic origin (Corfu et al., 2003).

The biotite-schist monazite is found in the biotite rich domains, which define the metamorphic foliation. No significant heterogeneity/zoning was observed in La, Y, and Ce X-ray compositional monazite maps, suggesting they represent a single metamorphic monazite generation (Salerno, 2017). The best estimates of the timing of monazite growth from two biotite schist samples reported by Salerno (2017) are weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ dates of 2670 ± 11 Ma (1σ) and 2676 ± 18 Ma (1σ) from sub-concordant spot analyses reflecting minor Pb-loss.

The Vermilion monazite crystals used in this study were obtained from several samples of the biotite schist (UTM 476489E/5354520N) collected from the same rock layer and same field location by one of the coauthors (Peter McSwiggen). The grains hand-picked from the heavy-minerals concentrate are translucent, yellowish/honey colored, and subhedral to euhedral in shape (Figure 5.1).

5.3 Analytical methods

The determination of major and trace element concentrations and U-Pb and Sm-Nd isotope compositions was undertaken in several laboratories and by a number of analytical techniques. It is important to note that all the Vermilion monazite crystals analysed were randomly hand-picked from a heavy-mineral concentrate and separated in different batches containing several grains for all the analytical methods in this study. Therefore, all the individual grains are different from each other, and they were labelled accordingly in each laboratory. The most transparent grains (200-600 μm in diameter), mostly free of imperfections and/or inclusions, were carefully selected and mounted on double-sided tape. These grains were fixed in a 2.5 cm diameter resin mount and then polished to obtain a smooth surface suitable for back-scattered electron imaging (BSE),

and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) at the Universidade de Brasília (UnB) and Universidade Federal de Ouro Preto (UFOP). A second aliquot of homogenous grains was separated for analyses by EPMA, LA-ICP-MS, ID-TIMS, and SHRIMP at independent laboratories (see Table 5.2). The details of the LA-ICP-MS technique (Table S1) and a complete dataset from all these methods are available in the Supplementary material.

5.3.1 Scanning electron microscopy

BSE images of the monazite were obtained using a JSM-6510 JEOL scanning electron microscope, operating with energy of 20kV. Images were acquired at the Laboratório de Microanálises - LMic (UFOP).

5.3.2 Electron-probe microanalysis (EPMA)

The major element compositions of the Vermilion monazite grains were analysed on a JEOL JXA-8200 electron probe micro-analyser, using a 15 kV accelerating voltage and a 20 nA beam current at McSwiggen & Associates, Minnesota, USA. They were analysed for the following elements with the specified X-ray lines: SiO₂ (K α), P₂O₅ (K α), CaO (K α), UO₂ (M β), ThO₂ (M α), PbO (M β), Y₂O₃ (L α), La₂O₃ (L α), Ce₂O₃ (L α), Pr₂O₃ (L β), Nd₂O₃ (L α), Sm₂O₃ (L β), Eu₂O₃ (L β), Gd₂O₃ (L β), Tb₂O₃ (L α), and Dy₂O₃ (L α).

5.3.3 Trace Elements

Trace element compositions were obtained at the Laboratório de Estudos Geodinâmicos, Geocronológicos e Ambientais of the Universidade de Brasília, Brazil, using a Thermo Finnigan Element XR high-resolution single-collector sector field ICP-MS coupled to a 193 nm Iridia laser ablation system. A second run of trace element analyses was determined by a Thermo Finnigan Element II single collector sector field (SF) ICP-MS, coupled to a CETAC UV Nd-YAG 213nm laser system, at the Laboratório de Geoquímica Isotópica (UFOP). A third run of trace element analyses was carried out using an Agilent 7500a Q-ICP-MS coupled to a 193 nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) at State Key Laboratory of Lithospheric Evolution (SKLLE), Institute of Geology and Geophysics, Chinese Academy of Sciences.

5.3.4 U-Pb dating ID-TIMS

The ID-TIMS analyses were performed at the TIMS U-Pb Laboratory at the University of Oslo (Norway) and the Jack Satterly Geochronology Laboratory (JSL) at the University of Toronto (Canada). The most translucent grains free of inclusions were selected.

5.3.5 U-Pb dating SHRIMP

U-Th-Pb isotopic analyses of monazite from the Vermilion sample were carried out on the SHRIMP II ion microprobe in the Research School of Earth Sciences (RSES), Australian National University (ANU), Canberra. Analytical procedures are similar to those described in Williams (1998 and references therein) and Ireland and Williams (2003). Several grains of the Vermilion monazite were hand-picked and cast into an epoxy disk together with the 44069 monazite reference material (Aleinikoff et al., 2006).

5.3.6 U-Pb dating LA-SF-ICP-MS

Monazite U-Pb dating was carried out at the Laboratório de Estudos Geodinâmicos, Geocronológicos e Ambientais, Universidade de Brasília (Brazil). The Vermilion monazite crystals were randomly selected and are not the same as the grains analysed in the other laboratories. A Thermo Finnigan Element XR high-resolution single-collector sector field ICP-MS coupled to a 193 nm Iridia laser ablation system was used to measure the masses of interest. The analyses used a spot diameter of 15 μm , with a repetition rate of 20 Hz, and a laser fluence of 2.0 J cm^{-2} . The Diamantina monazite (Gonçalves et al., 2018) was used for normalisation, and the USGS 44069 (Aleinikoff et al., 2006), Steenkampskraal (Knoper et al., 2000, Liu et al., 2012, Kaur et al., 2016), Thompson Mine (Williams et al., 1996) and Bananeira (Gonçalves et al., 2016) monazites were used for quality control. Systematic uncertainty of ca. 1% is propagated on each final date referred as $\pm \alpha/\beta$ (without/with systematic uncertainties), following Horstwood et al. (2016). No common lead correction was applied. Dates are quoted at 2σ .

5.3.7 U-Pb dating LA-MC-ICP-MS

Monazite U-Pb analyses were conducted using a Thermo Scientific Neptune Plus Multicollector ICP-MS instrument coupled to a 193nm HelEX Photon Machine Laser ablation system at the Laboratório de Geoquímica Isotópica (UFOP, Brazil). The laser fluence in the sample was set to 6 J/ cm^2 and the beam diameter and laser repetition rate

were set to 40 μm and 5 Hz, respectively. The primary reference material used for calibration was Itambé monazite (Gonçalves et al., 2016), while the 44069 (Aleinikoff et al., 2006) and Steenkampskral (also known as Namaqualand, Knoper et al., 2000, Liu et al., 2012, Fischer et al., 2020, or Namaqua, Kaur et al., 2016) monazites were used for quality control. A systematic uncertainty of ca. 1% was propagated for the final spot dates indicated as $\pm \alpha/\beta$ (without/with systematic uncertainties), following Horstwood et al. (2016).

5.3.8 U-Pb dating LA-Q-ICP-MS

An Agilent 7500a Q-ICP-MS coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) was used to determine U-Pb monazite spot dates at the State Key Laboratory of Lithospheric Evolution (SKLLE), Institute of Geology and Geophysics, Chinese Academy of Sciences. A different mount of Vermilion monazite crystals was analysed in this laboratory. The matrix-matched monazite reference material 44069 (Aleinikoff et al., 2006) was used as the primary reference material to correct $^{207}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, and $^{208}\text{Pb}/^{232}\text{Th}$ ratios. The energy density (fluence) at the ablation spots was $\sim 2.5 \text{ J cm}^{-2}$ and laser beam diameters were 24 μm at a repetition rate of 3 Hz.

U-Pb analyses at the University of Portsmouth - UK were obtained in a single session using a Jena PlasmaQuant Elite ICP-MS coupled to an ASI RESOLUTION 193 nm ArF excimer Laser. Analyses used 5 μm spot size, laser fluence of 2.0 J.cm^{-2} (measured on the spot) and repetition rate of 1 Hz. Trebilcock monazite (Tomascak et al., 1996) was used as a primary reference material with KMO (MacLachan et al., 2004; Goudie et al., 2014) and Itambé (Gonçalves et al., 2016) monazites used as quality control. The systematic uncertainty of ca. 1% is propagated on the final acquired dates for both laboratories represented as $\pm \alpha/\beta$ (without/with systematic uncertainties), following Horstwood et al. (2016).

5.3.9 Nd isotope composition ID-TIMS at UnB

The isotope dilution method for Nd isotopic analysis, separation procedures and analytical method applied at UnB was described by Gioia and Pimentel (2000). The obtained aliquot was analysed using a Thermo Scientific TRITON™ Plus Thermal Ionization Mass Spectrometer (TIMS) operating in static multi-collector mode. Mass fractionation was corrected by normalizing the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$.

Approximately 11 mg of a few monazite crystals were mixed with a $^{149}\text{Sm}/^{150}\text{Nd}$ spike and dissolved in PTFE beakers. The mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio obtained for the JMC solution standard was 0.512262 ± 0.000007 (2σ), in agreement with its preferred value from the GeoREM database website (Jochum et al., 2005).

5.3.10 Nd isotope solution MC-ICP-MS at UnB

The dissolution and wet chemistry procedures used for solution MC-ICP-MS analyses were the same as employed for the ID-TIMS analyses (section 3.9, above; Gioia and Pimentel, 2000). An aliquot was analyzed in a Thermo-Fisher Neptune MC-ICPMS instrument at the same laboratory. The samples were introduced in the spectrometer using a nebulizer with a flux of 100 $\mu\text{L}/\text{min}$. Seven blocks of 10 cycles each with an integration time of 4.194 seconds were considered for each analysis. After correcting for any (rare) ^{144}Sm interference, $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were corrected for instrumental mass fractionation using the exponential fractionation law and assuming $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$.

The mean $^{143}\text{Nd}/^{144}\text{Nd}$ obtained during the course of this study for the USGS BHVO-2 standard was 0.513007 ± 0.000006 (2σ), which is consistent with the most recently published values (e.g., 0.512979 ± 0.000014 (1SD), Jochum et al., 2016).

5.3.11 Sm-Nd isotope composition LA-ICP-MS (MC) at UFOP

A batch of six Vermilion monazite fragments was analysed for the Sm-Nd isotope composition using a Thermo-Finnigan Neptune MC-ICP-MS, coupled with a 193nm HelEx Photon Machine laser ablation system, in the Laboratório de Geoquímica Isotópica, UFOP. Analyses were performed with a laser fluence of 6 J/cm^2 , a spot diameter set to 60 μm and a repetition rate of 5 Hz. Data reduction was conducted using an in-house Excel spreadsheet following Gonçalves et al. (2018). The calibration reference material was Steenkampskral monazite (or Namaqualand; Liu et al., 2012). To perform quality control, the 44069 (Aleinikoff et al., 2006), Itambé (Gonçalves et al., 2016) and Diamantina (Gonçalves et al., 2017) monazite reference materials were also analysed.

5.3.12 Sm-Nd isotope composition LA-ICP-MS (MC) at SKLLE

Five Vermilion monazite grains were selected for in situ analysis of their Sm-Nd isotopic composition at SKLLE, Institute of Geology and Geophysics, Chinese Academy of Sciences. A Neptune Plus MC-ICP-MS coupled to a 193 nm ArF excimer laser ablation

system was employed to obtain Nd isotope analyses. The Neptune Plus MC-ICP-MS was tuned and optimized for maximum sensitivity using a JNdi-1 standard solution before laser analysis. The laser spot size and repetition rate were set to 24 μm and 3 Hz, respectively.

Table 5.2: Summary of the analytical techniques used to investigate and analyse the Vermilion monazite grains

	Imaging	Chemical composition				U-Pb dating							Sm-Nd isotope composition			
Technique/ Facility	SEM - BSE	EPMA	LA- SF- ICP- MS	LA- SF- ICP- MS	LA-Q- ICP- MS	ID-TIMS		SHRIMP	LA-SF- ICP- MS	LA-MC- ICP-MS	LA-Q- ICP-MS	LA-Q-ICP- MS	ID- TIMS	solution MC- ICP-MS	LA-MC-ICP-MS	
	UFOP	Minnesota	UnB	UFOP	SKLLE	Oslo	Toronto	ANU	UnB	UFOP	SKLLE	Portsmouth	UnB	UnB	UFOP	SKLLE
Number of grains analysed	12	11 (n = 20)	4 (n = 20)	5 (n = 30)	5 (n = 41)	4	3	6 (n = 27)	5 (n = 48)	6 (n = 58)	5 (n = 41)	4 (n = 52)	2	1	6 (n = 58)	5 (n = 50)

n = number of spots analysed

5.4 Results

5.4.1 Chemical composition

The BSE images show that Vermilion monazite grains are generally homogeneous, except for rare weak patchy sector zoning. Crystals may have some inclusions and small fractures, but those are easily identified and avoided under transmitted light of the laser ablation system (Figure 5.1).

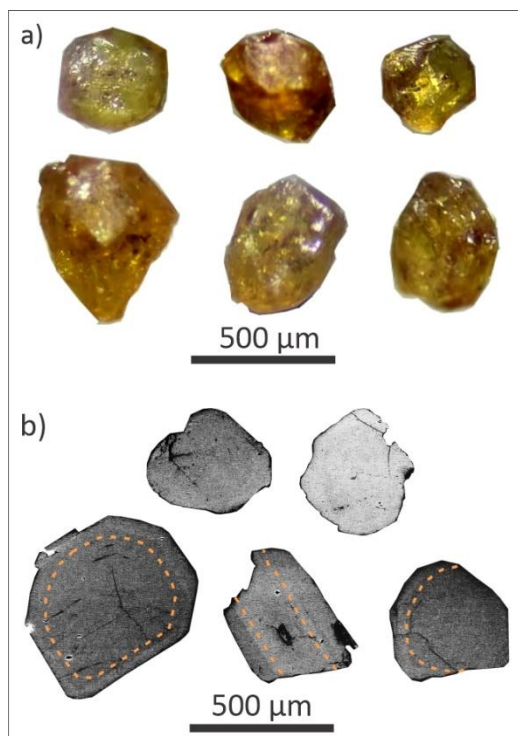


Figure 5.1: a) translucent grains from Vermilion monazite exhibiting a yellow/honey colour; b) BSE (back-scattered electron) images of Vermilion monazite showing small fractures with delicate zoning.

Major element analyses obtained by EPMA from eleven grains confirm the relative chemical homogeneity of Vermilion monazite (Table 5.3). Comparison between the major element concentrations shows small variations (<7 %RSD) for P_2O_5 , Y_2O_3 , La_2O_3 , Ce_2O_3 , Nd_2O_3 and Pr_2O_3 and significant (<15 %RSD) variations for CaO , SiO_2 , ThO_2 , Gd_2O_3 , PbO and Sm_2O_3 . The mean chemical composition of the Vermilion monazite is Ce_2O_3 (30.23 wt%), P_2O_5 (29.40 wt%), La_2O_3 (14.08 wt%), Nd_2O_3 (11.23 wt%), Y_2O_3 (0.70 wt%), CaO (0.92 wt%) and SiO_2 (0.79 wt%). Moderate variations in the concentration of ThO_2 (5.32–7.47 wt%), UO_2 (0.0 – 0.08 wt%) and PbO (0.60–0.90 wt%) can be observed between the different grains (Table 5.3).

Chondrite-normalised REE patterns, based on LA-ICP-MS analyses of all three laboratories involved in this study, are consistent (Figure 5.2). Data from UnB of four

monazite crystals shows a strong negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.074\text{-}0.078$). A significant variation is observed in the LREE (1-11 %RSD) and HREE (2-26 %RSD) for all the samples analysed. The Th, Pb and U contents are in the range of 50827-63125 ppm (mean 55438 ppm), 10391-13108 ppm (mean 11403 ppm), and 641-830 ppm (mean 706 ppm), respectively. It should be noted that these Pb values will differ from EPMA measurements because the measured masses via laser ablation are converted to ppm based on their respective natural abundance and do not take into account the radioactive decay of Th and U. The Th/U varies from 73.9 to 84.9 (Table 5.4). Data from five different monazite grains analysed at UFOP are marked by slightly higher Eu/Eu* anomaly (0.079-0.082) with a variation in the LREE (1-7 %RSD) and HREE (2-18 %RSD) between the analysed crystals. The analysed crystals have Th, Pb and U contents in the range 56841-68294 ppm (mean 64465 ppm), 9495-11996 ppm (mean 10981 ppm) and 666-817 ppm (mean 742 ppm), respectively. The Th/U varied from 83.8 to 90.2 (Table 5.4). Data from other five monazite crystals analysed at SKLLE show Eu anomalies in the range of 0.083-0.085 with variations in the LREE (1-7 %RSD) and HREE (4-17 %RSD) for all the analyses. The mean Th, Pb and U contents are 59527 ppm, 7159 ppm and 749 ppm, respectively. The Th/U ranged from 75.8 to 86.3 (Table 5.4).

Table 5.3: Major element composition (wt.%) of Vermilion monazite determined by EPMA

	V1 (n=4)	V2 (n=1)	V3 (n=1)	V4 (n=1)	V5 (n=1)	V6 (n=2)	V7 (n=3)	V8 (n=1)	V9 (n=1)	V10 (n=4)	V11 (n=1)	Average	%RSD
SiO ₂	0.76	0.77	0.75	0.80	0.80	0.74	0.91	0.66	0.91	0.76	0.81	0.79	9.0
P ₂ O ₅	29.12	29.19	29.67	29.16	29.57	29.38	29.25	29.73	29.33	29.65	29.33	29.40	0.7
CaO	0.85	0.71	1.06	0.85	0.80	0.91	0.93	0.87	1.00	0.91	1.20	0.92	14.5
Y ₂ O ₃	0.65	0.65	0.66	0.72	0.81	0.71	0.72	0.73	0.73	0.67	0.66	0.70	7.1
La ₂ O ₃	14.41	14.00	13.85	13.86	13.85	14.81	13.94	14.24	13.46	14.03	14.42	14.08	2.6
Ce ₂ O ₃	30.20	30.64	29.70	30.34	29.91	30.02	29.58	30.75	30.04	30.46	30.94	30.23	1.4
Pr ₂ O ₃	3.37	3.60	3.39	2.96	3.69	3.38	3.17	3.25	3.28	3.19	2.98	3.30	6.8
Nd ₂ O ₃	11.57	11.82	11.67	11.69	11.18	11.19	10.96	11.19	11.04	10.84	10.37	11.23	3.9
Sm ₂ O ₃	1.51	1.76	1.47	1.56	1.54	1.58	1.31	1.36	1.32	1.43	0.96	1.44	14.4
Eu ₂ O ₃	0.01	<b.d	<b.d	<b.d	<b.d	0.07	0.03	<b.d	<b.d	0.12	<b.d	0.06	-
Gd ₂ O ₃	0.84	0.79	1.09	1.03	0.83	0.97	0.95	0.60	0.85	0.78	0.94	0.88	15.4
Tb ₂ O ₃	0.01	0.05	<b.d	<b.d	<b.d	0.01	0.11	0.03	0.10	0.02	<b.d	0.05	-
Dy ₂ O ₃	0.08	0.11	0.10	0.19	0.05	0.11	0.11	0.17	0.13	0.14	0.05	0.11	40.2
PbO	0.67	0.60	0.72	0.81	0.77	0.73	0.89	0.72	0.90	0.75	0.82	0.76	11.7
ThO ₂	5.90	5.32	6.00	6.44	6.91	6.36	7.22	5.66	7.47	5.86	6.29	6.31	10.6
UO ₂	0.02	<b.d	0.04	<b.d	0.04	<b.d	0.08	0.02	0.04	0.01	0.04	0.04	-
Total	99.97	100.00	100.16	100.41	100.74	100.96	100.18	99.98	100.59	99.62	99.79	100.22	0.4
Mole fractions													
ThSiO ₄													0.09
(La-Sm)PO ₄													0.86
(Th, Ca, U, Pb)(PO ₄) ₂													0.03
Y(Gd-Lu)PO ₄													0.02
Sum													1.00

n = number of spots

<b.d = below detection limit

Mole fractions based on four oxygens per formula unit (Pyle et al., 2001)

Table 5.4: Trace elements compositions (ppm) for Vermilion monazite acquired by LA-ICP-MS

Sample	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Pb	Th	U	Th/U	Eu/Eu*	(La/Gd) _N	(Gd/Lu) _N
LA-SF-ICP-MS at UnB																					
V1 (n = 5)	156930	34115	118889	16486	296	8174	644	2258	268	448	32	115	10	-	13108	63125	830	77.8	0.076	16	105
%RSD	11.39	9.03	7.92	7.46	9.11	6.86	5.17	5.11	5.43	4.19	3.55	4.14	6.33	-	13.58	13.13	23.64	13.2	-	-	-
V2 (n = 5)	163840	36472	125293	17285	293	8102	656	2254	265	434	30	107	9	-	11324	56477	666	84.9	0.074	17	115
%RSD	2.63	2.42	3.78	3.87	2.89	4.49	1.46	2.24	2.03	2.56	1.50	3.63	3.47	-	5.01	2.28	4.70	2.6	-	-	-
V3 (n = 5)	140558	29916	104450	13826	256	6776	528	1810	211	352	25	89	8	-	10787	50827	688	73.9	0.078	17	113
%RSD	4.04	2.26	3.14	3.62	4.45	5.32	4.58	5.65	7.13	5.88	5.62	5.38	3.93	-	4.35	3.38	3.29	3.1	-	-	-
V4 (n = 5)	142691	31398	110033	14782	273	7255	553	1860	211	339	24	82	7	-	10391	51325	641	83.5	0.078	16	133
%RSD	5.14	2.97	2.01	1.31	1.47	2.41	3.09	4.92	11.34	18.61	23.90	25.69	24.85	-	16.90	17.01	27.95	18.1	-	-	-
LA-SF-ICP-MS at UFOP																					
V1 (n = 6)	155796	28579	111832	16591	323	8551	773	2557	323	531	36	143	12	0.4	11996	68294	817	83.8	0.080	15	93
%RSD	0.70	1.39	1.15	2.24	2.56	2.58	3.57	5.11	5.40	6.45	6.71	8.28	7.63	46.0	4.12	4.56	8.37	4.3	-	-	-
V2 (n = 6)	156501	28648	114599	16073	314	8492	786	2545	318	530	37	143	12	0.7	11384	66629	749	90.2	0.080	15	93
%RSD	2.86	1.70	1.38	2.56	3.72	4.51	4.42	6.21	8.06	7.54	7.01	8.03	7.29	55.6	9.35	9.51	17.15	10.2	-	-	-
V3 (n = 6)	155937	28306	114829	16178	316	8679	803	2638	331	555	39	153	12	0.5	11105	65523	742	89.1	0.079	15	90
%RSD	2.91	2.29	2.43	5.84	3.74	7.31	8.85	11.97	12.97	13.35	17.34	17.59	16.43	55.9	8.85	9.59	16.20	7.3	-	-	-
V4 (n = 6)	161470	27846	110569	14681	292	7646	695	2230	272	464	32	125	10	0.6	9495	56841	666	85.4	0.082	18	95
%RSD	2.09	1.55	1.48	1.79	1.00	1.94	1.77	1.76	3.07	3.86	4.35	3.50	5.36	53.0	4.53	4.25	3.88	3.6	-	-	-
V5 (n = 6)	157049	28314	116073	15620	312	8405	775	2470	303	515	35	137	11	0.9	10925	65036	735	89.7	0.081	16	97
%RSD	1.72	1.51	1.53	3.47	4.70	3.97	5.56	7.77	9.16	9.82	13.17	15.26	16.94	69.34	9.50	10.04	19.18	9.0	-	-	-
LA-Q-ICP-MS at SKLLE																					
V1 (n = 9)	139370	28301	105653	14697	289	7742	621	2121	255	385	28	100	9	-	7581	63048	783	80.8	0.080	15	112
%RSD	2.72	1.43	1.93	3.71	3.67	4.61	4.72	4.56	4.43	5.54	6.00	7.40	9.70	-	8.19	7.06	9.39	5.6	-	-	-
V2 (n = 8)	143606	27832	103816	13836	273	7030	557	1922	232	350	26	93	8	-	6683	56209	708	79.5	0.082	17	108
%RSD	2.67	1.76	2.94	4.16	3.38	4.65	3.87	3.65	4.05	5.05	5.76	7.02	5.84	-	5.07	4.98	5.45	6.0	-	-	-
V3 (n = 8)	144999	28084	103032	14031	279	7341	584	2039	242	370	28	100	9	-	7066	59268	762	78.0	0.082	17	108
%RSD	2.85	2.30	3.40	5.99	5.63	7.44	7.56	7.01	6.35	5.25	5.69	5.95	4.55	-	7.96	8.11	8.14	6.8	-	-	-
V4 (n = 8)	141346	28140	103795	14262	280	7545	588	2028	237	362	27	95	8	-	6656	55066	646	86.3	0.080	16	120
%RSD	2.79	2.03	2.95	5.58	3.69	7.40	8.24	9.74	11.16	12.10	14.17	14.65	16.70	-	8.26	8.05	15.08	9.8	-	-	-
V5 (n = 8)	143551	28283	105547	14606	300	8000	630	2191	262	395	29	106	9	-	7754	63605	844	75.8	0.082	15	112
%RSD	0.66	0.77	1.17	2.47	3.95	4.01	5.69	6.76	7.23	9.12	9.32	8.74	10.35	-	6.88	5.75	11.22	6.2	-	-	-

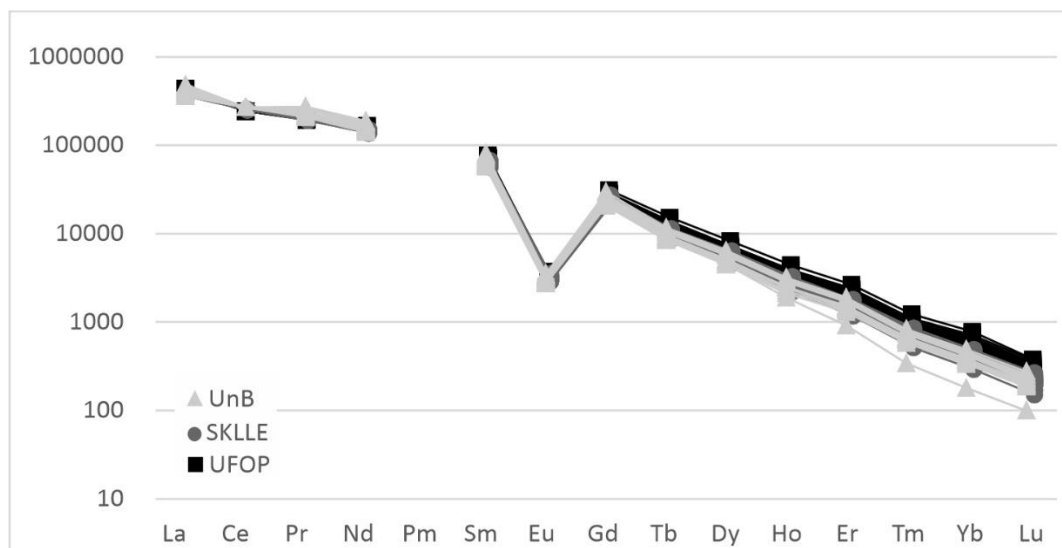


Figure 5.2: Chondrite-normalised (Taylor and McLennan, 1985) REE pattern of Vermilion monazite grains analysed at UnB, UFOP and SKLLE.

5.4.2 Isotopic characterisation

5.4.2.1 ID-TIMS U-Pb data

Four Vermilion monazite crystals were analysed by ID-TIMS at the University of Oslo and three crystals at the Jack Satterly Geochronology Laboratory (Table 5.5). The data acquired from both laboratories show low common/non-radiogenic lead (Pb_c) contents (1.6-7.7 pg) and, consequently, high $^{206}Pb/^{204}Pb$ (16153 to 56630). The U content and the Th/U ratio range from 177 to 1470 ppm and from 66.3 to 75.5, respectively.

The results obtained in Oslo are concordant and sub-concordant, with one result showing minor reverse discordancy (-0.1-0.6% disc.) and the other three overlapping on the concordia uncertainty envelope (Figure 5.3). The analyses yielded weighted mean dates of $^{206}Pb^*/^{238}U = 2671.6 \pm 9.8$ Ma (2 σ ; MSWD = 7.2; n = 4), $^{207}Pb^*/^{235}U = 2668.9 \pm 4.9$ Ma (2 σ ; MSWD = 7.4; n = 4) and $^{207}Pb^*/^{206}Pb^* = 2666.8 \pm 1.8$ Ma (2 σ ; MSWD = 4.0; n = 4). The weighted mean $^{206}Pb^*/^{238}U$ and $^{207}Pb^*/^{206}Pb^*$ ratios obtained are 0.5135 ± 0.0023 (2 σ ; MSWD = 7.2; n = 4) and 0.1815 ± 0.0002 (2 σ ; MSWD = 3.9; n = 4), respectively.

The ID-TIMS data from the Toronto laboratory returned sub-concordant dates, with minor radiogenic Pb loss (1.0-1.8 % disc.) in all three grains analysed (Figure 5.3). Pooled together, the $^{206}Pb^*/^{238}U$, $^{207}Pb^*/^{235}U$, $^{207}Pb^*/^{206}Pb^*$ ratios from the three individual grains gave weighted mean dates of 2636 ± 26 Ma (2 σ ; MSWD = 16), 2655 ± 12 Ma (2 σ ; MSWD = 14) and 2668.6 ± 1.8 Ma (2 σ ; MSWD = 1.3), respectively. The measured

$^{206}\text{Pb}^*/^{238}\text{U}$ and $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratios are 0.5051 ± 0.0060 (2σ ; MSWD = 16; $n = 3$) and 0.1817 ± 0.0002 (2σ ; MSWD = 1.3; $n = 3$), respectively. Despite the minor radiogenic Pb loss, the weighted mean $^{206}\text{Pb}^*/^{238}\text{U}$, $^{207}\text{Pb}^*/^{235}\text{U}$ and $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ dates still agree (within uncertainty) with results from the Oslo laboratory.

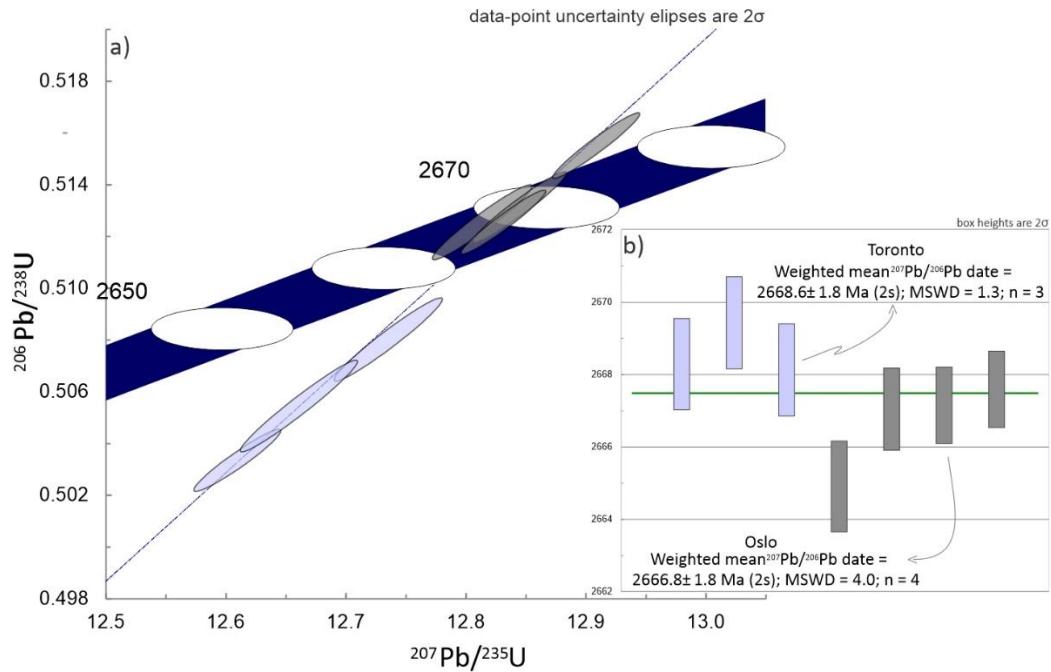


Figure 5.3: a) ID-TIMS U-Pb concordia diagram of Vermilion monazite analysed in Oslo (light grey ellipses) and Toronto (light blue ellipses); b) weighted mean $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ date diagram from both laboratories.

Table 5.5: ID-TIMS U-Pb data for Vermilion monazite

Sample	Weight	U	Th/U	Pbc	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}^*/^{235}\text{U}$	2σ	$^{206}\text{Pb}^*/^{238}\text{U}$	2σ	rho	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$	2σ	$^{206}\text{Pb}^*/^{238}\text{U}$	2σ	$^{207}\text{Pb}^*/^{235}\text{U}$	2σ	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$	2σ	Disc.
	(ug)	(ppm)		(pg)	measured		(abs)		(abs)			(abs)		(abs)	(abs)	(abs)	(abs)	(abs)	(%)
<i>Oslo</i>																			
V1	12	177	73.1	3.6	18612	12.8138	0.0340	0.5126	0.0012	0.96	0.1813	0.0001	2667.6	5.0	2666.1	2.5	2664.9	1.3	-0.1
V2	18	374	75.5	7.7	27576	12.8450	0.0320	0.5131	0.0011	0.96	0.1815	0.0001	2670.1	4.8	2668.3	2.3	2667.1	1.1	-0.1
V3	3	668	67.5	3.9	16153	12.8315	0.0289	0.5126	0.0010	0.96	0.1816	0.0001	2667.6	4.3	2667.4	2.1	2667.2	1.1	0.0
V4	6	469	68.2	5.0	17859	12.9089	0.0297	0.5155	0.0010	0.96	0.1816	0.0001	2680.2	4.4	2673.0	2.2	2667.6	1.1	-0.6
<i>Toronto</i>																			
V1	12	259	66.3	1.6	56630	12.6095	0.0297	0.5034	0.0010	0.95	0.1817	0.0001	2628.2	4.2	2650.9	2.2	2668.3	1.3	1.8
V2	8	334	66.5	2.3	33095	12.7355	0.0369	0.5080	0.0013	0.97	0.1818	0.0001	2648.2	5.6	2660.3	2.7	2669.5	1.3	1.0
V3	3	1470	74.1	3.9	31592	12.6609	0.0400	0.5055	0.0014	0.97	0.1817	0.0001	2637.2	6.2	2654.8	3.0	2668.2	1.3	1.4
Recommended values	-	-	-	-	-	12.8310	0.0180	0.5128	0.0006	-	0.1815	0.0003	2668.4	2.6	2667.3	1.3	2666.5	3.0	-

Notes:

Th/U calculated from radiogenic $^{208}\text{Pb}/^{206}\text{Pb}^*$ ratio and $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ age assuming concordance.

PbC is total amount of common Pb in picograms; assigned the isotopic composition of laboratory

blank

 $^{206}\text{Pb}/^{204}\text{Pb}$ corrected for fractionation and common Pb in the

spike.

Pb/U ratios corrected for fractionation, common Pb in the spike, and blank.

Error Corr is correlation coefficients of X-Y errors on the concordia plot.

Disc is percent discordance for the given $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ age

The recommended values are the weighted mean calculated for the concordant points

5.4.2.2 SHRIMP U-Pb data

The SHRIMP acquired data from six Vermilion monazite crystals yielded concordant results (Table 5.6 and Figure 5.4). A total of twenty-eight spot analyses indicated high homogeneity of the U-Pb and Pb-Pb ratios and resulted in a weighted mean $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ date and ratio of 2662 ± 2 Ma (2σ ; MSWD = 1.04) and of 0.1810 ± 0.0002 (2σ ; MSWD = 1.04), respectively. For the weighted mean $^{206}\text{Pb}^*/^{238}\text{U}$ date and ratio, excluding one spot, values of 2680 ± 10 Ma (2σ ; MSWD = 0.87) and 0.5153 ± 0.0024 (2σ ; MSWD = 0.88) were obtained, respectively (Fig. 5.4). It is noteworthy that the weighted mean $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ date is slightly younger (around 0.2%) than the ID-TIMS $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ date if considering only the internal/random uncertainties.

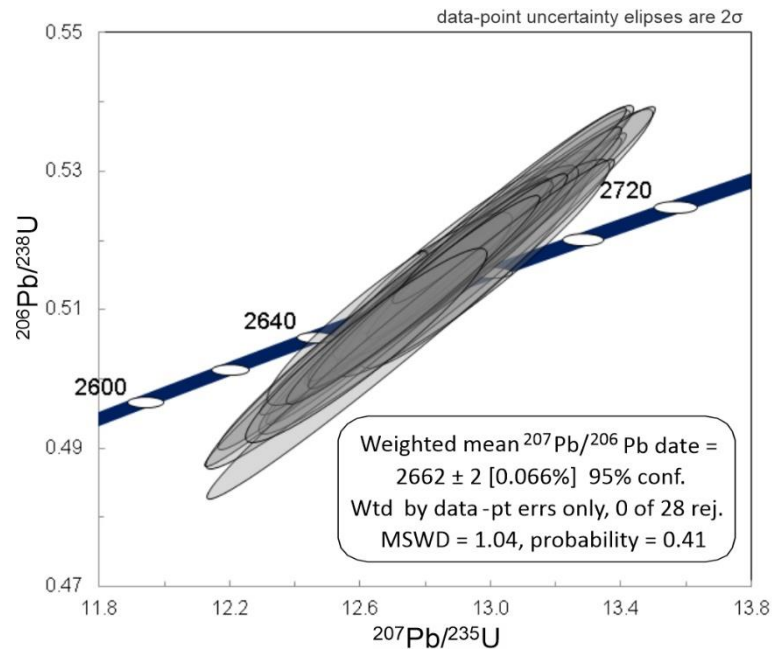


Figure 5.4: SHRIMP U-Pb data from Vermilion monazite. Internal/random uncertainties are reported at 2σ confidence interval.

Table 5.6: SHRIMP U-Pb data for Vermilion monazite

Sample	Th/U	$\frac{^{207}\text{Pb}^*}{^{206}\text{Pb}^*}$	2 σ	$\frac{^{207}\text{Pb}^*}{^{235}\text{U}}$	2 σ	$\frac{^{206}\text{Pb}^*}{^{238}\text{U}}$	2 σ	$\frac{^{208}\text{Pb}^*}{^{232}\text{Th}}$	2 σ	$\frac{^{206}\text{Pb}^*}{^{238}\text{U}}$	2 $\sigma\%$	$\frac{^{207}\text{Pb}^*}{^{235}\text{U}}$	2 $\sigma\%$	$\frac{^{207}\text{Pb}^*}{^{206}\text{Pb}^*}$	2 $\sigma\%$	$\frac{^{208}\text{Pb}^*}{^{232}\text{Th}}$	2 $\sigma\%$
V1 (n = 5)	84.5	2664	10	2669	23	2675	51	2679	34	0.5144	2.3	12.86	2.4	0.1813	0.59	0.1417	1.4
V2 (n = 4)	73.2	2664	11	2684	23	2711	51	2722	37	0.5228	2.3	13.06	2.4	0.1812	0.64	0.1442	1.5
V3 (n = 4)	82.0	2658	10	2664	26	2672	60	2674	35	0.5136	2.7	12.79	2.8	0.1806	0.60	0.1414	1.4
V4 (n = 6)	87.3	2664	11	2671	24	2681	54	2711	42	0.5156	2.5	12.88	2.5	0.1812	0.67	0.1436	1.7
V5 (n = 4)	72.0	2660	10	2668	25	2679	57	2696	37	0.5152	2.6	12.84	2.7	0.1808	0.58	0.1427	1.5
V6 (n = 5)	82.9	2661	11	2665	28	2670	62	2724	47	0.5131	2.8	12.80	2.9	0.1809	0.66	0.1443	1.8

Note: all the ratios were corrected for ^{204}Pb

5.4.2.3 LA-ICP-MS U-Pb data

The LA-ICP-MS U-Pb results for the Vermilion monazite analysed in different laboratories are shown in Table 5.7. At UnB, LA-SF-ICP-MS data acquired from five fragments (total of forty-eight spot dates) yielded a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ date and ratio of $2664 \pm 4/27$ Ma (2σ ; MSWD = 1.02) and 0.1818 ± 0.0004 (2σ ; MSWD = 1.02), respectively, and a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date and ratio of $2675 \pm 11/29$ Ma (2σ ; MSWD = 3.6) and 0.5145 ± 0.0027 (2σ ; MSWD = 3.6), respectively. Some spots were slightly discordant due to minor Pb loss in one of the investigated crystals (Figure 5.5a). The UFOP LA-MC-ICP-MS data obtained from six grains show a high degree of U-Pb isotope homogeneity. Fifty-eight laser spot analyses pooled from the six crystals produced a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ date and ratio of $2666 \pm 1/27$ Ma (2σ ; MSWD = 0.9) and of 0.1814 ± 0.0001 (2σ ; MSWD = 0.9), respectively, and a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date and ratio of $2667 \pm 1/27$ Ma (2σ ; MSWD = 0.021) and 0.5125 ± 0.0002 (2σ ; MSWD = 0.021), respectively (Fig. 5.5b). The data acquired by LA-Q-ICP-MS (at SKLLE) of five crystals, combining forty-one spot dates produced a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ date and ratio of $2665 \pm 5/27$ Ma (2σ ; MSWD = 0.97) and of 0.1813 ± 0.0005 (2σ ; MSWD = 0.96), respectively, and a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date and ratio of $2652 \pm 7/27$ Ma (2σ ; MSWD = 1.3) and 0.5088 ± 0.0017 (2σ ; MSWD = 1.3), respectively, showing minor discordance (Fig. 5.5c). Lastly, the U-Pb data acquired by Jena PlasmaQuant Elite ICP-MS at Portsmouth from four crystals (total of fifty-two spots) returned a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ date and ratio of $2672 \pm 8/28$ Ma (2σ ; MSWD = 0.77) and of 0.1821 ± 0.0008 (2σ ; MSWD = 0.78), respectively, and a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date and ratio of $2610 \pm 13/29$ Ma (2σ ; MSWD = 0.71) and 0.5026 ± 0.0030 (2σ ; MSWD = 0.77), respectively. The $^{206}\text{Pb}/^{238}\text{U}$ date and ratios are slightly lower due to some Pb loss (Fig. 5.5d). All individual spot dates are equivalent within uncertainty of each other, and the results are consistent with the ID-TIMS and SHRIMP dates.

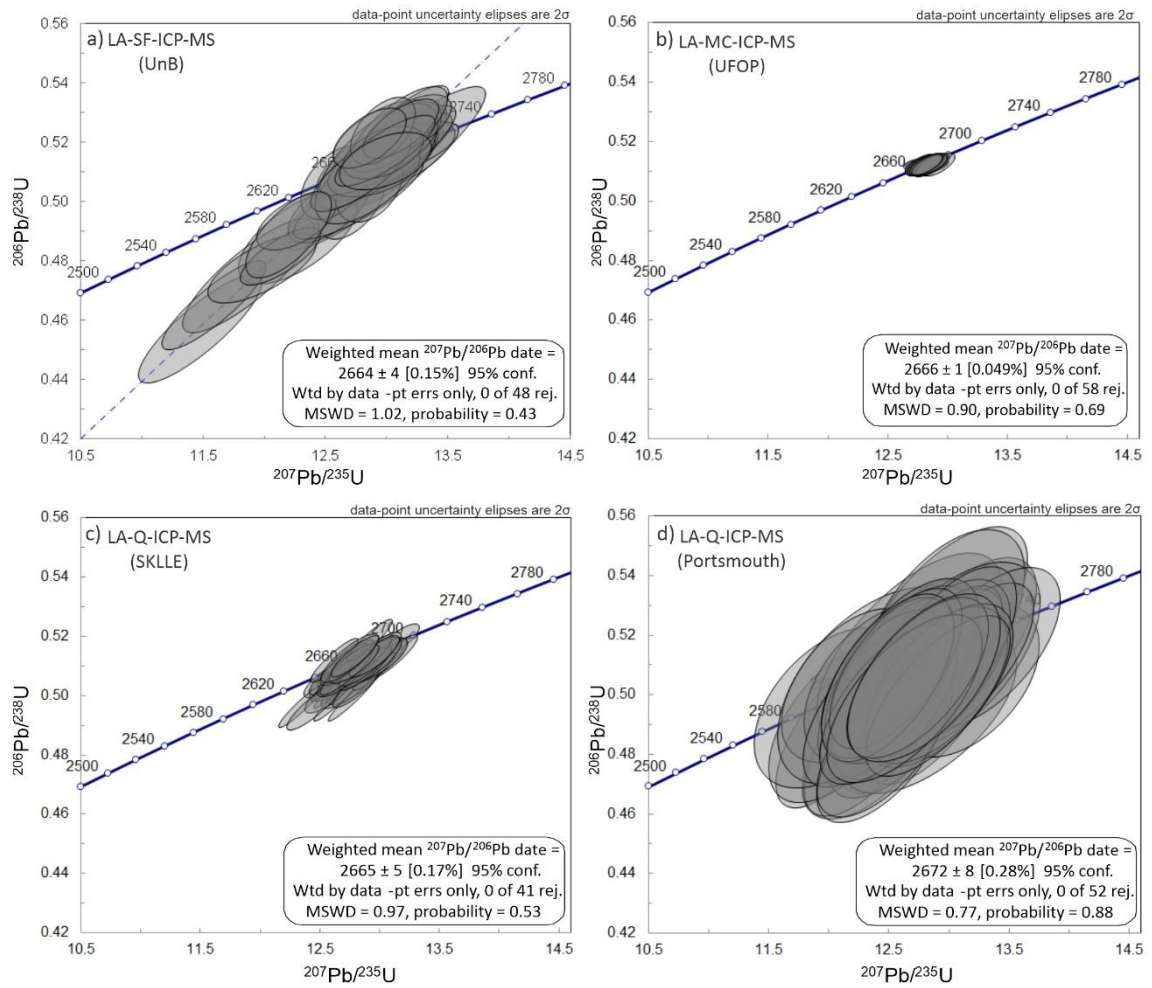


Figure 5.5: U-Pb data from Vermilion monazite analysed in different laboratories using different techniques. Internal/random uncertainties are reported at 2σ confidence interval.

Table 5.7: LA-ICP-MS U-Pb data obtained for Vermilion monazite in different laboratories

Sample	U (ppm)	Th/U	$^{207}\text{Pb}/$ ^{206}Pb	2 σ %	$^{207}\text{Pb}/$ ^{235}U	2 σ %	$^{206}\text{Pb}/$ ^{238}U	2 σ %	Rho	$^{208}\text{Pb}/$ ^{232}Th	2 σ %	$^{206}\text{Pb}/$ ^{238}U	2 σ	$^{207}\text{Pb}/$ ^{235}U	2 σ	$^{207}\text{Pb}/$ ^{206}Pb	2 σ	$^{208}\text{Pb}/$ ^{232}Th	2 σ
<i>LA-SF-ICP-MS at UnB</i>																			
V1 (n = 8)	500	84.3	0.1839	1.84	12.7690	2.67	0.5032	2.18	0.63	0.1427	1.25	2683	31	2626	47	2659	25	2695	32
V2 (n = 10)	513	87.6	0.1818	1.77	12.5181	2.65	0.4978	2.04	0.75	0.1416	1.35	2666	29	2602	43	2639	25	2676	34
V3 (n = 10)	531	87.3	0.1820	1.85	12.9695	2.34	0.5134	1.81	0.64	0.1465	1.11	2666	31	2669	39	2674	22	2763	29
V4 (n = 10)	514	86.8	0.1808	1.76	12.9329	2.48	0.5158	1.95	0.65	0.1454	1.21	2654	29	2679	43	2670	23	2745	31
V5 (n = 10)	477	96.9	0.1806	1.74	12.9173	2.21	0.5170	1.81	0.63	0.1446	1.08	2654	29	2685	40	2670	21	2730	28
<i>LA-MC-ICP-MS at UFOP</i>																			
V1 (n = 11)	657	80.7	0.1809	0.58	12.7834	0.65	0.5124	0.29	0.45	-	-	2667	6	2664	6	2661	10	-	-
V2 (n = 6)	651	81.5	0.1810	0.53	12.7898	0.76	0.5125	0.55	0.72	-	-	2667	12	2664	7	2662	9	-	-
V3 (n = 10)	833	79.8	0.1819	0.62	12.8516	0.71	0.5124	0.33	0.47	-	-	2667	7	2669	7	2670	10	-	-
V4 (n = 11)	669	86.6	0.1813	0.66	12.8117	0.72	0.5125	0.26	0.37	-	-	2667	6	2666	7	2665	11	-	-
V5 (n = 11)	645	86.2	0.1814	0.67	12.8179	0.88	0.5124	0.56	0.64	-	-	2667	12	2666	8	2666	11	-	-
V6 (n = 9)	840	84.2	0.1819	0.60	12.8499	0.84	0.5125	0.59	0.70	-	-	2667	13	2669	8	2670	10	-	-
<i>LA-Q-ICP-MS at SKLLE</i>																			
V1 (n = 9)	705	80.8	0.1814	1.92	12.7100	2.24	0.5070	1.83	0.82	-	-	2644	40	2658	21	2665	32	-	-
V2 (n = 8)	637	79.5	0.1810	1.82	12.9171	2.06	0.5127	1.77	0.86	-	-	2668	39	2674	19	2662	30	-	-
V3 (n = 8)	685	78.0	0.1815	1.85	12.6928	2.06	0.5033	1.84	0.90	-	-	2628	40	2657	19	2667	31	-	-
V4 (n = 8)	581	86.3	0.1821	2.04	12.7750	2.30	0.5079	1.93	0.85	-	-	2648	42	2663	22	2672	34	-	-
V5 (n = 8)	760	75.8	0.1804	1.82	12.8180	2.24	0.5127	1.92	0.85	-	-	2668	42	2666	21	2657	30	-	-
<i>LA-Q-ICP-MS at Portsmouth</i>																			
V1 (n = 13)	-	-	0.1820	3.19	12.5115	3.66	0.4971	4.35	0.61	0.1474	7.41	2588	93	2621	35	2671	53	2769	192
V2 (n = 14)	-	-	0.1813	3.90	12.7464	4.31	0.5094	4.64	0.57	0.1483	7.42	2636	100	2631	41	2665	65	2786	193
V3 (n = 13)	-	-	0.1829	3.24	12.7131	3.72	0.5048	4.40	0.62	0.1493	7.42	2619	95	2638	36	2679	54	2802	197
V4 (n = 12)	-	-	0.1820	3.18	12.6550	3.76	0.5020	4.40	0.62	0.1476	7.51	2607	95	2627	35	2671	53	2771	193

Note: all the ratios, dates and uncertainties are mean values of spot analyses carried out on individual fragments

5.4.2.4 Sm-Nd isotope composition

Two aliquots of Vermilion monazite analysed by ID-TIMS yielded $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.510698 ± 0.000003 (2σ) and of 0.510692 ± 0.000003 (2σ), with a weighted mean of 0.510694 ± 0.000040 (2σ ; MSWD = 9.6) (Table 5.8, Figure 5.6a). The bulk Nd isotope composition obtained by solution mode MC-ICP-MS gave a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.510726 ± 0.000014 (2σ) consistent, within uncertainties, with the weighted mean ID-TIMS data.

A total of fifty-eight LA-MC-ICP-MS Sm-Nd isotope measurements were obtained from six fragments at UFOP (Table 5.8; Figure 5.6a, b). The results have a mean of 0.51068 ± 0.00002 (2σ) (0.007 %RSD), and a variation among individual grains from 0.51065 ± 0.00002 (2σ) to 0.51072 ± 0.00002 (2σ) (Table 5.8). The $^{147}\text{Sm}/^{144}\text{Nd}$ ratio shows significant variation among different grains but is homogeneous within a given individual monazite crystal. The mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratio from all grains is 0.0869 ± 0.0002 (2σ) (2.5 %RSD), and individual grains have mean values that vary from 0.0850 ± 0.0002 (2σ) to 0.0901 ± 0.0002 (2σ) (Table 5.8 and Figure 5.6). The calculated ϵNd_i (initial epsilon Nd) gave a small dispersion, ranging from -0.8 ± 0.5 (2σ) to -0.2 ± 0.5 (2σ). The variation in $^{147}\text{Sm}/^{144}\text{Nd}$ ratios among grains of the Vermilion monazite is greater than that for Steenkampskraal/Namaqua (Liu et al. 2012; Fisher et al., 2020), Itambé (Gonçalves et al., 2016) and Diamantina (Gonçalves et al., 2018) monazite used as reference materials (Figure 5.6 and Supplementary material). In contrast, within individual Vermilion monazite grains, the variation in the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio is small (0.001 to 0.008 %RSD). In the diagram of $^{147}\text{Sm}/^{144}\text{Nd}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ (Figure 5.7), the Vermilion monazite data cluster in two distinct groups, but overlap with the reference isochron of 2667 Ma (ID-TIMS date). The value for $^{145}\text{Nd}/^{144}\text{Nd}$ (0.34842 ± 1 ; 2σ) agrees with the canonical value from Wasserburg et al., (1981).

As highlighted above, the results of fifty LA-MC-ICP-MS Sm-Nd isotope measurements obtained at SKLLE (Table 5.8) also indicate that the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is relatively homogeneous and that there is high reproducibility between the grains, consistent with the ID-TIMS results (Figure 5.6a, b). The measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are similar and range from 0.51065 ± 0.00001 (2σ) to 0.51069 ± 0.00001 (2σ), giving a mean of 0.51067 ± 0.00001 (2σ) (0.007% RSD) (Table 5.8). It is relevant to note that the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are slightly heterogeneous for both laboratories, as observed in the two clusters with higher and lower weighted mean values of 0.51071 ± 0.00001 (2σ ; MSWD

= 13; n = 51) and of 0.51065 ± 0.00001 (2σ ; MSWD = 7.6; n = 57) (Figure 5.6a), respectively, which still agree with the ID-TIMS results. The $^{147}\text{Sm}/^{144}\text{Nd}$ ratio results for all grains show an overall mean of 0.0835 ± 0.0001 (2σ) (2.2 %RSD) and exhibit a small variation (Figure 5.6). The V8 and V9 crystals have very low inter-grain $^{147}\text{Sm}/^{144}\text{Nd}$ heterogeneity, with mean values of 0.0823 ± 0.0001 (2σ) and 0.0828 ± 0.0001 (2σ), respectively. The V7, V10 and V11 crystals were more heterogeneous, ranging from 0.0839 ± 0.0001 (2σ) to 0.0845 ± 0.0001 (2σ). The ϵNdi results agree, within uncertainty, and range from 0.4 ± 0.4 (2σ) to 0.6 ± 0.4 (2σ). The ϵNdi data are slightly different from those reported above, possibly related to an analytical artifact (-0.8 ± 0.5 to -0.2 ± 0.5 ; 2σ ; UFOP). The Vermilion monazite samples from this batch are comparable to those reported before in the $^{147}\text{Sm}/^{144}\text{Nd}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ diagram (Figure 5.7). The obtained value for the $^{145}\text{Nd}/^{144}\text{Nd}$ ratio of 0.34840 ± 1 (2σ) is in agreement with the value proposed by Wasserburg et al., (1981).

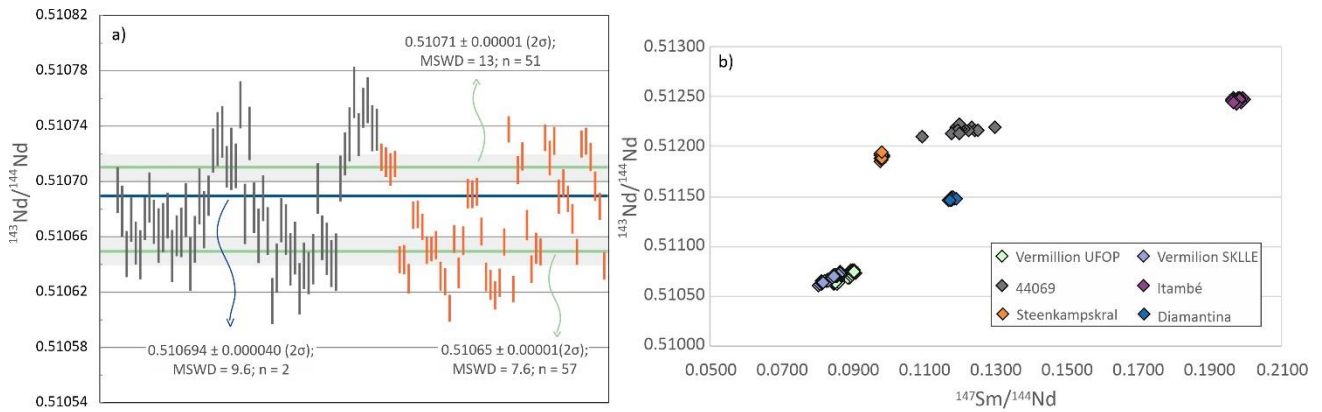


Figure 5.6: a) Comparison of $^{143}\text{Nd}/^{144}\text{Nd}$ ratios obtained by ID-TIMS (blue line) and LA-MC-ICP-MS in two laboratories (green lines). The data reveal significant heterogeneities of the grains between UFOP (grey error bars; 2σ) and SKLLE (orange error bars; 2σ) laboratories; b) $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{147}\text{Sm}/^{144}\text{Nd}$ diagram exhibiting the slightly variation in these ratios compared to others reference materials (Steenkampskraal-Knoper et al., 2000, 44069-Aleinikoff et al., 2006, Itambé-Gonçalves et al., 2016 and Diamantina-Gonçalves et al., 2018). The 2SE error bars are smaller than the symbols for each spot data.

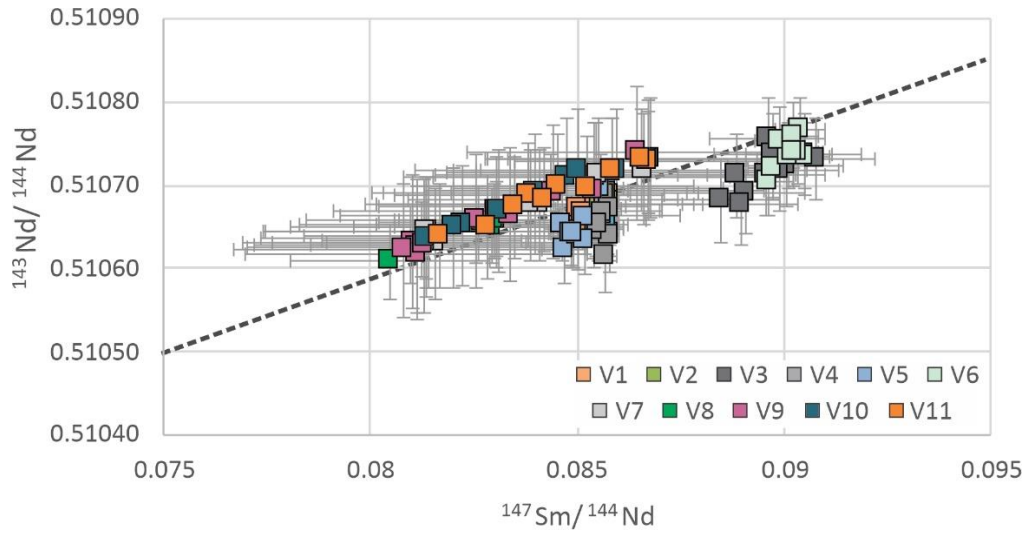


Figure 5.7: Sm-Nd isotope data from eleven grains of Vermilion monazite obtained at UFOP (V1-V6) and SKLLE (V7-V11). The reference isochron is based on an $^{207}\text{Pb}/^{206}\text{Pb}$ date of ca. 2667 Ma, obtained by ID-TIMS.

Table 5.8: Sm-Nd isotopic composition of the Vermilion monazite acquired by ID-TIMS and LA-MC-ICP-MS

Sample	$^{147}\text{Sm}/^{144}\text{Nd}$	$\pm 2\sigma$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2\sigma$	$^{143}\text{Nd}/^{144}\text{Ndi}$	$\pm 2\sigma$	$^{145}\text{Nd}/^{144}\text{Nd}$	$\pm 2\sigma$	eNdi	$\pm 2\sigma$	Reference age
ID-TIMS at UnB											
V1	-	-	0.510698	0.000003	-	-	-	-	-	-	
V2	-	-	0.510692	0.000003	-	-	-	-	-	-	
solution MC-ICP-MS at UnB											
V1	-	-	0.510726	0.000014	-	-	-	-	-	-	
LA-MC-ICP-MS at UFOP											
V1 (n = 11)	0.0854	0.0003	0.51067	0.00002	0.50917	0.00002	0.34842	0.00001	-0.2	0.5	2667
V2 (n = 9)	0.0857	0.0002	0.51067	0.00002	0.50916	0.00002	0.34842	0.00001	-0.4	0.5	
V3 (n = 11)	0.0896	0.0002	0.51072	0.00002	0.50914	0.00002	0.34842	0.00001	-0.8	0.5	
V4 (n = 9)	0.0857	0.0002	0.51066	0.00002	0.50915	0.00002	0.34842	0.00001	-0.6	0.5	
V5 (n = 9)	0.0850	0.0002	0.51065	0.00002	0.50915	0.00002	0.34842	0.00001	-0.5	0.5	
V6 (n = 9)	0.0901	0.0002	0.51068	0.00002	0.50915	0.00002	0.34842	0.00001	-0.5	0.5	
LA-MC-ICP-MS at SKLLE											
V7 (n = 10)	0.0839	0.0001	0.51068	0.00001	0.50920	0.00001	0.34840	0.00001	0.5	0.4	
V8 (n = 10)	0.0823	0.0001	0.51065	0.00001	0.50920	0.00001	0.34840	0.00001	0.4	0.4	
V9 (n = 10)	0.0828	0.0001	0.51066	0.00001	0.50920	0.00001	0.34840	0.00001	0.4	0.4	
V10 (n = 10)	0.0842	0.0001	0.51069	0.00001	0.50921	0.00001	0.34840	0.00001	0.6	0.4	
V11 (n = 10)	0.0845	0.0001	0.51069	0.00001	0.50920	0.00001	0.34840	0.00001	0.5	0.4	

Notes: (i) = initial isotope ratio calculated

5.5 Discussion

5.5.1 Assessing the potential of Vermilion monazite as a primary reference material

To investigate and demonstrate the suitability of Vermilion monazite as a primary reference material, four U-Pb data acquisition runs (named Round 1 to 4) were performed using an LA-SF-ICP-MS at UFOP. All results are shown in Table 5.9 and Figure 5.8. Vermilion monazite was used as the main calibrant to analyse other reference materials, treated as unknowns, and other monazite samples of known ages (see Table 5.9). The analytical conditions were the same as acquired for monazite in Gonçalves et al., (2016). A complete dataset is shown in the Supplementary material. The values of Vermilion monazite obtained by ID-TIMS (see Discussion) were used in the data reduction performed in the Saturn software (Silva et al., 2023). A ^{207}Pb -based common Pb correction was applied in some analyses of the unknowns.

For Bananeira monazite (Th = 6.8 wt.%; Gonçalves et al., 2016), the analyses in Round 1 and 2 produced weighted mean $^{206}\text{Pb}/^{238}\text{U}$ dates of $510 \pm 4/6$ Ma (2σ , MSWD = 0.20, $n = 7$) and $510 \pm 4/6$ Ma (2σ , MSWD = 0.045, $n = 7$), respectively. The age offset for Bananeira monazite relative to the accepted value of the $^{206}\text{Pb}/^{238}\text{U}$ date is ca. 0.70% (Table 5.9). Combining data from both runs, the weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date was $510 \pm 3/6$ Ma (2σ , MSWD = 0.113, $n = 14$) (Figure 5.8a) and the weighted mean $^{207}\text{Pb}/^{235}\text{U}$ date was $512 \pm 3/6$ Ma (2σ , MSWD = 0.24, $n = 14$). The results are within the uncertainties of the ID-TIMS values reported by Gonçalves et al. (2016; $^{206}\text{Pb}/^{238}\text{U}$ date of 513.6 ± 1.2 Ma; $^{207}\text{Pb}/^{235}\text{U}$ date of 507.7 ± 1.3 Ma). No matrix effects, at least within the precision of the LA-ICP-MS technique, was observed.

Diamantina monazite (Th = 0.4 wt.%; Gonçalves et al. 2018; $^{206}\text{Pb}/^{238}\text{U}$ ID-TIMS date of 495.26 ± 0.54) was investigated in Round 1 and gave a concordia age of $498 \pm 5/7$ Ma (2σ , MSWD of conc. + equi. = 0.25, $n = 7$) (Figure 5.8b), within uncertainty and deviating about ca. 0.55% from the recommended age of Gonçalves et al. (2018; Table 5.9). As this monazite has a low U content, a ^{207}Pb -based Pb_c correction was applied to spots that contained very little radiogenic Pb.

The Itambé monazite (Th = 8.9 wt.%; Gonçalves et al., 2016) was dated in Rounds 1 to 4, and gave weighted mean $^{206}\text{Pb}/^{238}\text{U}$ dates of $515 \pm 4/7$ Ma (2σ , MSWD = 0.10, $n = 7$), $506 \pm 4/6$ Ma (2σ , MSWD = 0.13, $n = 7$), $512 \pm 4/6$ Ma (2σ , MSWD = 0.019, $n = 8$), and $512 \pm 3/6$ Ma (2σ , MSWD = 0.13, $n = 11$), respectively. Combining all points, we

obtained a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean date of $511 \pm 2/5$ Ma (2σ , MSWD = 0.41, $n = 33$) (Figure 5.8c), which is consistent with the value published by Gonçalves et al., (2016; $^{206}\text{Pb}/^{238}\text{U}$ ID-TIMS date of 511.79 ± 0.52 Ma). The offsets from the certified $^{206}\text{Pb}/^{238}\text{U}$ date varied from ca. -1.13% to +0.63% (Table 5.9). However, the $^{207}\text{Pb}/^{235}\text{U}$ weighted mean date of $517 \pm 2/6$ Ma (2σ , MSWD = 0.66, $n = 33$) is slightly higher than the accepted $^{207}\text{Pb}/^{235}\text{U}$ date of 506.44 ± 0.73 Ma (Gonçalves et al., 2016).

The Thompson Mine monazite (Th = 7-19 wt.%; Buick et al., 2011; Williams et al., 1996) was also analysed in Rounds 1 to 4. The obtained values returned weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ dates of $1782 \pm 12/21$ Ma (2σ , MSWD = 0.102, $n = 5$), $1785 \pm 9/20$ Ma (2σ , MSWD = 1.00, $n = 6$), $1795 \pm 28/33$ Ma (2σ , MSWD = 3.5, $n = 7$), and $1773 \pm 6/19$ Ma (2σ , MSWD = 1.08, $n = 8$), respectively. The results of all compiled tests yielded a $^{207}\text{Pb}/^{206}\text{Pb}$ weighted mean date of $1783 \pm 7/19$ Ma (2σ , MSWD = 2.1, $n = 25$) (Figure 5.8d), with offset values ranging from ca. +0.40% to +1.64% (Table 5.9). The results overlap with the ID-TIMS age published by Williams et al., (1996) of 1766 Ma (uncertainties unpublished). No matrix effects were observed, at least within the precision of the technique.

Reference material USGS 44069 (Th = 1.3-5.0 wt.%; Buick et al., 2011) with $^{206}\text{Pb}/^{238}\text{U}$ ID-TIMS date of 424.9 ± 0.4 Ma (Aleinikoff et al., 2006) was tested in three runs (Round 1 to 3). It gave $^{206}\text{Pb}/^{238}\text{U}$ weighted mean dates of $431 \pm 3/5$ Ma (2σ , MSWD = 0.085, $n = 12$), $425 \pm 3/5$ Ma (2σ , MSWD = 0.42, $n = 7$), and $426 \pm 4/6$ Ma (2σ , MSWD = 0.016, $n = 7$). ^{207}Pb -correction was applied in three individual spots. The $^{206}\text{Pb}/^{238}\text{U}$ weighted mean combining all the individual spots yielded a date of $428 \pm 2/5$ Ma (2σ , MSWD = 0.46, $n = 26$) (Figure 5.8e), with the offset varying from ca. +0.02% to +1.44% (Table 5.9). The results are within the uncertainties of the accepted values, with no apparent matrix effects.

Paraíso monazite (Th = 8.3 wt.%; Gonçalves et al. 2016; $^{207}\text{Pb}/^{235}\text{U}$ date of 509.6 ± 5.4 Ma) was dated in Round 2 and gave a weighted mean $^{207}\text{Pb}/^{235}\text{U}$ date of $510 \pm 4/6$ Ma (2σ , MSWD = 0.019, $n = 7$) (Figure 5.8f). The result agrees with the published data (Table 5.9) and apparently do not show matrix effects.

The Steenkampskraal monazite (Th = 8.3 wt.%; Liu et al., 2012) reference material (also known as Namaqualand, Liu et al., 2012, or Namaqua, Kaur et al., 2016) was analysed in Round 3, and returned a concordia age of $1033 \pm 8/13$ Ma (2σ , MSWD conc/equi. = 1.9, $n = 15$) (Figure 5.8g). This result agrees with the values previously

published by Knoper et al. (2000; SHRIMP date of ca. 1033 Ma), Kaur et al., (2016; ID-TIMS date of 1027 ± 1 Ma) and Fisher et al. (2020; 1026 ± 1.5 Ma). The offset for the U-Pb date obtained for Steenkampskraal monazite is ca. +0.58% (Table 5.9).

The Madagascar monazite (known as M1-M4, Th = 7.7-10.5 wt.%; Liu et al., 2012) was analysed in Round 4 and gave a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of $526 \pm 3/6$ Ma (2σ , MSWD = 0.15, $n = 7$) (Figure 5.8h). This result is consistent with previously published weighted mean Q-ICP-MS $^{206}\text{Pb}/^{238}\text{U}$ dates from Liu et al. (2012) from four crystals analysed of M1 = 524.8 ± 3.7 Ma, M2 = 523.3 ± 3.6 Ma, M3 = 520.8 ± 3.8 Ma, and M4 = 519.0 ± 3.7 Ma. The offset obtained for Madagascar monazite is ca. +0.23% (considering the reference age of M1 monazite fragment from Liu et al., 2012) (Table 5.9).

Lastly, a megacryst of Paleoproterozoic magmatic/hydrothermal Houtenbek monazite (Th = 2.4-3.2 wt.%; Buick et al., 2011), which has been related to emplacement of the Bushveld-age granites (e.g., Buick et al., 2011) was investigated here in Round 3 and 4. This monazite is not a reference material. It shows porous zones of alteration but was included to test the use of Vermilion monazite to date a relatively old monazite. Dating of this sample yielded concordant to sub-concordant spot dates and weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ dates of $2047 \pm 10/23$ Ma (2σ , MSWD = 0.61, $n = 6$) and $2045 \pm 7/22$ Ma (2σ , MSWD = 1.3, $n = 14$) for the two analytical sessions, respectively. Combining all the analytical spots from this monazite, in which only one spot received $^{207}\text{Pb}_c$ -correction, gave a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ date of $2044 \pm 5/21$ Ma (2σ , MSWD = 1.09, $n = 20$) (Figure 5.8i), in agreement with previous SHRIMP and LA-ICP-MS weighted mean dates of 2059.2 ± 3.5 Ma and 2046 ± 10 Ma, respectively, reported by Buick et al. (2011), corresponding to age offsets of -0.79% (Round 3) and 0.59% (Round 4).

Despite the wide variability between age and Th content between the Vermilion monazite and the samples used on the round-robin, no apparent matrix effects were observed at the precision of the LA-ICP-MS technique. For SIMS/SHRIMP analyses, matrix effects related to Th composition have been observed for U-Pb geochronology and oxygen isotopes determination (e.g., Stern and Berman, 2000; Fletcher et al., 2010; Rubatto et al., 2014). Matrix effects related to significant differences between age of the RM and unknown have also been reported for LA-ICP-MS and SIMS/SHRIMP (Stern and Berman, 2000; Kohn, 2009; Fletcher et al., 2010) but are relatively difficult to observe and quantify its contribution. This round-robin test thus shows that it is possible

to use an Archean monazite to date younger samples with relative ease and negligible matrix-related offsets, at the current precision achieved by LA-ICP-MS method.

Table 5.9: LA-ICP-MS U-Pb results from the round-robin analysis using Vermilion monazite as primary reference material

Sample	U (ppm)	Th/U	$^{207}\text{Pb}/^{206}\text{Pb}$	2 σ %	$^{207}\text{Pb}/^{235}\text{U}$	2 σ %	$^{206}\text{Pb}/^{238}\text{U}$	2 σ %	Rho	$^{206}\text{Pb}/^{238}\text{U}$	2 σ	$^{207}\text{Pb}/^{235}\text{U}$	2 σ	$^{207}\text{Pb}/^{206}\text{Pb}$	2 σ	Age offset (%)
<i>Round 1</i>																
Bananeira (n = 7)	3268	22.0	0.0579	1.50	0.6567	2.73	0.0823	2.28	0.83	510	11	513	12	524	33	-0.70%
Diamantina (n = 7)	204	28.6	0.0572	4.04	0.6338	4.82	0.0803	2.60	0.55	498	12	498	20	501	92	0.55%
Itambé (n = 7)	3033	19.0	0.0584	1.38	0.6685	2.73	0.0831	2.35	0.86	514	12	520	12	543	31	0.63%
Thompson Mine (n = 5)	2133	70.2	0.1089	1.54	4.7045	2.99	0.3132	2.56	0.86	1756	39	1768	27	1782	28	0.91%
USGS 44069 (n = 12)	3601	9.0	0.0558	1.65	0.5315	2.90	0.0691	2.36	0.82	431	10	433	11	444	37	1.44%
<i>Round 2</i>																
Bananeira (n = 7)	3245	18.1	0.0576	1.63	0.6542	3.05	0.0824	2.58	0.84	510	13	511	13	515	36	-0.70%
Itambé (n = 7)	5281	19.1	0.0580	1.48	0.6522	2.69	0.0816	2.21	0.84	506	11	510	11	528	33	-1.13%
Paraíso (n = 7)	3445	18.2	0.0577	1.37	0.6523	2.63	0.0821	2.25	0.85	508	11	510	11	517	30	0.08%
Thompson Mine (n = 7)	2198	62.2	0.1096	1.42	4.7570	2.78	0.3148	2.38	0.87	1764	37	1777	25	1793	26	1.08%
USGS 44069 (n = 6)	3387	9.1	0.0556	1.54	0.5224	2.78	0.0682	2.30	0.83	425	9	427	10	436	35	0.02%
<i>Round 3</i>																
Houtenbek (n = 6)	1396	23.4	0.1263	1.59	6.5276	4.01	0.3747	3.63	0.89	2052	64	2050	38	2048	28	-0.59%
Itambé (n = 8)	2459	34.0	0.0585	1.48	0.6658	2.86	0.0826	2.44	0.86	512	12	518	12	547	33	0.04%
Steenkampskraal (n = 15)	1499	43.6	0.0740	1.77	1.7555	3.53	0.1721	3.05	0.87	1024	29	1029	24	1040	36	0.58%
Thompson Mine (n = 7)	1543	57.0	0.1098	1.81	4.7537	3.50	0.3141	2.98	0.85	1761	46	1777	31	1795	33	1.64%
USGS 44069 (n = 7)	2613	9.1	0.0557	1.85	0.5246	3.42	0.0683	2.88	0.84	426	12	428	12	441	42	0.26%
<i>Round 4</i>																
Houtenbek (n = 14)	1785	23.6	0.1260	1.34	6.3684	3.15	0.3665	2.80	0.87	2013	49	2027	30	2043	24	-0.79%
Itambé (n = 11)	2490	32.7	0.0584	1.25	0.6655	2.39	0.0827	2.04	0.85	512	10	518	10	543	28	0.04%
Madagascar (n = 7)	3656	42.0	0.0583	1.48	0.6831	2.28	0.0850	1.66	0.76	526	8	529	10	541	33	0.23%
Thompson Mine (n = 8)	3033	46.3	0.1090	1.14	4.7365	2.01	0.3152	1.64	0.82	1766	25	1774	19	1782	21	0.40%

n = number of spots analysed

Note: all the ratios, dates and uncertainties are mean values of spot analyses carried out on individual fragments

Age offset = offset of the obtained age compared to the reference value. References: Bananeira, Itambé, Paraíso - Gonçalves et al. (2016); Diamantina - Gonçalves et al. (2018); Thompson Mine - Williams et al. (1996); USGS 44069 - Aleinikoff et al. (2006); Houtenbek - Buick et al. (2010); Steenkampskraal - Kaur et al. (2016); Madagascar - Liu et al. (2012).

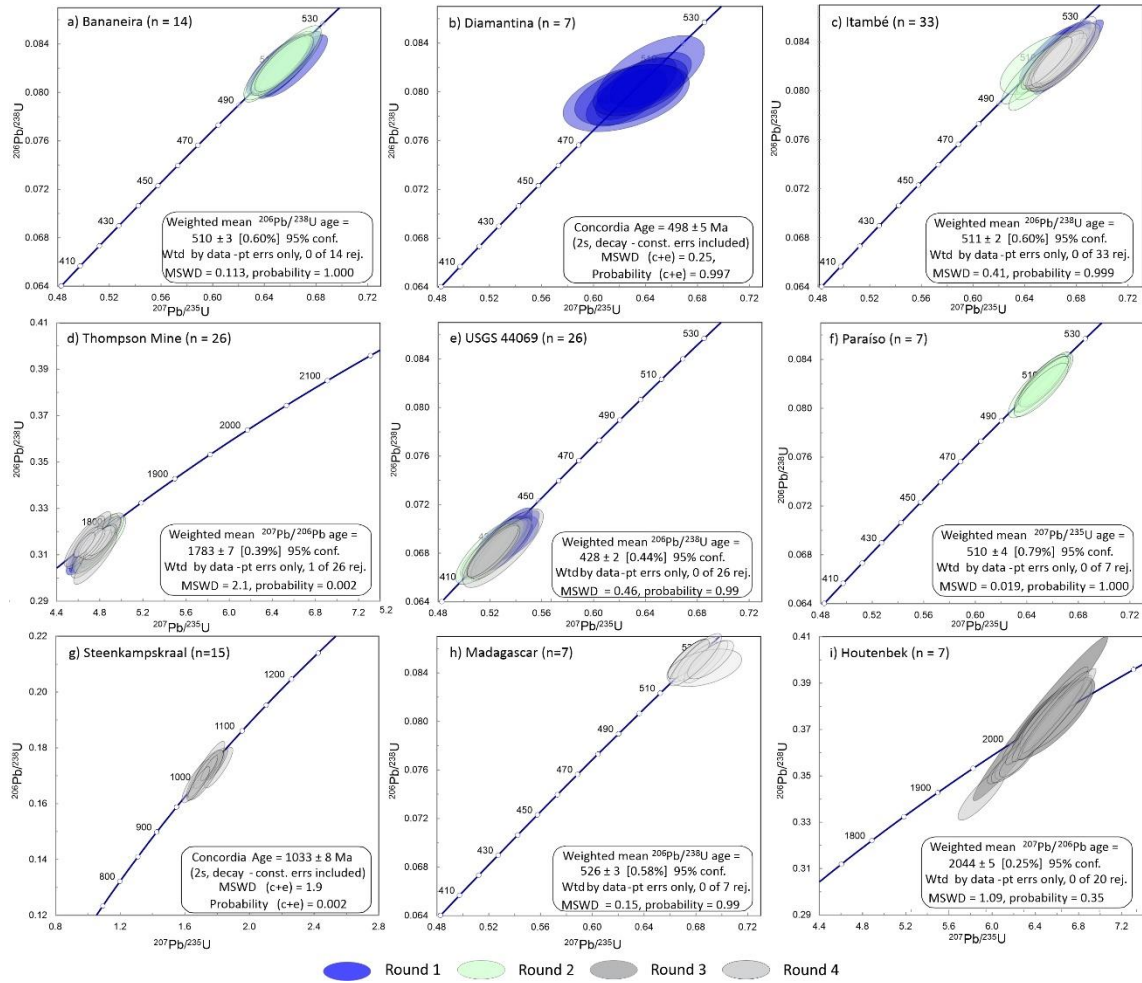


Figure 5.8: U-Pb LA-SF-ICP-MS results from the round-robin runs using Vermilion monazite as primary reference material to calibrate other monazite reference materials, treated as unknowns. Data-point uncertainties ellipses are 2σ .

5.5.2 Evaluating the potential of Vermilion monazite as an Archean calibrant for U-Pb and Sm-Nd analyses

The results presented in this research demonstrate that the Vermilion monazite is relatively homogeneous in terms of major and trace element concentrations. Back-scattered electron images confirm the relative chemical homogeneity of the grains, which rarely exhibit weak zoning, and are only locally affected by small fractures. Vermilion monazite has homogeneous U-Pb isotope compositions and, when used as a primary calibrant for LA-ICP-MS U-Pb geochronology, reproduces the certified ages of several monazite reference materials analysed as unknowns. Sm-Nd isotope compositions are homogeneous for $^{143}\text{Nd}/^{144}\text{Nd}$, but show somewhat more variation for $^{147}\text{Sm}/^{144}\text{Nd}$. Hence, we conclude that Vermilion monazite has the necessary prerequisites to be classified as an ideal reference material for U-Pb dating and useful as a secondary

reference material for trace elements analyses and Sm-Nd isotope compositions as discussed below.

The ID-TIMS U-Pb analytical data show that Vermilion monazite has low Pb_c contents (<1.6-7.7 pg, which includes the analytical blank), moderate to high concentrations of U (177-1470 ppm), moderate to high Th contents (12899 - 108867 ppm) and slightly variable Th/U (66.3 - 75.5). The results acquired from Toronto are slightly discordant (1.0-1.8%) due to some recent Pb loss. One of the spots analysed in Oslo is slightly reversely discordant (-0.6%) (Figure 5.3) and this could indicate an excess of ^{206}Pb associated with initial excess of ^{230}Th . Disregarding the discordant datapoints, the recommended ratios/dates for the Vermilion monazite are: weighted mean $^{207}Pb^*/^{206}Pb^*$ date of 2666.5 ± 3.0 Ma (2σ ; MSWD = 4.5; $n = 3$) and ratio of 0.1815 ± 0.0003 (2σ ; MSWD = 4.4; $n = 3$); the $^{206}Pb^*/^{238}U$ date of 2668.4 ± 2.6 (2σ ; $n = 3$; MSWD = 0.36) and ratio of 0.5128 ± 0.0006 (2σ ; $n = 3$; MSWD = 0.36), and the $^{207}Pb^*/^{235}U$ date of 2667.3 ± 1.3 (2σ ; $n = 3$; MSWD = 0.9) and ratio of 12.8310 ± 0.0180 (2σ ; $n = 3$; MSWD = 0.89).

The U-Pb SHRIMP data yielded a slightly younger (0.2% relative) weighted mean $^{207}Pb/^{206}Pb$ date of 2662 ± 2 Ma (2σ ; MSWD = 1.4) compared to the ID-TIMS data when evaluating only the internal/random uncertainties. The LA-ICP-MS results from UnB, UFOP, SKLLE and Portsmouth are in agreement with both the ID-TIMS and SHRIMP data.

The Vermilion monazite Th contents (5.1-6.8 wt%) are broadly equivalent to those of other monazite reference materials (e.g. Itambé, Bananeira, Steenkampskraal, TS-Mnz, USGS 44069, Iveland) and with the Th totals of many metamorphic and igneous monazites. One of the advantages of using Vermilion monazite as reference material is the calibration of the $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ measurements for older samples. Young monazite reference materials have isotopic ratios that are very different from Archean and Paleoproterozoic samples, which can bring potential problems with matrix effects. In addition, the results obtained using Vermilion together with younger reference materials demonstrate that at least considering the LA-ICP-MS precision, no potential matrix effects were observed. In this context, it is worth noting that using Vermilion monazite with these other reference materials in SIMS analyses, there should be little or no matrix matching required, as some laboratories perform a matrix correction based on Th content. The SIMS technique may require some matrix-effect correction for the $^{206}Pb/^{238}U$ ratios.

In addition, our round-robin results show that no matrix effect was noticeable using Vermilion monazite as the main calibrant to analyse other monazite reference materials with a similar Th range (e.g., Itambé, Steenkampskraal, Manangoutry, USGS 44069). However, testing the younger Diamantina monazite, we observed an analytical issue in the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios due to the low-Th and -U contents (and consequently low contents of radiogenic Pb) for this reference material. This can be associated with the tuning configuration applied for the reference materials with high-U and Th contents treated as unknowns, causing an improper measurement of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios for the Diamantina monazite. We suggest caution when using Vermilion monazite as reference material to date low-U and Th samples and/or apply common Pb corrections as demonstrated in this study.

Several LA-ICP-MS sessions using Vermilion monazite as the primary reference material to date reference monazites as unknowns have returned U-Pb dates within uncertainty of their recommended values. Hence, Vermilion monazite can be used as a reference material for calibration or quality control in U-Pb LA-ICP-MS analyses (Table 5.9 and Figure 5.8). Although some of the TIMS data returned slightly discordant dates, the U-Pb data from Vermilion monazite (-0.6 to 1.8%) have a similar range of age variations to those of other reference materials, such as Diamantina (-0.1 to +1.0%; Gonçalves et al., 2018), Itambé (-6.6 to 5.2%; Gonçalves et al., 2016); TS-Mnz (-1.6% to -1.2%; Budzýn et al., 2021). In addition, Wall et al., (2016) and Stern et al., (2009) proposed two Archean zircons reference materials, Stillwater AN2 and OG1, for U-Pb geochronology with a discordancy (-0.07 to +0.32%; +0.3 to +2.9%, respectively) similar to the variation observed in Vermilion monazite.

The experiments using a Paleoproterozoic monazite demonstrate the usefulness of Vermilion monazite to interpret ancient crustal processes. The Houtenbek monazite U-Pb results are consistent with the value of 2054 Ma for the emplacement age of the main phase of the Lebowa Granite Suite of the Bushveld Complex (Skursch et al., 2022).

The $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ measurements of the Vermilion monazite acquired by both LA-MC-ICP-MS laboratories confirm only limited variations in $^{143}\text{Nd}/^{144}\text{Nd}$ (0.51065 ± 0.00002 (2σ) to 0.51072 ± 0.00002 (2σ)) between and within different monazite crystals, with a small relative standard deviation of 0.007% for all the spot analyses from each laboratory. In addition, these results are consistent with the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios obtained by ID-TIMS and solution mode MC-ICP-MS. Variation in

the $^{147}\text{Sm}/^{144}\text{Nd}$ ratios are more significant (2.2-2.5 %RSD), ranging from 0.0823 ± 0.0001 (2σ) to 0.0901 ± 0.0002 (2σ) for all spot analyses. The variation seen in $^{147}\text{Sm}/^{144}\text{Nd}$ is towards the high end of that observed for other reference materials (Figure 5.6) e.g. Steenkampskraal (0.3 %RSD), Diamantina (0.5 %RSD), Itambé (0.6% RSD) and 44069 (3.3 %RSD) (Liu et al., 2012; Gonçalves et al., 2016, 2018; Fisher et al., 2020). At this stage, we suggest that Vermilion monazite may be suitable as a secondary reference material for Sm-Nd isotope measurements. Grains with patchy domains, overgrowth and recrystallisation can be used to determine when the opening of the Sm-Nd isotopic system happened and/or whether variations in the initial isotopic signatures occurred (McFarlane and McCulloch, 2007; Fisher et al., 2017).

5.5.3 A Case Study: Investigating monazite crystallisation and recrystallisation in the 3360 Ma São José do Campestre Massif, NE Brazil

To assess Vermilion monazite as a U-Pb calibrant for investigating Archean processes, a case study was undertaken on monazite samples from a trondhjemitic gneiss and leucosome veins from the Presidente Juscelino Migmatite Complex (PJ Complex), located in the São José do Campestre Massif (SJCM), Borborema Province, NE Brazil (Dantas et al., 1998, 2004, 2013). The Borborema Province itself (Almeida et al., 1981; Neves et al., 2021) is an orogenic system that resulted from the convergence of the West African – São Luís – São Francisco-Congo paleocontinents during amalgamation of Western Gondwana (Figure 5.9a, b). It comprises heterogeneous Archean and Paleoproterozoic migmatite-gneiss terranes that experienced reworking and differentiation processes, with subsequent Neoproterozoic metamorphism, shear zone development and granitic intrusions (e.g. Van Schmus et al., 2008). One sample (Sample CE-118) was collected from a plagioclase-rich leucosome vein within the migmatite in the southern part of the PJ Complex (Figure 5.9). It is interpreted that these rocks are crystallised under upper amphibolite facies metamorphism (Dantas et al., 2004).

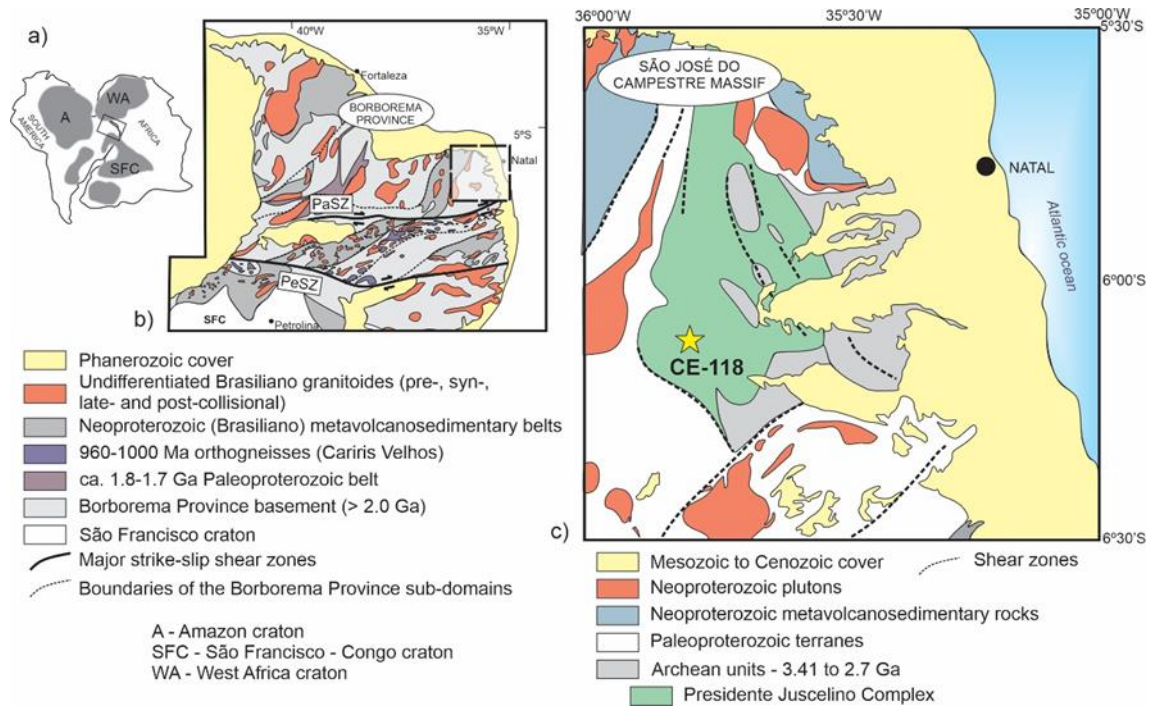


Figure 5.9: (a) Western Gondwana context of Borborema Province. (b) Location of the SJCM in the province, highlighting the Patos (PaSZ) and Pernambuco (PeSZ) shear zones, that divide the Borborema Province into northern, central, and southern tectonic domains (modified from Caxito et al., 2016). (c) Simplified SJCM map showing the sample locality (modified from Dantas et al., 2004).

Monazite grains from this sample are subhedral crystals that vary in colour from dark- to pale-yellow and are ca. 100 μm in diameter. BSE images showed that some grains contain complex and irregular compositional zoning, while others showed little compositional zoning (Figure 5.10c).

Thirty spot U-Pb LA-ICP-MS analyses were obtained from sixteen monazite grains (Supplementary material). The data define two clusters with older and younger age populations, with no clear relationship between the darker and brighter domains on BSE images (Figure 5.10). The oldest monazite data, plotted on a Wetherill concordia diagram, define a discordia line reflecting some Pb-loss. The great majority of the analyses are slightly discordant (1-7 % discordant), cluster near an upper intercept at 3094 ± 14 Ma (2σ ; MSWD = 0.22; $n = 17$) and yield a $^{207}\text{Pb}/^{206}\text{Pb}$ weighted mean date at 3077 ± 13 Ma (2σ , MSWD = 0.22, $n = 15$; two spots were excluded). The two age estimates are consistent within uncertainties (Figure 5.10a). Two more discordant analyses control the lower intercept and suggest that Pb loss occurred at c. 500 Ma. (Figure 5.10a). The younger set of monazite analyses is marked by low common Pb contents (Figure 5.10b). For this group we obtained a lower intercept on a Tera-Wasserburg diagram at 536 ± 4 Ma (2σ ; MSWD = 2.4; $n = 13$; $\text{Pb}_c = 0.827$) and a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean date at 543

± 4 Ma (2σ , MSWD = 2.4, $n = 12$; one spot was excluded) in agreement within uncertainties (Figure 5.10b). The two age populations can be explained by a Cambrian event involving Pb loss and/or by fluid induced dissolution/precipitation processes as indicated by the porous textures on the younger domains (Figure 5.10c).

The older monazite age obtained here dates metamorphism and crystallisation of leucosomes at 3094 ± 14 Ma in the Paleoarchean rocks of the Presidente Juscelino Complex. The complex was later affected by Brasiliano-age metamorphism at ca. 543 Ma.

The main feature of the Brasiliano reworking in the entire Borborema Province is the development of large-scale shear zones that record multiple $^{206}\text{Pb}/^{238}\text{U}$ dates. Two main clusters are observed; from ca. 572 to ca. 552 Ma, and from ca. 544 to 519 Ma (Dantas et al., 2004; Archanjo et al., 2013; Viegas et al., 2014; Cioffi et al., 2021). Metamorphic zircon grains seem to register the peak temperature at ca. 580 Ma (Dantas et al., 2004). We interpret this 40 Ma age difference between metamorphic zircon and monazite as part of the result of a long-lived history of shearing, fluid-circulation and deformation in the Borborema Province.

The Archean to latest Neoproterozoic monazite ages found in the Presidente Juscelino Complex contribute to the understanding of accretional history and continental crust evolution through time. The complex itself can be seen as the result of Archean “cratonic basement inliers” amalgamated during the Paleoproterozoic and then again during the ca. 600-500 Ma Brasiliano–Pan African orogeny.

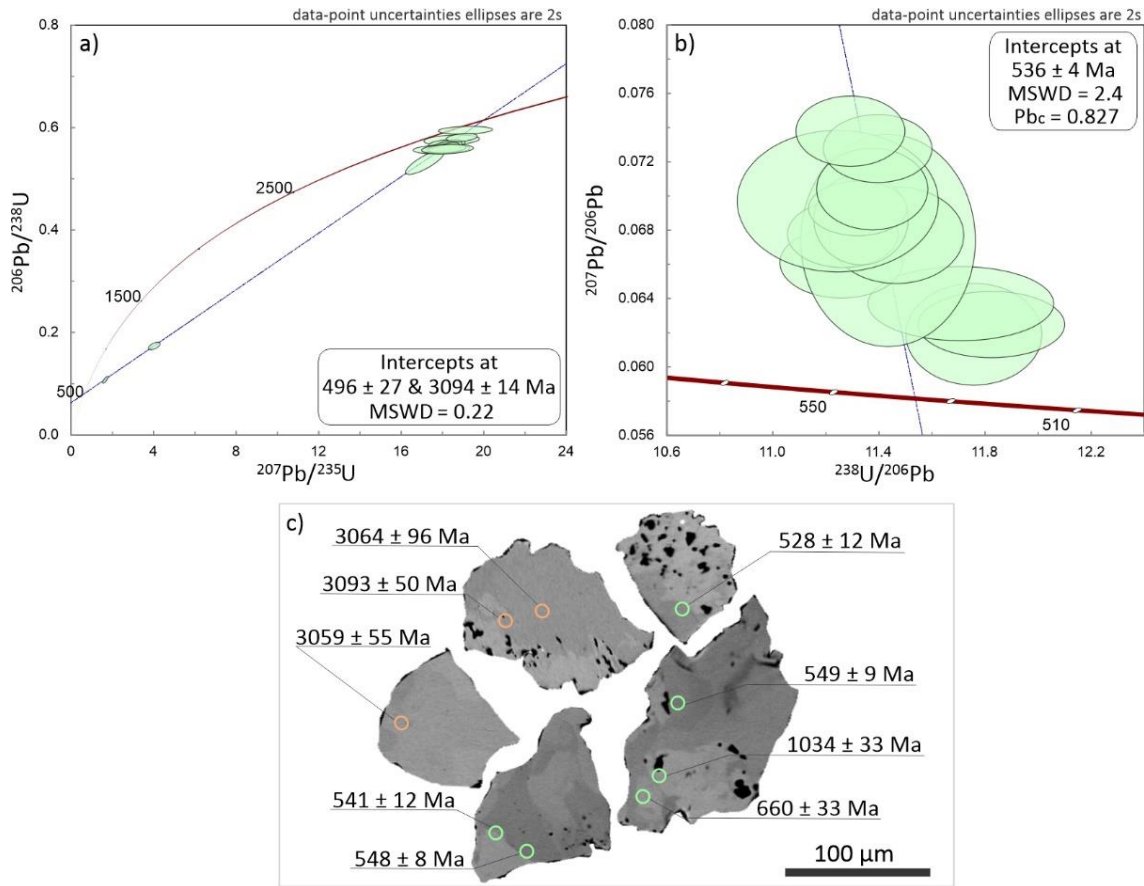


Figure 5.10: a) U-Pb Wetherill concordia diagram exhibiting the upper and lower intercepts for the older cluster of monazite sample CE-118; b) U-Pb Tera-Wasserburg diagram showing the obtained younger ages for the recrystallised monazite sample CE-118 that incorporated low common Pb contents; c) BSE images of some of the monazite grains showing porosity related to selective recrystallisation by dissolution/reprecipitation processes. Note that some monazites are zoned, and others are uniform. The coloured dots (spot size = 10 µm) represent spots ablated by LA-MC-ICP-MS. The green and the orange dots refer to the $^{206}\text{Pb}/^{238}\text{U}$ and the $^{207}\text{Pb}/^{206}\text{Pb}$ dates, respectively.

Therefore, the application of Vermilion monazite for U-Pb dating makes it feasible to investigate geological events such as evidence of >1.5 Ga monazite crystallisation during mineralisation (e.g., Rasmussen et al., 2006), metamorphism and magmatism. The use of Vermilion monazite for investigating unknown monazite samples of Paleoproterozoic and Archean dates helps to avoid compositional matrix-effects. Analyses of Archean monazites can contribute to a better understanding of the timing of growth of host metamorphic minerals associated with different metamorphic events. This contributes to a better understanding of the Archean rocks evolution and their regional significance (Stern and Berman, 2000). Considering the Archean age of Vermilion, this is the oldest monazite available as a reference material for the scientific community.

5.6 Conclusion

Vermilion monazite is homogeneous in terms of U-Pb age and relatively homogeneous for Nd isotope systematics, and trace element concentrations, showing slight zoning according to major element variations. It is ideal for investigating Archean and Paleoproterozoic samples as it has a similar age and ratio for calibration purposes, which aids avoiding compositional matrix-effect. We propose it as a primary reference material for U-Pb LA-ICP-MS analyses, as confirmed by the round-robin results using the Vermilion monazite to reproduce the ages of the reference materials, and as a secondary reference material for Sm-Nd studies. All the results accomplished by LA-ICP-MS U-Pb geochronology agree with the ID-TIMS and SHRIMP data. The weighted mean $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ date of 2666.5 ± 3.0 Ma (2σ ; MSWD = 4.5; $n = 3$) and ratio of 0.1815 ± 0.0003 (2σ ; MSWD = 4.4; $n = 3$); the $^{206}\text{Pb}^*/^{238}\text{U}$ date of 2668.4 ± 2.6 (2σ ; $n = 3$; MSWD = 0.36) and ratio of 0.5128 ± 0.0006 (2σ ; $n = 3$; MSWD = 0.36), and the $^{207}\text{Pb}^*/^{235}\text{U}$ date of 2667.3 ± 1.3 (2σ ; $n = 3$; MSWD = 0.9) and ratio of 12.8310 ± 0.0180 (2σ ; $n = 3$; MSWD = 0.89), obtained by ID-TIMS are the recommended values for calibration using the Vermilion monazite reference material. There are large quantities of the Vermilion monazite reference material available to be distributed.

5.7 Acknowledgements

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CAPÍTULO 6

**UNRAVELLING FLUID INTERACTION
PROCESSES IN THE HYDRATED ZONE
OF THE SOUTHERN MARGINAL ZONE
OF THE LIMPOPO BELT - SOUTH
AFRICA: U-Pb AND Sm-Nd
SYSTEMATICS USING MONAZITE AND
APATITE IN METAPELITES**

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ABSTRACT

The Southern Marginal Zone (SMZ) of the Limpopo Belt contains dispersed fragments of retrogressed metapelites with ubiquitous amphibolite facies assemblages which include retrograde biotite, orthoamphibole, kyanite and a 2nd generation of garnet-replaced orthopyroxene and partially replaced cordierite. The hydrated metapelites contain graphite intergrown with the retrograde assemblages, indicating a mixed H₂O-CO₂ fluid and a rock-dominated system. According to prior investigations, there are several hypotheses for the origin of the fluid involved in the retrogression, but the source of the fluids which triggered the retrogression hydration event is still unknown. Here we use the chemical composition of garnet, monazite, apatite, and amphibole of the metapelites from the hydrated zone to constrain the fluid source and geochemical mobility of trace elements during fluid dissolution-precipitation reactions. Garnet REE patterns show two distinct populations described as Grt1 (Eu/Eu*=0.26-0.36) and Grt2 Eu/Eu*=1.51-1.69). Monazite shows a relatively homogeneous LREE pattern for individual samples with a slight variation in HREE and negative Eu anomaly (Eu/Eu*=0.20-0.38). Apatite also displays distinct REE patterns, relatively enriched in REE (Σ REE = 1054-3009 ppm), depleted in REE (Σ REE = 141-159 ppm) or both. U-Pb monazite ages ranging from 2741 Ma to 2707 Ma suggest that the amphibolite-facies assemblages are mainly related to a Neoarchean, ca. 2.7 Ga granulite-facies event. U-Pb apatite analyses yielded younger ages of ca. 2050 Ma. Sm-Nd isochron of monazite, amphibole and apatite from individual samples presented an initial ¹⁴³Nd/¹⁴⁴Nd ratio of 0.50894 ± 0.00006 (2s; n = 21; MSWD = 2.6), yielding a Sm-Nd isochron age of 2684 ± 51 Ma (2s). The Sm-Nd isochron indicates that monazite and apatite crystallised at ca. 2.7 Ga during the granulite facies partial melting of the SMZ metapelites and that amphibole grew during hydration of the SMZ during the Neoarchean. All mineral phases remained closed for Sm-Nd systematic, except for a minor proportion of apatite and amphibole that plotted slightly

below the isochron. We propose that the retrogressed zone of the SMZ experienced a Neoarchean peak granulite-facies followed by amphibolite-facies retrogression at ca. 2.7 Ga, in which an internally derived fluid interacted with the metapelites. This is supported by published Sm-Nd bulk rock compositions from unretrogressed granulite facies and hydrated amphibolite samples that follow the same evolution trend as these samples, ruling out the contribution of an externally derived fluid. A later lower-temperature Paleoproterozoic re-heating event at 2.05 Ga was responsible for resetting the U-Pb apatite system by volume diffusion, consistent with the reported rutile U-Pb ages. Initial $^{87}\text{Sr}/^{88}\text{Sr} = 0.7130 \pm 0.0014$ (2s; n = 19; MSWD = 13) indicates a continental origin for the fluids that crystallised the apatite.

6.1 Introduction

Comprehending the geological processes in polymetamorphic terrains that experienced high pressure and temperature conditions requires an association between chemical composition and isotope geochemistry data integrated with the petrology of the rocks under study. The U-Pb geochronology and Sm-Nd isotopic composition in accessory minerals associated with the chemical composition of the mineral phases aid in assessing the processes involving the formation of distinct garnets generations that underwent secondary growth/dissolution reprecipitation reactions (e.g. Hermann and Rubatto, 2003; Buick et al., 2006a; Kelly et al., 2006; Buick et al., 2010).

The Southern Marginal Zone (SMZ) within the Limpopo Belt is a well-known region that experienced granulite-facies conditions and was intensely hydrated in the southern portion under retrogressed amphibolite-facies conditions (e.g. Van Reeneen and Smith, 1992; Stevens, 1997; Kreissig et al., 2001; Van Reeneen et al., 2011; Nicoli et al., 2015; Madlakana et al., 2020) (Fig. 6.1). Previous studies have proposed different interpretations for the source of the fluids that caused the retrogression hydration event, as being an externally derived CO_2 - and H_2O -rich fluid that infiltrated the Hout River Shear Zone (HRSZ) (e.g. Van Reenen, 1986; Koizumi et al., 2014; Van Reenen et al., 2014), or as being an internally derived fluid from crystallising melt produced during the cooling of the former granulites (Stevens, 1997). Additionally, Vennemann and Smith (1992) suggested that the amphibolites-facies rock never recorded granulite facies conditions, based on similar carbon isotope compositions within the same lithologies that excluded an externally derived fluid. Madlakana et al. (2020) argued for a Paleoproterozoic retrogression at ca. 2.1 Ga based on U-Pb rutile ages suggesting that the

SMZ is a polymetamorphic terrain and that the retrogression is not related to the main granulite facies event of ca. 2.7 Ga. However, the timing of hydration and the source of the fluids that contributed to this event remain uncertain.

In this study, for investigating the amphibolite-facies rocks from the hydrated portion of the SMZ we used the LA-SF-ICP-MS technique for trace element analyses (garnet, monazite and apatite) and the LA-MC-ICP-MS analytical method for the U-Pb geochronology and Sm-Nd isotope compositions (monazite and apatite) and Sr-Sr analyses (apatite). The Sm-Nd isotope measurements for the orthoamphiboles were obtained by solution MC-ICP-MS. The results provide new insights regarding the timing of the retrogression hydration event related to the sources of fluids that hydrated the former granulites in the SMZ constraining the metamorphic evolution based on the accessory mineral chemical and isotopic signatures.

6.2 Geology background

The Limpopo Belt is an Archean terrain formed by high-grade metamorphic rocks located between the South Africa-Zimbabwe-Botswana borders (e.g. Stevens 1997). The Central Zone of the Limpopo Belt (Fig. 6.1a) represents a polymetamorphic terrain that records granulite-facies conditions in distinct events at 3.2-3.1 Ga (Holzer et al., 1998) and 2.0 Ga (Kreissig et al., 2001; Buick et al., 2006; Zeh et al., 2010). The Northern and Southern Marginal Zone of the Limpopo Belt (Fig. 6.1a) contain high-grade granitoid and greenstone belt lithologies that experienced granulite-facies metamorphic conditions during the collision and crust exhumation of the Zimbabwe and Kaapvaal Craton between 2.69-2.62 Ga (e.g., Kreissig et al., 2001; Van Reenen et al., 2011).

The Southern Marginal Zone (SMZ) of the Limpopo Belt is located along the northern edge of the Kaapvaal Craton (Fig. 6.1b). It is composed of grey tonalitic and trondjemitic gneisses (Baviaanskloof Gneiss) with supracrustal successions of metasedimentary, metaafic and metaultramafic rocks (Bandelierkop Formation) (e.g. Du Toit et al., 1983). The SMZ metapelites are a dominant portion of the Bandelierkop Formation and occur mostly as granulites in the northern area but the most southerly portion of the SMZ is retrogressed under amphibolite facies conditions to the north of the Kaapvaal craton (e.g. Stevens, 1997). The granulite-facies metamorphism occurred during a Neoarchean continental collision between the Kaapvaal and Zimbabwe cratons at ca. 2.7 Ga (Barton et al., 1992; Kreissig et al., 2000), or, more likely, during arc accretion at this time (Nicoli et al., 2015). The Hout River Shear Zone (HRSZ) separates

the SMZ from the Kaapvaal craton, in which the granulites have been thrust over the lower grades rocks of the northern Kaapvaal craton due to orogenic collapse before 2.68 Ga (e.g. Barton and van Reenen, 1992; Barton et al., 1992). The granulites in the north of the SMZ are partially retrogressed, with this incomplete retrogression reflecting the same P-T conditions as the amphibolite metapelites in the southern portion. This suggests that different extents of fluid availability in the two domains have controlled the degree of observed retrogression in these regions (Madlakana et al., 2020). However, in the amphibolite-facies metapelites, there is no indication of the granulite facies event of ca. 2.7 Ga, thus what these rocks from the hydrated zone reveal remains unclear.

Previous studies have shown that H₂O-CO₂-dominant fluids of uncertain origin infiltrated the granulites through the HRSZ during the orogenic collapse phase and reacted with the granulites under amphibolite facies conditions (Van Reenen, 1986). Evidence in the region points that CO₂-rich and brine fluids with reduced water activity caused a pervasive retrogression (Van Reenen et al., 2014) and that during this event anhydrous minerals such as orthopyroxene reacted with fluid to form orthoamphibole. Vennemann & Smith (1992) reported that the variations observed in the carbon isotope ratios of the metapelitic rocks indicated that an externally derived CO₂-rich fluid was inconsistent with the results. Stevens (1997) proposed that amphibolite metapelites are a product of graphite-bearing granulites that reacted with an internally derived fluid produced from crystallising melts. Madlakana et al. (2020) suggested a thermal anomaly in the mantle as the probable heat source that caused the retrogression in the SMZ during a younger Paleoproterozoic event at ca. 2.1 Ga recorded by rutile ages. The resulting reaction textures are also intergrown with remobilised graphite (e.g. Stevens, 1997), indicating that the fluids either introduced additional carbon to the rocks or oxidised carbon in some areas and precipitated it in the hydration zones. Nevertheless, the source of the fluids that caused the retrogression and the timing of these reactions present limited information available.

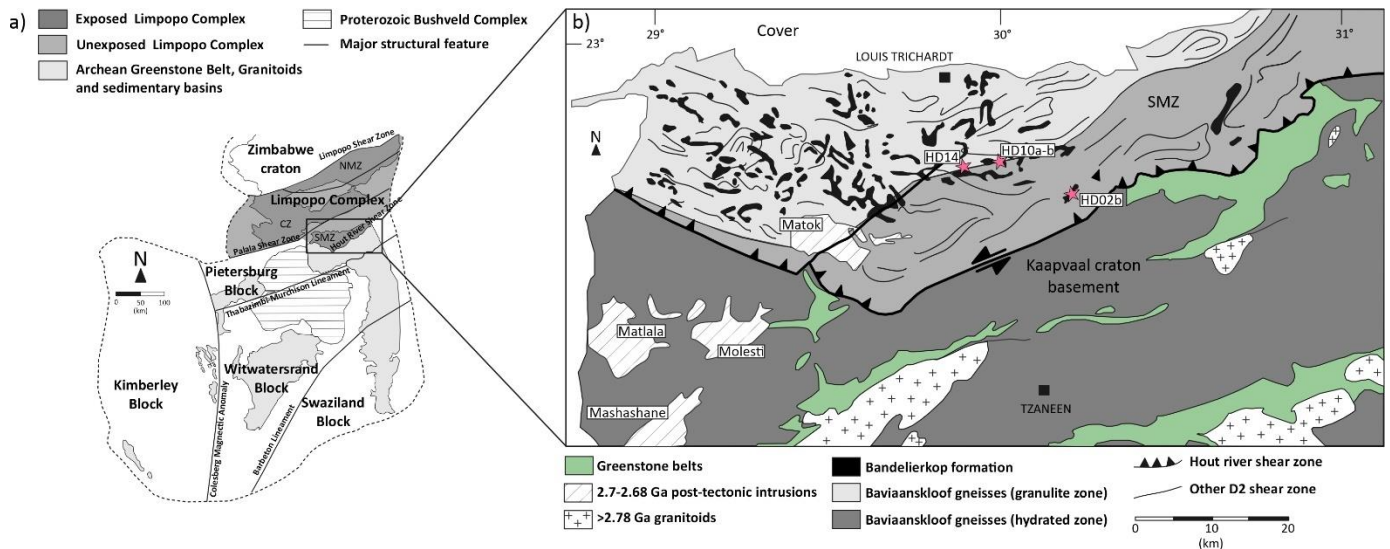


Figure 6.1: a) Simplified overview of the Kaapvaal Craton and northern terranes (modified after Hunter, 1974; de Wit et al., 1992c; Poujol et al., 2003; Eglington and Armstrong, 2004; Vezinet et al., 2018). The three zones of the Limpopo Belt are represented as follows: the Central Zone (CZ), the Northern Marginal Zone (NMZ) and the Southern Marginal Zone (SMZ); b) Geology of the Southern Marginal Zone located on the northern part of the Kaapvaal Craton (modified after Stevens 1997; Nicoli et al., 2015; Vezinet et al., 2018; Carranza, 2018) with the sample locations.

6.3 Methodology

Analyses were performed along with hand-picked apatite, monazite, and amphibole grains for a petrographic description and to investigate major and trace element chemical compositions and isotope composition of the samples selected for this study. The hand-picked monazite and apatite crystals were embedded in a 2.5 cm diameter resin mount and polished before being analysed for electron microscopy imaging and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) at Stellenbosch University (SU) and Universidade Federal de Ouro Preto (UFOP). These grains were used to measure trace elements and for U-Pb dating and Sm-Nd and Sr-Sr isotope compositions. The hand-picked amphiboles were analysed by solution MC-ICP-MS at Universidade de Brasília (UnB). A complete dataset for the analytical methods is given in the Electronic Supplement. All mineral abbreviations follow the nomenclature presented in Whitney and Evans (2010).

6.3.1 Chemical Compositions

6.3.1.1 Electron microscopy imaging and major elements compositions

Electron microscope imaging and major element compositions of the thin section samples were obtained at the Electron Microscopy Unit of the Central Analytical Facility at Stellenbosch University. For the petrographic study, backscattered electron images and

major element compositions were acquired using a Zeiss EVO SEM equipped with an Oxford Instruments × Max 20 mm² EDS detector, an Oxford Instruments Wave Dispersive X-ray Spectrometer, and Oxford INCA software. The beam analytical setups for obtaining the quantitative data were a working distance of 8.5 mm, an accelerating voltage of 20 kV, a specimen beam, and a probe current of 20.00 nA and 1.0 A, respectively. The EDS detector counting time was 10 s live-time and 60 s on peak. For investigating the zonation of hand-picked apatite, the cathodoluminescence (CL) images were conducted using a Zeiss Merlin FE-SEM in a cold stage mode cooled down to -180 °C with nitrogen gas, operating at 20 kV accelerating voltage, 11 nA probe current, with a working distance of 8.5 mm.

Backscattered electron images of hand-picked monazite were obtained at Universidade Federal de Ouro Preto (UFOP) using a JSM-6510 JEOL scanning electron microscope. The images were conducted operating at the energy of 20 kV and a current of 20 nA.

6.3.1.2 Trace Elements

Trace element compositions of monazite mounted in epoxy were obtained using a Resolution 193 nm Excimer laser from Applied Spectra connected to an Agilent 8800 QQQ ICP-MS in the Central Analytical Facility at Stellenbosch University. Analyses were performed using a beam diameter of 40 µm, laser fluence of 3 J/cm², and a repetition rate of 10 Hz. The ablation takes place in the sample cell flushed with He gas (50 ml/min), where the ablated material is mixed with Ar gas (1.0 l/min) and N₂ gas (3.5 ml/min) before introduction in the ICP-MS. The ablation time was set to 35 s and the background acquisition time was set to 15 s. Oxygen gas (0.68 ml/min) was used as a reactive cell gas to measure all the analytes. The masses analysed in this study were: ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴³Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁷Hf, ²⁰⁸Pb, ²³²Th, ²³⁸U. The data reduction software package LADR from Norris Scientific (Norris et al., 2021) was used for data processing. The ¹⁴⁰Ce (28 wt%) was used as an internal standard to correct variations observed in the matrix effect between the reference material and the unknown samples. NIST 610 (Jochum et al., 2005, 2016) were used as primary reference material and Diamantina and Itambé monazite (Gonçalves et al., 2016; 2018) were used as secondary reference material. The accuracy based on repeated analyses of the reference materials is better than 10%.

Trace element analyses of apatite and garnet crystals were conducted using a Thermo Finnigan Element II single collector sector field (SF) ICP-MS, coupled to a CETAC UV Nd-YAG 213 nm laser system at the Laboratório de Geoquímica Isotópica, Universidade Federal de Ouro Preto (UFOP). Trace elements analyses of hand-picked apatite grains embedded in a resin mount followed the same analytical protocols. The sample cell was flushed with helium gas (0.3 l/min) to minimise aerosol deposition and mixed with argon gas (0.95 l/min) downstream of the ablation cell. The following masses were investigated: ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{177}Hf , ^{208}Pb , ^{232}Th , ^{238}U , ^{55}Mn , ^{88}Sr , ^{89}Y . The analyses were conducted with a spot size of 40 μm , a laser fluence of 10.0 J/cm², and a laser repetition rate of 10 Hz. Each analysis comprised sample ablation of 60 s and background measurement of 20 s. NIST-610 glass was used as the primary reference material and BHVO glass was used for quality control (Jochum et al. 2011). All glass reference materials and unknown samples were analysed in a bracketed mode. The data were processed offline using Saturn – Trace Elements software (Figueiredo, 2022). The matrix effect between the glass reference materials and the unknown samples was corrected based on the CaO content of apatite (55 wt.%) and the Si content of garnet (36 wt.%) used as an internal standard. The accuracy of the BCR-2 and BHVO glass reference materials was within 5-10% of the accepted values.

6.3.2 Isotope Geochemistry

6.3.2.1 U-Pb geochronology by LA-MC-ICP-MS

U-Pb data of monazite and apatite were performed in epoxy mount using a Thermo Scientific Neptune Plus Multicollector ICP-MS instrument coupled to a 193 nm HelEX Photon Machine Laser ablation system at the Laboratório de Geoquímica Isotópica at UFOP. The laser sampling procedures employed a total ablation time for each spot of 60 s, with 20 s of gas background and 40 s of signal ablation. The following ion counters (ICs) were used to measure the signals during the analyses of the relevant masses simultaneously measured: ^{208}Pb on IC6, ^{207}Pb on IC1B, ^{206}Pb on IC2, $^{204}\text{Hg} + \text{Pb}$ on IC5 and ^{202}Hg on IC4. Faraday cups H2 and H4 were used to measure ^{232}Th and ^{238}U , respectively. For the U-Pb monazite dating, the individual spots were analysed with a beam diameter of 10 μm , a frequency of 5 Hz, and a fluence of 3.03 J cm⁻². For the U-Pb apatite dating, the spot size was set to 40 μm , and the frequency and fluence were set to

5 Hz of 6 J cm^{-2} , respectively. The raw data were processed offline using the data reduction software Saturn (Silva et al., 2023) to correct for background noise, instrumental mass discrimination, and laser-induced elemental fractionation LIEF.

The monazite U-Pb dating analyses were obtained in two sessions. The primary reference material used in both analytical sessions was the Vermilion monazite (Mazoz et al., 2024) for matrix-matched calibration purposes. One unknown sample was analysed in the first round and two other unknown samples were analysed in the second round. The Steenkampskraal (also known as Namaqualand, Knoper et al. 2000, Liu et al. 2012, Fischer et al. 2020, or Namaqua, Kaur et al. 2016) and Thompson Mine (Williams et al. 1996) monazites were used as quality control.

The results on Steenkampskraal obtained in both sessions returned concordia ages of $1037 \pm 4/11 \text{ Ma}$ (2s; MSWD_{c+e} = 0.48; n = 7) and $1032 \pm 3/11 \text{ Ma}$ (2s; MSWD_{c+e} = 0.79; n = 16) relatively consistent with the ID-TIMS age of $1038 \pm 0.6 \text{ Ma}$ (Fisher et al. 2020). Analyses on Thompson Mine monazite for both rounds yielded weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ ages of $1757 \pm 11/21 \text{ Ma}$ (2s; MSWD = 1.00; n = 5) and $1773 \pm 8/19 \text{ Ma}$ (2s; MSWD = 0.9; n = 13) in agreement with the age of 1766 Ma published by Williams et al. (1996; uncertainties unpublished).

The apatite U-Pb dating was acquired in one analytical session. NIST 612 (Jochum et al., 2005; Jochum et al., 2016) were used as primary reference material to normalise the data in each session on a bracketed mode. Madagascar green apatite (MAD1; Thomson et al., 2012) was used to calculate the offset (2.5%) between the primary reference material and the apatite secondary reference materials and unknown samples. Several secondary reference materials were used as quality control to monitor the variations and drift in $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ ratios of repeated analyses during a session. The following apatite secondary reference materials were used: Madagascar blue (MAD 2; Thomson et al., 2012), 401 (Thompson et al., 2016), Durango (Chew et al., 2011), Ipirá (*in house*), Sumé (Lana et al., 2022) and McClure Mountain (Schoene and Bowring, 2006). The acquired lower intercept ages were calculated on Tera-Wasserburg diagrams using the Stacey and Kramers (1975) method based on an anchored regression through Pb_c . The data are not Pb_c -corrected.

The calculated lower intercept age of Madagascar green apatite of $482 \pm 2/5 \text{ Ma}$ (2s; MSWD = 0.61; n = 14) agrees within uncertainties with the published values of $486.58 \pm 0.85 \text{ Ma}$ (MAD1) from Thomson et al., (2012). The lower intercept age for

Madagascar blue apatite of $466 \pm 2/5$ Ma (2s; MSWD = 0.92; n = 16) is slightly younger compared to the age value reported by Thomson et al., (2012; 474.25 ± 0.41 Ma). The Sumé apatite lower intercept age of $570 \pm 2/6$ Ma (2s; MSWD = 0.95; n = 16) is consistent with the published values of Lana et al., (2022; 568.0 ± 3.1 Ma). The obtained lower intercept for 401 apatite of $521 \pm 2/6$ Ma (2s; MSWD = 0.58; n = 14) and McClure apatite of $525 \pm 3/6$ Ma (2s; MSWD = 1.4; n = 12) is, in general, consistent, within uncertainties, with the reported values by Thompson et al., (2016; 530.3 ± 1.5 Ma) and Schoene and Bowring (2006; 523.51 ± 1.47 Ma), respectively. The Durango apatite lower intercept of $32 \pm 1/1$ Ma (2s; MSWD = 1.3; n = 18) is consistent with the results from Chew et al., (2011; 2014; 31.97 ± 0.59 Ma). The in-house Ipirá apatite yielded a lower intercept of $2088 \pm 4/21$ Ma (2s; MSWD = 0.58; n = 40) in agreement with the results obtained in our routine dating.

6.3.2.2 Sm-Nd isotope composition by solution MC-ICP-MS

Analyses of amphiboles were done at the Laboratório de Estudos Geodinâmicos, Geocronológicos e Ambientais, Universidade de Brasília - UnB (Brazil). The separation procedures and analytical method applied were reported by Gioia and Pimentel (2000). The samples were washed and weathered parts were removed, then crushed and pulverised to a very fine size powder. Approximately 10 ng of amphibole powder was mixed with $^{149}\text{Sm}/^{150}\text{Nd}$ rapid solution and dissolved in Savillex capsules. The samples used for Sm-Nd extraction were subjected to conventional cation exchange techniques based on Teflon® columns containing LN-Spec resin (HDEHP - Di-(2-ethylhexyl) phosphoric acid supported by polytetrafluoroethylene powder). The samples were analysed in solution in a Thermo-Fisher Neptune MC-ICPMS and were introduced in the spectrometer using a nebuliser with a flux of 100 $\mu\text{L}/\text{min}$. For Sm, the tuned masses were ^{146}Nd , ^{147}Sm , ^{148}Sm , ^{149}Sm , ^{150}Sm , ^{152}Sm and ^{154}Sm . Five blocks of 10 cycles each with an integration time of 4.194 seconds were considered for each analysis. Mass bias correction was done by normalisation to $^{147}\text{Sm}/^{152}\text{Sm}$ (true value of 0.556083) using the exponential law. For Nd the tuned masses were ^{142}Nd , ^{143}Nd , ^{144}Nd , ^{145}Nd , ^{146}Nd , ^{147}Sm , ^{148}Nd and ^{150}Nd . Seven blocks of 10 cycles each with an integration time of 4.194 seconds were considered for each analysis. After correcting any (rare) ^{144}Sm interference, $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were corrected for instrumental mass fractionation using the exponential fractionation law and assuming $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. The average

$^{143}\text{Nd}/^{144}\text{Nd}$ obtained for the USGS BHVO-2 standard was 0.512970 ± 0.00002 (2s) during this study, which is consistent with the most recently published values (e.g., 0.512979 ± 0.000014 (SD), Jochum et al. 2016). The precision in Sm/Nd and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were better than $\pm 0.5\%$ (2s) and $\pm 0.0005\%$ (2s), respectively, based on repeated analysis of the international BHVO-2 and BCR-1 rock standards. T_{DM} values were calculated based on the model by DePaolo (1981). The measured $^{143}\text{Nd}/^{144}\text{Nd}$ sample ratios are expressed in Epsilon notation (ϵ_{Nd}) as the fractional deviation in part per 10^4 (units) from the $^{143}\text{Nd}/^{144}\text{Nd}$ value of the Chondritic Uniform Reservoir (CHUR).

6.3.2.3 Sm-Nd isotope composition by LA-MC-ICP-MS

Analyses of monazite and apatite were conducted on an epoxy mount at the Laboratório de Geoquímica Isotópica (UFOP) using a Thermo Fisher Neptune Plus LA-(MC)-ICP-MS coupled with a 193 nm HeEX Photon Machine laser ablation system. The protocols used are described in detail in Gonçalves et al., (2018). Data was acquired in static mode (^{142}Nd -Ce, ^{143}Nd , ^{144}Nd -Sm, ^{145}Nd , ^{146}Nd , ^{147}Sm , ^{148}Nd -Sm, ^{149}Sm , ^{150}Nd -Sm). The measured data were processed offline to correct for background, mass interference, and mass bias using an *in-house* Excel spreadsheet as shown in Gonçalves et al. (2018). Helium gas (0.3 l/min) was utilised as carrier gas at the ablation cell and mixed with N_2 (0.3 l/min) and Ar (0.95 l/min) sample carries gas prior introduction in the ICP-MS to optimize the signal intensity. The monazite analyses were acquired with a spot size of 60 μm , a pulse rate of 5 Hz, and a laser energy density at the sample site of 6 J/cm^2 . The apatite analyses were done with a spot size of 80 μm , repetition rate of 5Hz, and laser fluence of 6 J/cm^2 .

The monazite Sm-Nd data employed the monazites Steenkampskraal (or Namaqualand, Liu et al. 2012; Knoper et al. 2000; Liu et al. 2012; Fischer et al. 2020; or Namaqua, Kaur et al. 2016) as primary reference materials used to calibrate the Sm-Nd and Nd-Nd ratios. Several natural monazite reference materials were used for quality control, including USGS 44069 (Aleinikoff et al. 2006), Thompson Mine (Williams et al., 1996), Vermilion (Mazoz et al., 2024), Bananeiro (Gonçalves et al., 2016), Diamantina (Gonçalves et al., 2018). Each reference material was analysed with ten spots and the results are given as arithmetic mean values. Analyses of USGS monazite yielded a mean $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.1215 ± 6 (2s) and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.51226 ± 8 (2s) and is consistent with the reported values of 0.1159 ± 64 (2s) and 0.512175 ± 46 , respectively

(Liu et al., 2012). Thompson Mine monazite returned $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ mean values of 0.0949 ± 7 (2s) and 0.51081 ± 8 (2s), respectively, in agreement with the published values reported by Iizuka et al., (2011; $^{147}\text{Sm}/^{144}\text{Nd} = 0.0946 \pm 0.0164$ (2SD), $^{143}\text{Nd}/^{144}\text{Nd} = 0.51084 \pm 0.00016$ (2SD)). Our results for $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of Vermilion monazite are 0.0872 ± 4 (2s) and 0.51069 ± 7 (2s), respectively, which also agrees with the analyses by Mazoz et al., (2024; $^{147}\text{Sm}/^{144}\text{Nd} = 0.0869 \pm 2$ (2s); 0.0835 ± 1 (2s), $^{143}\text{Nd}/^{144}\text{Nd} = 0.510694 \pm 40$ (2s)). Bananeiro monazite yielded $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.2877 ± 26 (2s) and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.51286 ± 22 (2s) in general in agreement with the reported values of 0.2775 ± 74 (2SD) and 0.512763 ± 38 (2SD), respectively (Gonçalves et al., 2016). The $^{147}\text{Sm}/^{144}\text{Nd}$ value of 0.1185 ± 0.0006 (2 σ) and $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.51143 ± 9 (2s) for the Diamantina monazite agrees, within uncertainties, with the values reported by Gonçalves et al. (2018; 0.1177 ± 0.0002 (2s), 0.51143 ± 0.00002 (2s), respectively).

The apatite Sm-Nd results were obtained using Madagascar blue apatite (Thomson et al., 2012) as primary reference material to normalise the Sm-Nd and Nd-Nd ratios. Well-characterised Durango apatite (Chew et al., 2011) and Madagascar blue apatite (Thomson et al., 2012) natural reference material was used as quality control material, together with 401 apatite (Thompson et al., 2016) and Madagascar green apatite (Thomson et al., 2012). We also took advantage of using the Khan River and Bear Lake titanite (Mazoz et al., 2022) as quality control, however, a matrix effect was observed in the Sm-Nd ratios, thus only the Nd-Nd were reported. Eleven spots analyses for Durango apatite returned mean $^{147}\text{Sm}/^{144}\text{Nd}$ values of 0.0863 ± 2 (2s) and $^{143}\text{Nd}/^{144}\text{Nd}$ values of 0.51242 ± 5 (2s), in agreement in general, within uncertainties, with the values of 0.0867 ± 1 (2s) and 0.512483 ± 8 (2s), respectively, published by Foster and Vence (2006). Madagascar blue apatite produced $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ values of 0.0783 ± 2 (2s) and 0.51134 ± 7 (2s), respectively, for ten laser spots, in agreement with the data reported by Fischer et al., (2020; 0.0779 ± 0.0005 (2SD), 0.511304 ± 0.000013 (2SD), respectively). Fifteen spots analyses for 401 apatite ($^{147}\text{Sm}/^{144}\text{Nd} = 0.0905 \pm 4$ (2s) and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512282 \pm 16$ (2s); Apen et al., 2022) pooled a mean $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.0844 ± 2 (2s) and $^{143}\text{Nd}/^{144}\text{Nd}$ values of 0.51223 ± 4 (2s). The Sm-Nd ratio for 401 apatite was a little bit higher compared to the reported value, however, this reference material is not yet well characterised (Apen et al., 2022). Our analyses for ten laser spots of Madagascar green apatite returned $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.0812 ± 2

(2s) of 0.51130 ± 1 (2s), which agree well with the analyses reported by Yang et al., (2014, 0.0811 ± 17 (2SD) and 0.511322 ± 53 (2SD), respectively). Khan River (fifteen laser spots) and Bear Lake (fourteen laser spots) titanites returned $^{143}\text{Nd}/^{144}\text{Nd}$ values of 0.51159 ± 6 (2s) and 0.51233 ± 8 (2s), respectively, which agree well with the published values by Mazoz et al., (2022; 0.511587 ± 0.000027 (2s) and 0.512321 ± 0.000004 (2s)).

6.3.2.4 Sr-Sr Isotope Composition by LA-MC-ICP-MS

Sr-Sr isotope compositions of apatite samples were acquired using a Thermo Fisher Neptune Plus LA-(MC)-ICP-MS coupled with a 193 nm HeEX Photon Machine laser ablation system at Laboratório de Geoquímica of UFOP, Brazil. The isotopic measurements have already been described by Wilson et al. (2017) and Yang et al. (2009, 2014) and followed all the procedures described in Lana et al. (2022). The ablation was conducted under a sample gas stream of Ar (0.8 l/min) used to flush out the ablation cell and mixed with He (0.5 l/min) and N₂ (0.005 l/min) before arrival at the ICP-MS. The laser was set up to an acquisition cycle of 30 s of measurement of the gas blank, followed by 60 s of sample ablation, with a spot size of 85 μm , a repetition rate of 6 Hz, and an energy density of 4 J/cm². The Kr isotopic ratios ($^{83}\text{Kr}/^{84}\text{Kr} = 0.20175$, $^{83}\text{Kr}/^{86}\text{Kr} = 0.66474$) (Christensen et al., 1995, Bizzarro et al., 2003) were applied to correct the isobaric interference of ^{84}Kr on ^{84}Sr and ^{86}Kr on ^{86}Sr using the Kr gas baseline measurement. The raw data was reduced offline using the *in-house* Sr - Saturn (Figueiredo et al., - unpublished). The NIST 610 glass was used at the beginning of each analytical cycle as primary reference material to correct the $^{87}\text{Rb}/^{85}\text{Rb}$ mass bias according to the Sr mass bias ($^{86}\text{Sr}/^{88}\text{Sr}$ relative to $^{86}\text{Sr}/^{88}\text{Sr}$ true = 0.1194). Quality control analytical measurements included Madagascar apatite (Thomson et al., 2012) and the *in-house* reference materials MIR (plagioclase provided by Dr. A. Gerdes, Frankfurt), TUB (megalodon teeth), and a belemnite fossil. Analyses of six individual spots for Madagascar apatite returned a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71185 ± 133 (2s) consistent with the value of 0.71179 ± 3 (2s) reported by Yang et al., (2014). MIR results for ten laser spots returned a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70305 ± 116 (2s) in agreement with the TIMS published values of Rankenburger et al. (2004; 0.70309 ± 7 (2s)). The *in-house* reference materials TUB ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70885$) and the belemnite ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70700$) presented $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.70884 ± 67 (2s) and 0.70705 ± 90 (2s), respectively.

6.4 Results

6.4.1 Mineral assemblages of the retrograde metapelites

The amphibolite facies metapelite samples (HD02b, HD10a, HD10b, and HD14) collected from the retrogressed hydrated zone (Fig. 6.1) are represented by metapelites that underwent partial melting producing stromatic and nebulitic leucosomes containing quartz, plagioclase, garnet, biotite and orthoamphibole (Stevens, 1997; Kreissig et al., 2001; Ferreira et al., 2024 - in prep.). The metapelite samples from the hydrated zone of the SMZ collected for this study were previously investigated and described in detail by Carranza (2018) and Ferreira et al. (2024 - in prep.). The samples selected for this study are archived material from previous projects. Therefore, a brief review of the textural relationships and metamorphic features will be presented.

Sample HD02b is in the retrogressed hydrated zone and presents the mineral assemblage $\text{Grt} + \text{Bt} + \text{Pl} + \text{Qz} + \text{OAmph} + \text{Ky} \pm \text{Gr}$ (Fig. 6.2a, b). Peritectic garnet (Grt1) is poikiloblastic with some inclusions of mostly quartz, and plagioclase. Zircon, monazite, rutile, and ilmenite occur as accessory minerals included in Grt1 and the matrix assemblage. In this sample, new garnet crystallisation (Grt2) is observed as rims in Grt1 as well as small idioblastic garnets (Grt2). In Grt2 rim quartz, biotite, rutile, kyanite, and iron oxides occur as inclusions representing the retrogressed features (Stevens, 1997). Small crystals of staurolite can be found in the Grt2 rim. All these mineral assemblages suggest a product of cordierite (from previous granulite facies) reaction with fluids (Stevens et al., 1997; Koizumi et al., 2014). Apatite crystals occur as intergrown with Grt2 rim (e.g. Fig. 6.2a) together with iron oxide and sulphides and disperse in the matrix assemblage. The mineral assemblage surrounding the Grt2 rim contains kyanite, plagioclase, and quartz. Orthoamphiboles are characterised by anthophyllite and gedrite are intergrown with quartz and biotite.

Samples HD10a, HD10b, and HD14 (Fig. 6.2c-g) were collected in the area to the north of the retrogressed hydrated zone (Fig. 6.1). No orthopyroxene from the granulite facies was found, although there are some cordierite remains that reacted with fluids to form kyanite, biotite, quartz, and orthoamphiboles (Fig. 6.2c-g; Stevens, 1997). The samples in general are more altered in the garnet surroundings indicating a more pervasive reaction. The same mineral assemblage and accessory minerals as HD02b are present in these samples. Apatite occurs as inclusions in garnets and the matrix assemblage in samples HD10a and HD10b, showing some zoning in a few grains (e.g. Fig. 6.2e). The

poikiloblastic Grt1 is observed in all these samples together with the garnet Grt2 (rim/small idioblastic) (Fig. 6.2b-g). For the latter, the Grt2 rim contains inclusions of retrogressed kyanite, quartz, orthoamphibole, and pyrite (Fig. 6.2b-f). Some graphite is noticed close to the retrogressed mineral assemblage portions (e.g. Fig. 6.2f).

6.4.2 Major element compositions

The chemical composition of phases related to the retrogression hydration event in the amphibolite zone of the samples investigated in this study is shown in Electronic Supplement 1. The mineral chemistry has been presented in detail by Stevens, (1997) and Ferreira et al., (2024 - in prep.), therefore a summarised data is presented here focused on the representative mineral analyses for this study.

Samples HD02b, HD10a, and HD14 contain garnet porphyroblasts (Grt1), and core and rim/small idioblastic garnets (Grt2) that are almandine-rich with an average composition of Alm₆₅Pyr₃₀ Grs₁Sps₁ and Alm₆₃Pyr₃₂Grs₃Sps₁, respectively. They exhibit weak major-element zoning compared to both garnet generations, besides the grossular increase content in Grt2. Orthoamphiboles from samples HD02b, HD10a, and HD10b are represented by anthophyllite and gedrite, with Mg# values ranging from 0.60 to 0.69. Anthophyllite represented the highest proportion of the orthoamphiboles analysed, returning Al content varying from $X_{Al} = 0.27$ to 1.45. Gedrite returned higher Al contents varying from $X_{Al} = 1.72$ to 2.54. Cordierite (HD10b) shows Mg# content that varies from 0.84 to 0.85. Staurolite found in some retrogressed portions (HD14) exhibits small variation contents of $X_{Mg} = 0.88$ to 1.03. For the accessory minerals, monazite from samples HD02b, HD10a, and HD14 are characterised as (Ce)-monazite and the average compositions include 33.68 wt% Ce₂O₃, 11.62 wt% Nd₂O₃, and 13.73 wt% La₂O₃. ThO₂ contents varied from 0.91 to 4.55 wt%. Due to the low-precision technique for analysing trace elements, UO₂ and PbO are below the detection limits. The apatite individual crystals analysed from samples HD02b, HD10a and HD10b are fluorapatite (F = 1.16 to 3.72 wt%). The major constituents of apatite presented little variations for CaO and P₂O₅, varying from 50.51 to 55.49 wt% and from 41.81 to 43.31 wt%, respectively. Small average values for Na₂O (0.05 wt%), SiO₂ (0.06 wt%), and FeO (0.17 wt%) were obtained but are, in general, below the detection limit for most of the individual spots analysed. Cl values were only detected for the HD02b sample, varying from 0.67 to 2.35 wt%.

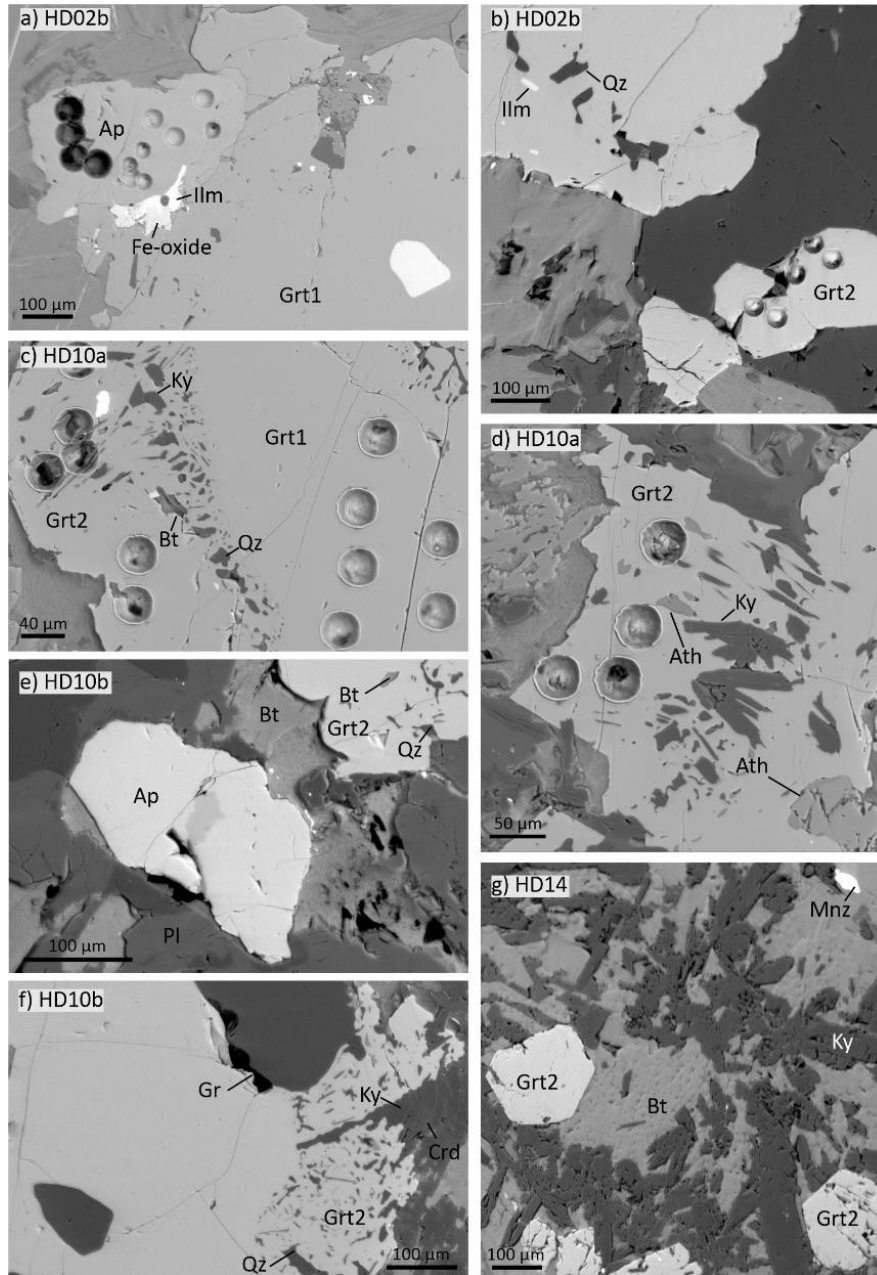


Figure 6.2: Back-scattered electron (BSE) images from the metapelite samples from the retrogressed hydrates zone of the SMZ. a) Apatite in association with ilmenite and Fe oxide along garnet Grt1; b) Garnet Grt2 occurring as rim containing ilmenite and quartz and occurring as small idioblastic garnet Grt2; c), d) Garnet Grt2 rim intergrown with retrogressed mineral assemblages (anthophyllite, kyanite, biotite and quartz); e) Apatite dispersed in the matrix with garnet Grt2 intergrown with biotite and quartz; f) Garnet Grt1 and garnet Grt2 rim with precipitated graphite associated with kyanite and cordierite; g) Small idioblastic garnet Grt2.

6.4.3 Trace element compositions

Garnets from samples HD02b, HD10a, and HD10b have similar chondrite-normalised REE patterns between them, presenting two garnet generations represented by the core (Grt1) and small idioblastic/rim (Grt2). The REE pattern for all samples is characterised by a large negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.26\text{-}0.36$) for Grt1 and by

enrichment in the MREE content, showing a positive Eu anomaly ($\text{Eu}/\text{Eu}^* = 1.51\text{-}1.69$) for Grt2 (Fig. 6.3; Electronic Supplement 2 - Table S1). Notably, small idioblastic garnet in sample HD02b showed positive and negative Eu anomalies, probably indicating a partial recrystallisation. In general, HD02b garnet Grt1 shows a strong increase in the LREE ($(\text{La}/\text{Gd})_N = 0.01$), with a flat enriched and variable pattern for the HREE ($(\text{Gd}/\text{Lu})_N = 0.33$). One garnet core revealed an HREE pattern slightly enriched ($(\text{Gd}/\text{Lu})_N = 0.03$) (Fig. 6.3). Garnet Grt2 reveals similar patterns for the LREE ($(\text{La}/\text{Gd})_N = 0.01$) and a more variable HREE ($(\text{Gd}/\text{Lu})_N = 0.97$) compared to Grt1. HD10a garnets are similar compared to the previous sample. Grt1 exhibits a steeper LREE pattern ($(\text{La}/\text{Gd})_N = 0.01$) with a smooth and more homogeneous HREE enriched pattern ($(\text{Gd}/\text{Lu})_N = 0.14$). A resemblant pattern of LREE ($(\text{La}/\text{Gd})_N = 0.02$) and HREE ($(\text{Gd}/\text{Lu})_N = 0.16$) is observed for garnet Grt2 related to Grt1. HD10b results yielded similar REE pattern behaviour for garnet Grt1 (LREE ($(\text{La}/\text{Gd})_N = 0.07$) and HREE ($(\text{Gd}/\text{Lu})_N = 0.22$)), and garnet Grt2 (LREE ($(\text{La}/\text{Gd})_N = 0.06$) and HREE ($(\text{Gd}/\text{Lu})_N = 0.91$)) compared to previous garnet generation samples. In general, it is possible to notice a decrease in Y (97 to 19 ppm), Sc (122 to 58 ppm), and Mn (4482 to 2856 ppm) average contents from core to rim/small idioblastic garnets new generations (Electronic Supplement 2) for sample HD02b. A similar variation trend was observed for Y (69 to 24 ppm, 57 to 27 ppm), Sc (109 to 63 ppm, 64 to 40 ppm), and Mn (4727 to 3187 ppm, 3002 to 2498 ppm) average contents for sample HD10a and HD10b, respectively (Electronic Supplement 2 - Table S1).

Monazites from samples HD02b, HD10a and HD14 are generally homogeneous in the REE chondrite-normalised diagram (Fig. 6.4), with smoothly fractionated and enriched LREE pattern ($(\text{La}/\text{Gd})_N = 7.2\text{-}9.5$) with negative Eu anomaly ($(\text{Eu}/\text{Eu}^* = 0.20\text{-}0.38$; Fig. 6.4). The HREE profiles for the three investigated samples are steeper and highly fractionated ($(\text{Gd}/\text{Lu})_N = 447.1\text{-}930.6$)), presenting a similar variation between the samples. Sample HD02b presented U and Th contents ranging from 3480 to 6902 ppm and 3172 to 28715, respectively. For sample HD10a the U contents varied from 4112 to 7523 ppm and the Th contents showed a wider range from 13821 to 35570 ppm. Lastly, sample HD14 showed a large range for U and Th contents varying from 758 to 7933 ppm and 8864 to 39458 ppm, respectively (Electronic Supplement 2 - Table S2).

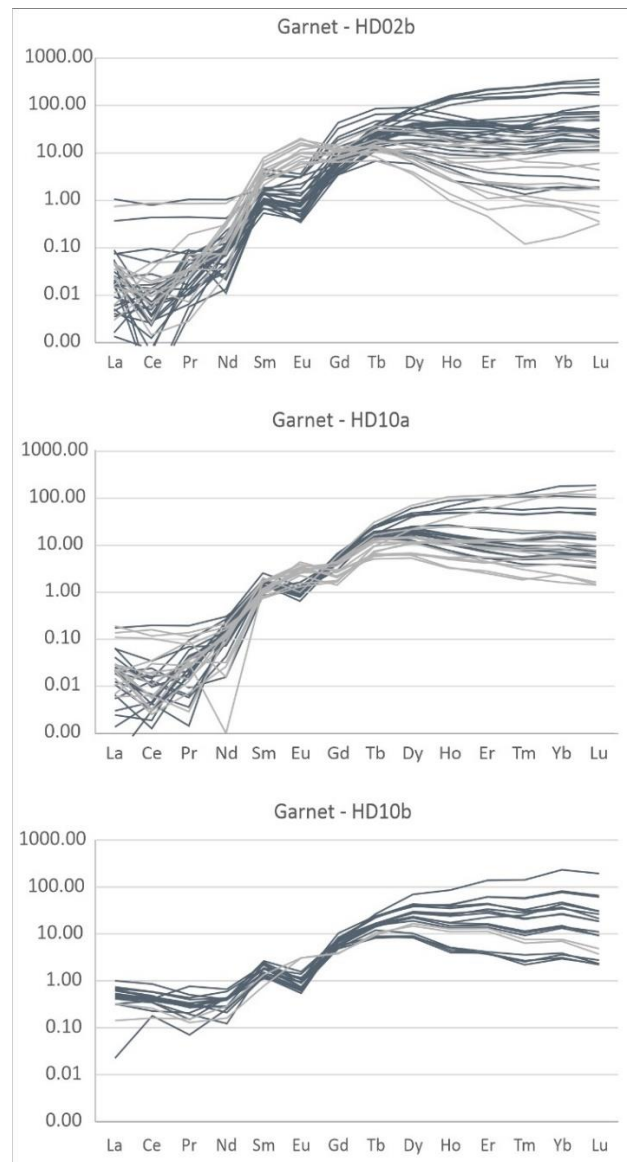


Figure 6.3: Chondrite-normalised REE patterns of the garnets analysed in this study. The dark grey lines represent the garnet Grt1 population, and the light grey lines represent the garnet Grt2 population. Concentrations were normalised by the chondrite values from Taylor and McLennan (1985).

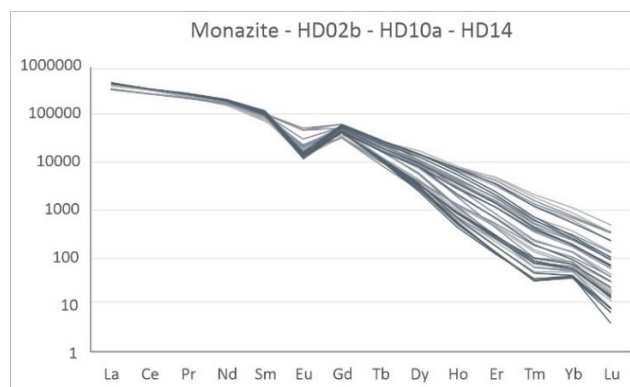


Figure 6.4: Chondrite-normalised REE patterns of the monazite from the samples investigated in this study. Concentrations were normalised by the chondrite values from Taylor and McLennan (1985).

The handpicked and *in-situ* apatite grains investigated in this study returned similar REE chondrite-normalised patterns within each sample (Fig. 6.5). However, only the REE-enriched group were observed for samples HD10a and HD10b. Apatite from sample HD02b ($\Sigma\text{REE} = 1962\text{-}3009$ ppm) is characterised by a slightly variable and enriched LREE profile ($(\text{La}/\text{Gd})_{\text{N}} = 0.86\text{-}1.74$) and moderate negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.56\text{-}0.67$) (Fig. 6.5). Interestingly, the three compositionally distinct populations observed in the HREE portion for the *in situ* analyses show a variable steeply fractionated sloping for the HREE pattern ($(\text{Gd}/\text{Lu})_{\text{N}} = 40.32\text{-}191.01$). This range is consistent with the results obtained in the apatite mount ($(\text{Gd}/\text{Lu})_{\text{N}} = 40.71$) (Fig. 6.5). The apatite samples present a positive Er anomaly and a slightly flat pattern from Tm to Lu. Notably, these variations occur between individual apatite grains (Fig. 6.5). Strontium is variable but is clustered for all populations ranging from 321 to 747 ppm (Fig. 6.6a). Yttrium contents are highly spread (16 to 429 ppm) and clearly evidence the different apatite compositional groups in this sample (Fig. 6.6b). Manganese concentrations overlap between the apatite distinct populations and vary from 110 to 496 ppm (Fig. 6.6c). Lutetium contents (0.1 to 1 ppm) are low compared to the other REEs but also variable (Fig. 6.6d). Sm and Nd contents range from 156 to 348 ppm and 377 to 1470 ppm, respectively, presenting a similar distribution pattern (Fig. 6.6e, f). Uranium and Th range from 18 to 34 ppm and 0 to 13 ppm, respectively (Fig. 6g, h) (Electronic Supplement 2 - Table S3).

In the HD10a sample, the apatite is represented by two distinct groups in the REE diagram. One population is characterised by an enriched REE pattern ($\Sigma\text{REE} = 1054\text{-}1160$ ppm), with a progressive increase in the LREE ($(\text{La}/\text{Gd})_{\text{N}} = 0.10\text{-}0.23$) and a slightly fractionated HREE pattern ($(\text{Gd}/\text{Lu})_{\text{N}} = 6.28\text{-}9.38$) compared to the previous sample (Fig. 6.5). The other group is represented by a depleted and flat REE profile ($\Sigma\text{REE} = 159$ ppm), with little inclined LREE ($(\text{La}/\text{Gd})_{\text{N}} = 3.79$) and smooth HREE pattern ($(\text{Gd}/\text{Lu})_{\text{N}} = 1.83$). Both populations presented similar negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.31\text{-}0.37$). A variation is observed in the chemical composition contents of the different REE population, however, they occur within individual apatite crystals indicating a mixture of apatite generations partially recrystallised observed in the *in-situ* results. Strontium contents are less variable (155 to 343 ppm; Fig. 6.6a). Yttrium has a wide range and indicates the two distinct apatite groups (21 to 1018 ppm; Fig. 6.6b). Manganese is slightly spread and variable (124 to 510 ppm; Fig. 6.6c), and Lu contents exhibited a large

range (0.3 to 5 ppm; Fig. 6.6d). Samarium and Nd contents vary from 5 to 192 ppm (Fig. 6.6e) and 18 to 339 ppm (Fig. 6.6f), respectively, exhibiting a similar behaviour pattern for both elements. Uranium (4 to 40 ppm), and Th (0 to 17 ppm) yielded generally higher variation (Fig. 6.6g, h).

Apatite from sample HD10b contains an REE-chondrite normalised diagram similar to sample HD10a (Fig. 6.5). Two REE patterns are also observed but show a slightly steeper HREE fractionation in the REE-enriched population. The LREE in the REE-enriched population ($\Sigma\text{REE} = 1163\text{-}1378$ ppm) is marked by a slight increase pattern ($(\text{La/Gd})\text{N} = 0.07\text{-}0.16$) with a more depleted HREE pattern ($(\text{Gd/Lu})\text{N} = 10.93\text{-}18.39$). The REE-poor group ($\Sigma\text{REE} = 141$ ppm) contains similar signatures for the decreasing LREE pattern ($(\text{La/Gd})\text{N} = 4.78$) and HREE flat pattern ($(\text{Gd/Lu})\text{N} = 1.31$) compared to HD10a. Smaller variations were observed for Sr (154 to 330 ppm; Fig. 6.6a). Yttrium contents (17 to 1081 ppm; Fig. 6.6b) follow the behaviour observed in the previous samples separating the two distinct groups with different chemical compositions. Manganese varied from 98 to 2444 ppm (Fig. 6.6c) and Lu varied from 0.3 to 5 ppm (Fig. 6.6d). The pattern observed for Sm (3 to 261 ppm; Fig. 6.6e) and Nd (17 to 591 ppm; Fig. 6.6f) marks the distinct populations but also presents a similar enrichment trend for both elements in all samples (Fig. 6.6e, f). U (3 to 96 ppm) and Th (0 to 27 ppm) present large chemical composition variations (Fig. 6.6g, h).

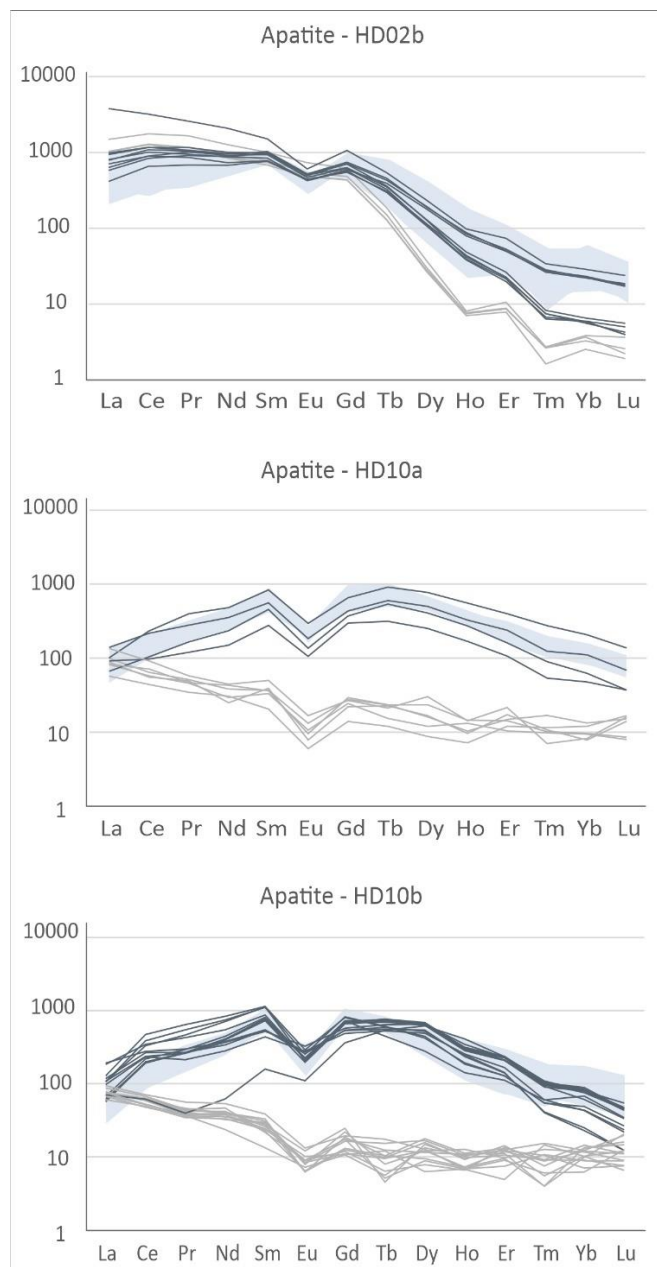


Figure 6.5: Chondrite-normalised REE concentrations of the apatite from the studied samples. The dark grey lines (in-situ analyses) and the blue shaded pattern (handpicked apatite) represent the REE-enriched apatite population, and the light grey lines (in-situ analyses) represent the REE-depleted apatite group. The blue shadowed pattern represents the handpicked apatite population. Concentrations were normalised by the chondrite values from Taylor and McLennan (1985).

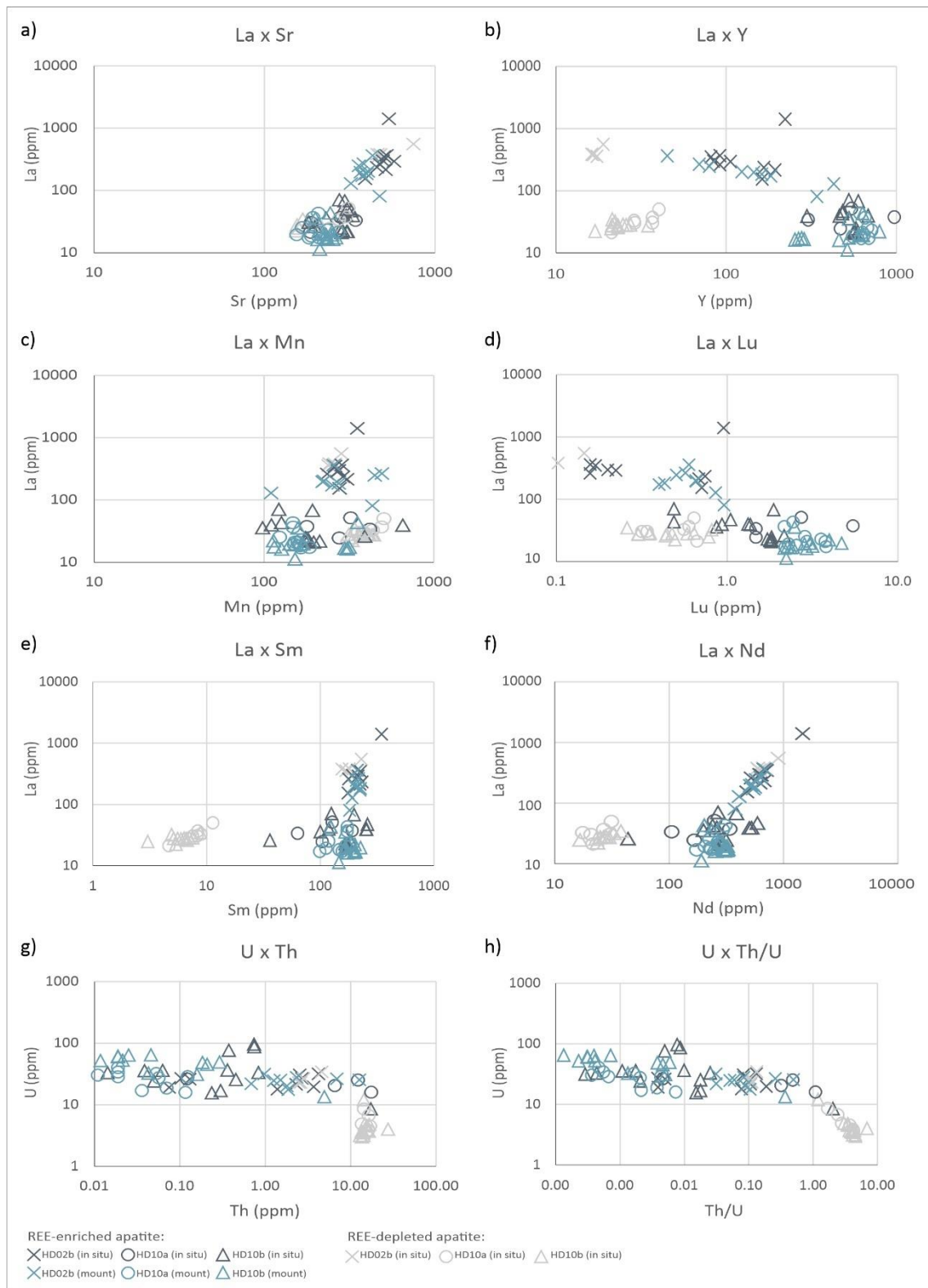


Figure 6.6: Apatite trace element diagram compositions for Sr, Y, Mn, Lu, Sm, Nd, Th and U. a) La versus Sr; b) La versus Y; c) La versus Mn; d) La versus Lu; e) La versus Sm; f) La versus Nd; g) U versus Th; h) U versus Th/U. Lanthanum presented similar concentrations for all the samples analysed between each element investigated. The “x”, circle and triangle symbols represent sample HD02b, HD10a and HD10b, respectively.

6.4.4 U-Pb geochronology

BSE images of monazite crystals from samples HD02b, HD10a, and HD14 are anhedral to subhedral, with some grains showing weak patchy zoning or brighter domains generally homogeneous with darker areas containing patchy patterns with delicate porous textures. Sample HD14 showed more fractured grains compared to samples HD02b and HD10a (Fig. 6.7a). U-Pb data acquired by LA-MC-ICP-MS returned concordant to subconcordant results (Fig. 6.8; Electronic Supplement 3- Table S4 and S5). The isotopic composition of twenty-seven analyses for seven crystals from sample HD02b yielded a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2707 ± 4 Ma (2s, MSWD = 0.45), showing a slight discordance pattern due to some Pb-loss (Fig. 6.8). For sample HD10a, thirty-one spot analyses for thirteen grains produced a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2742 ± 4 Ma (2s, MSWD = 1.9) (Fig. 6.8). Finally, sample HD14 showed a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2716 ± 5 Ma (2s, MSWD = 2.7) for thirty spots analysed from sixteen crystals, exhibiting a slightly reverse data probably related to excesses of ^{206}Pb associated with high ^{230}Th contents (Fig. 6.8).

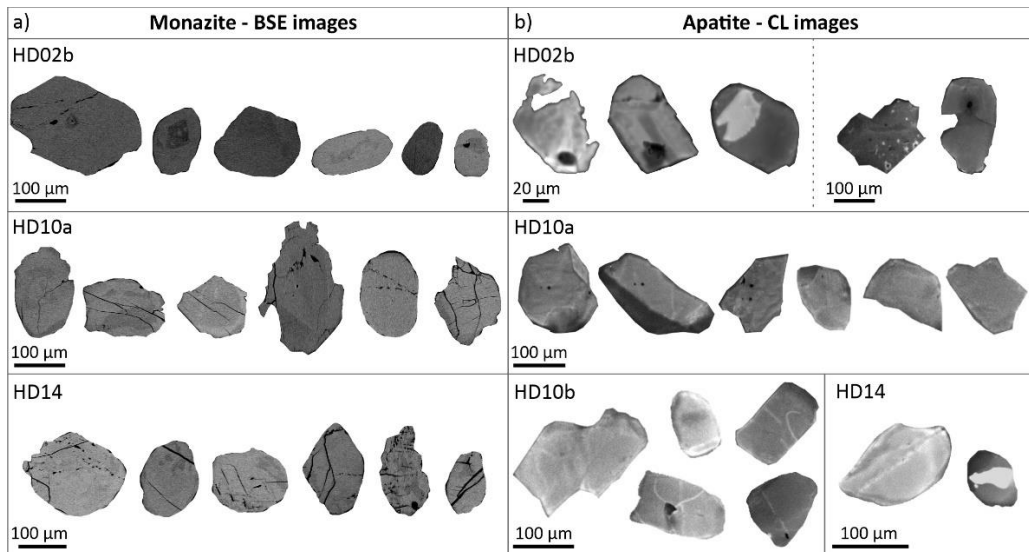


Figure 6.7: a) Monazite BSE images showing some crystals with slight zoning and fractures. Some grains present delicate porous textures; b) Apatite CL images containing patchy textures and oscillatory zoning in some crystals with overgrowth (e.g. HD02b, HD14) and porous textures (e.g. HD02b, HD10a).

Cathodoluminescence (CL) images for apatite grains from samples HD02b, HD10a, HD10b, and HD14 exhibit various zoning types (Fig. 6.7b). The crystal fragments are anhedral to subhedral, showing some grains with darker and brighter areas and little heterogeneous portions with discontinuous zoning and porous texture. The isotopic data for sample HD02b of thirteen individual spots from ten grains yielded a

lower intercept of 2056 ± 17 Ma (2s, MSWD = 0.99) (Fig. 6.9; Electronic Supplement 3 - Table S6). For this sample, the lower intercept age was obtained without anchoring to an initial $^{207}\text{Pb}/^{206}\text{Pb}$, that is, the data alone determined the upper intercept. This was done to avoid misinterpretations of the age, which probably experienced some disturbance in the U-Pb system. Individual spot data of twenty analyses from twelve grains for sample HD10a and fifteen analyses from nine grains for sample HD10b returned lower intercept ages of 2051 ± 7 Ma (2s, MSWD = 1.6, $\text{Pb}_c = 1.004$) and 2048 ± 6 Ma (2s, MSWD = 0.93, $\text{Pb}_c = 1.004$), respectively, consistent within uncertainties (Fig. 6.9). Sample HD14 presented a lower intercept age of 2055 ± 17 Ma (2s, MSWD = 0.35, $\text{Pb}_c = 1.008$) for three analyses from one grain as this sample has only a few apatites (Fig. 6.9). Three spots were discarded due to signal problems related to the crystal size and imperfections (e.g., fractures and inclusions).

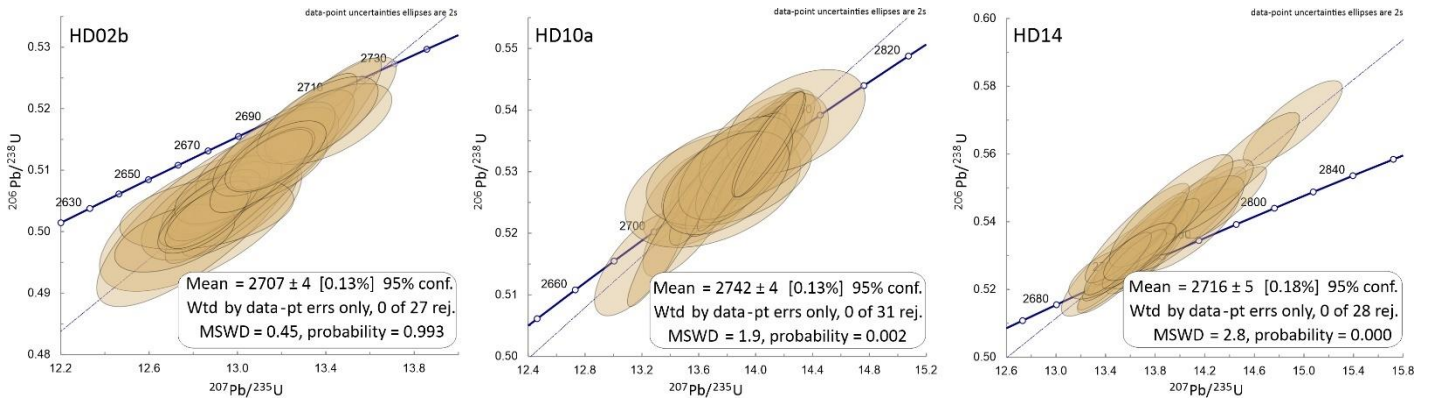


Figure 6.8: Wheterhill concordia diagrams of U-Pb data from monazite samples obtained by LA-MC-ICP-MS.

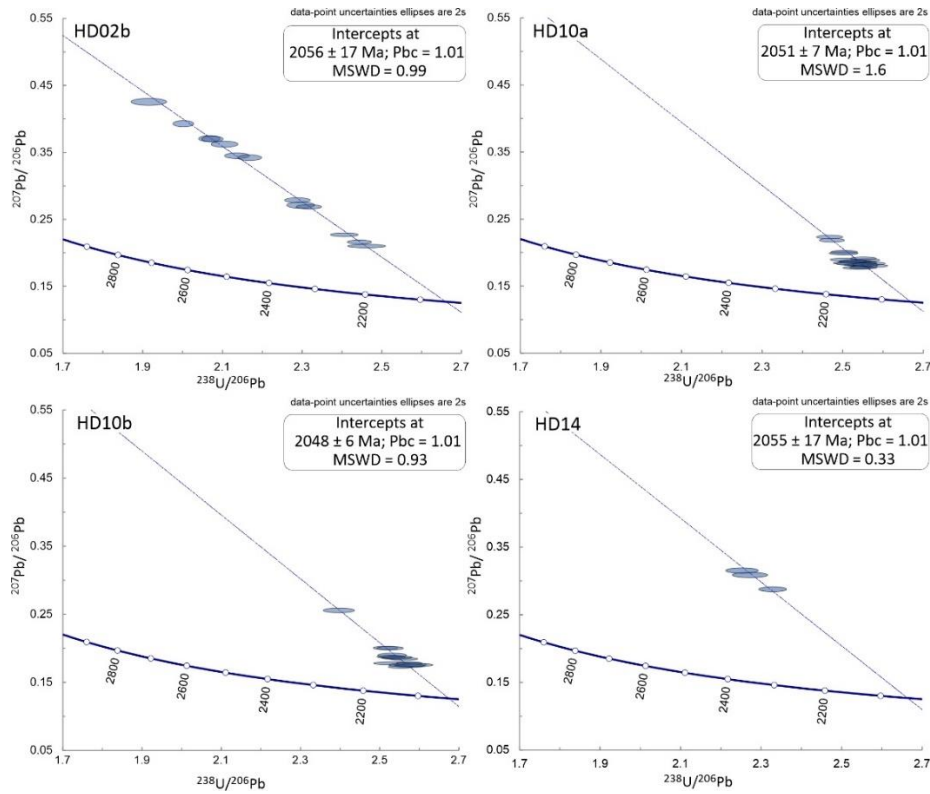


Figure 6.9: Tera-Wasserburg concordia diagrams of U–Pb data from apatite samples obtained by LA-MC-ICP-MS.

6.4.5 Sm-Nd isotope systematics

6.4.5.1 Solution mode-MC-ICP-MS

Amphiboles aliquot from sample HD02b yielded $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of 0.1255 ± 0.0002 (2s) and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.51107 ± 0.00015 (2s). The results for sample HD10b showed $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of 0.1488 ± 0.0004 (2s) and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.51091 ± 0.00036 (2s) (Fig. 6.10; Table 6.1). The obtained data for $^{143}\text{Nd}/^{144}\text{Nd}$ ratios agree within uncertainties between these samples. The ϵNd values obtained for samples HD02b and HD10b are -30.6 and -33.7 (uncertainties not reported), respectively (Table 6.1).

6.4.5.2 LA-MC-ICP-MS

Monazite from samples HD02b, HD10a and HD14 and apatite from samples HD02b, HD10a and HD10b were investigated for Sm-Nd isotope compositions (Fig. 6.10; Table 6.1 and Electronic Supplement 3 - Table S7 and S8). All monazite results have similar $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (Fig. 6.10; Table 6.1 and Electronic Supplement 3 - Table S7), producing an initial $^{143}\text{Nd}/^{144}\text{Nd}$ isochron intercept of 0.50882 ± 0.00030 (2s; MSWD = 0.81; n = 30) and a weighted average initial $^{143}\text{Nd}/^{144}\text{Nd}$ value

of 0.50891 ± 0.00002 (2s; MSWD = 0.88; n = 30), which agree within uncertainties. The weighted average initial $^{143}\text{Nd}/^{144}\text{Nd}$ value was calculated according to the age of ca. 2.7 Ga obtained in the monazite U-Pb dating (Electronic Supplement 3 - Table S4 and S5). All the samples have a moderate scatter in initial ϵNd (-5.7 ± 1.2 to -0.2 ± 4.4 ; 2s), considering the calculated U-Pb age (Table 6.1).

In contrast to monazite, apatite analyses are complex and markedly more radiogenic, showing two distinct populations with variable $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (Fig. 6.10). In order to investigate the apatite isotopic behaviour, we considered the two apatite spreads on the isochron (Fig. 6.10). Considering the population aligned with the isochron regression line, we obtained an initial $^{143}\text{Nd}/^{144}\text{Nd}$ isochron intercept of 0.50919 ± 0.00056 (2s; MSWD = 5.8; n = 13) and a weighted average initial $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.50882 ± 0.00006 (2s; MSWD = 1.3; n = 12), consistent within uncertainties with each other and between the monazite results (Table 6.1 and Electronic Supplement 3 - Table S7 and S8).

For the apatite containing different slope on the isochron diagram (Fig. 6.10), we acquired an initial $^{143}\text{Nd}/^{144}\text{Nd}$ isochron intercept of 0.50880 ± 0.00170 (2s; MSWD = 6.7; n = 13), consistent with the previous data within uncertainties, and a weighted average initial $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.50833 ± 0.00006 (2s; MSWD = 1.04; n = 11) (Table 6.1 and Electronic Supplement 3 - Table S8). The apatite weighted average initial $^{143}\text{Nd}/^{144}\text{Nd}$ values were calculated for the main granulite facies event at ca. 2.7 Ga, as considering the U-Pb age of ca. 2.05 Ga the results were not in agreement with their respective isochron values. The samples aligned in the isochron presented variable initial ϵNd (-9.7 ± 3.4 to 2.9 ± 1.4 ; 2s) (Fig. 6.11; Table 6.1). In contrast, the population aligned below the isochron yielded a large scatter and more negative values in initial ϵNd varying from -31.9 ± 3.4 (2s) to -11.7 ± 3.1 (2s) (Fig. 6.11; Table 6.1).

Using the entire dataset of monazite, apatite and amphibole (population with collinear array), we generate an initial $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.50894 ± 0.00006 (2s; MSWD = 2.6; n = 43), consistent with the individual initial $^{143}\text{Nd}/^{144}\text{Nd}$ results for both apatite and monazite mineral phases, with a $^{147}\text{Sm}/^{143}\text{Nd}$ - $^{144}\text{Nd}/^{143}\text{Nd}$ isochron age of 2685 ± 50 Ma (Fig. 6.10). Plotting the apatite and amphiboles in the lower isochron, we obtained an initial $^{143}\text{Nd}/^{144}\text{Nd}$ values of 0.50798 ± 0.00047 (2s; MSWD = 1.01; n = 14), with values slightly lower to the previous main isochron result.

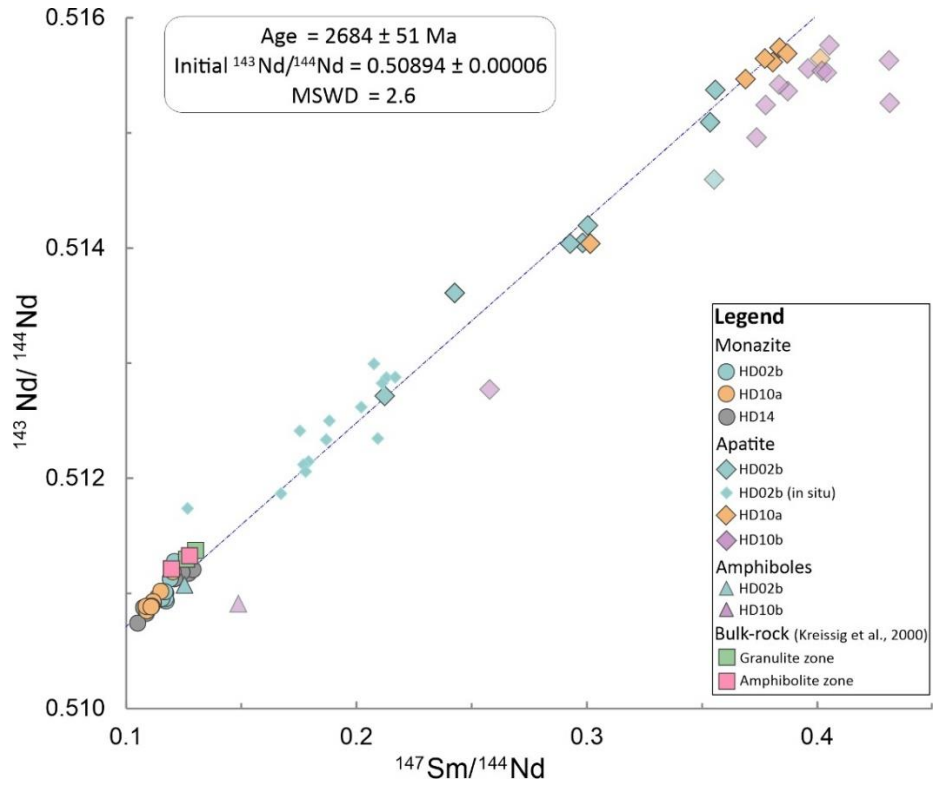


Figure 6.10: Sm-Nd isochron for the monazite and apatite analysed by LA-MC-ICP-MS and orthoamphibole obtained by solution MC-ICP-MS compared with the Sm-Nd bulk rock data from Kreissig et al. (2001) for the granulite and amphibolite retrogressed hydrated zone from the SMZ. The apatite population plotting below the main isochron are represented by the translucent spots.

Table 6.1: Sm-Nd isotope data of monazite and apatite analysed by LA-MC-ICP-MS and orthoamphibole analysed by solution MC-ICP-MS.

Identifier	$^{147}\text{Sm}/^{144}\text{Nd}$	$\pm 2s$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2s$	$^{143}\text{Nd}/^{144}\text{Ndi}$	$\pm 2s$	ϵNdi	$\pm 2s$
Monazite								
HD02b-1	0.1175	0.0007	0.51094	0.00010	0.50883	0.00010	-5.7	1.2
HD02b-2	0.1172	0.0007	0.51095	0.00010	0.50886	0.00010	-5.2	1.2
HD02b-3	0.1210	0.0028	0.51128	0.00038	0.50911	0.00038	-0.2	4.4
HD02b-4	0.1137	0.0006	0.51097	0.00009	0.50893	0.00009	-3.7	1.1
HD02b-5	0.1156	0.0008	0.51096	0.00009	0.50889	0.00009	-4.6	1.1
HD02b-6	0.1192	0.0007	0.51113	0.00009	0.50899	0.00009	-2.5	1.2
HD02b-7	0.0999	0.0006	0.51072	0.00009	0.50893	0.00009	-3.8	1.2
HD02b-8	0.1170	0.0006	0.51101	0.00010	0.50892	0.00010	-4.0	1.2
HD10a-1	0.1151	0.0006	0.51102	0.00008	0.50896	0.00008	-3.2	1.0
HD10a-2	0.1119	0.0007	0.51092	0.00011	0.50892	0.00011	-4.1	1.3
HD10a-3	0.1096	0.0006	0.51087	0.00010	0.50890	0.00010	-4.0	1.2
HD10a-4	0.1117	0.0006	0.51093	0.00008	0.50891	0.00008	-3.6	1.0
HD10a-5	0.1107	0.0006	0.51088	0.00007	0.50889	0.00007	-4.1	0.8
HD10a-6	0.1112	0.0007	0.51089	0.00009	0.50888	0.00009	-4.2	1.1
HD10a-7	0.1204	0.0007	0.51119	0.00011	0.50902	0.00011	-1.5	1.3
HD10a-8	0.1090	0.0006	0.51085	0.00009	0.50890	0.00009	-4.4	1.2
HD10a-9	0.1087	0.0006	0.51089	0.00010	0.50894	0.00010	-3.5	1.2
HD10a-10	0.1109	0.0006	0.51088	0.00006	0.50890	0.00006	-4.4	0.8

HD14-1	0.1088	0.0005	0.51083	0.00008	0.50888	0.00008	-4.8	1.0
HD14-2	0.1099	0.0006	0.51087	0.00009	0.50890	0.00009	-4.4	1.2
HD14-3	0.1094	0.0006	0.51088	0.00007	0.50891	0.00007	-3.5	0.9
HD14-4	0.1167	0.0007	0.51094	0.00009	0.50883	0.00009	-5.0	1.1
HD14-5	0.1271	0.0008	0.51117	0.00008	0.50887	0.00008	-4.1	1.0
HD14-6	0.1173	0.0013	0.51100	0.00009	0.50888	0.00009	-3.9	1.1
HD14-7	0.1144	0.0006	0.51097	0.00009	0.50890	0.00009	-3.7	1.1
HD14-8	0.1051	0.0009	0.51074	0.00007	0.50886	0.00007	-5.1	0.9
HD14-9	0.1076	0.0006	0.51088	0.00007	0.50895	0.00007	-3.3	0.9
HD14-10	0.1291	0.0007	0.51121	0.00010	0.50890	0.00010	-4.4	1.2
HD14-11	0.1243	0.0008	0.51118	0.00012	0.50896	0.00012	-3.2	1.4
HD14-12	0.1211	0.0007	0.51113	0.00010	0.50896	0.00010	-3.1	1.3
<i>Apatite</i>								
HD02b-1	0.2982	0.0011	0.51404	0.00017	0.50871	0.00017	-8.1	2.8
HD02b-2	0.2123	0.0007	0.51271	0.00010	0.50892	0.00010	-4.0	1.6
HD02b-3	0.2927	0.0047	0.51404	0.00030	0.50880	0.00030	-6.3	4.8
HD02b-4	0.3535	0.0023	0.51509	0.00075	0.50877	0.00075	-6.9	12.1
HD02b-5	0.3004	0.0005	0.51420	0.00011	0.50882	0.00011	-5.9	1.7
HD02b-7	0.2426	0.0004	0.51361	0.00009	0.50927	0.00009	2.9	1.4
HD02b-8	0.3553	0.0013	0.51459	0.00016	0.50824	0.00016	-17.3	2.6
HD02b-9	0.3557	0.0008	0.51537	0.00023	0.50901	0.00023	-2.2	3.8
HD10a-1	0.3015	0.0006	0.51404	0.00021	0.50859	0.00021	-9.7	3.4
HD10a-2	0.3836	0.0019	0.51574	0.00020	0.50880	0.00020	-5.5	3.2
HD10a-3	0.3807	0.0009	0.51561	0.00020	0.50873	0.00020	-6.9	3.3
HD10a-4	0.4013	0.0010	0.51565	0.00019	0.50839	0.00019	-13.6	3.1
HD10a-5	0.3689	0.0025	0.51547	0.00019	0.50880	0.00019	-5.6	3.0
HD10a-8	0.3773	0.0014	0.51564	0.00018	0.50882	0.00018	-5.1	2.8
HD10a-9	0.3870	0.0011	0.51569	0.00028	0.50869	0.00028	-7.7	4.5
HD10b-1	0.3960	0.0080	0.51556	0.00027	0.50840	0.00027	-13.4	4.3
HD10b-2	0.3777	0.0009	0.51524	0.00018	0.50841	0.00018	-13.2	3.0
HD10b-3	0.2578	0.0094	0.51277	0.00029	0.50811	0.00029	-19.1	4.6
HD10b-4	0.4020	0.0013	0.51554	0.00020	0.50827	0.00020	-16.0	3.2
HD10b-5	0.4041	0.0013	0.51552	0.00020	0.50822	0.00020	-17.0	3.2
HD10b-8	0.3871	0.0008	0.51536	0.00018	0.50836	0.00018	-14.2	2.9
HD10b-9	0.3834	0.0009	0.51542	0.00019	0.50849	0.00019	-11.7	3.1
HD10b-10	0.3736	0.0246	0.51496	0.00034	0.50820	0.00034	-17.3	5.6
HD10b-11	0.4052	0.0013	0.51576	0.00041	0.50843	0.00041	-12.7	6.6
<i>Amphiboles</i>								
HD02b	0.1255	0.0002	0.51107	0.00015	0.50885	-	-30.6	-
HD10b	0.1488	0.0004	0.51091	0.00036	0.50828	-	-33.7	-

6.4.6 Sr-Sr isotope compositions

The analysed apatite from samples HD02b, HD10a, and HD10b yielded heterogeneous $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between the grains investigated in each sample (Table 6.2 - Electronic Supplement 3 - Table S9). The individual values present a relatively large scatter but with

similar average $^{87}\text{Sr}/^{86}\text{Sr}$ values for sample HD02b of 0.7122 ± 0.0016 (2s; n = 8), varying from 0.7067 to 0.7147, and HD10b of 0.7122 ± 0.0027 (2s; n = 5), varying from 0.7033 to 0.7176. Sample HD10a returned higher average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7184 ± 0.0029 (2s; n = 7), with less variation, ranging from 0.7129 to 0.7178. Plotting all samples (one outlier spot removed) we obtained a weighted mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7130 ± 0.0014 (2s; MSWD = 13; n = 20).

Table 6.2: Sr-Sr data of apatite analysed by LA-MC-ICP-MS

Identifier	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2s$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2s$	$^{84}\text{Sr}/^{86}\text{Sr}$	$\pm 2s$	$^{84}\text{Sr}/^{88}\text{Sr}$	$\pm 2s$
<i>Apatite</i>								
HD02b-1	0.7129	0.0017	0.7129	0.0017	0.0547	0.0015	0.0065	0.0002
HD02b-2	0.7067	0.0024	0.7067	0.0024	0.0547	0.0021	0.0065	0.0003
HD02b-3	0.7119	0.0017	0.7119	0.0017	0.0549	0.0016	0.0066	0.0002
HD02b-4	0.7139	0.0009	0.7139	0.0009	0.0557	0.0011	0.0067	0.0001
HD02b-5	0.7146	0.0016	0.7146	0.0016	0.0544	0.0015	0.0065	0.0002
HD02b-6	0.7091	0.0013	0.7091	0.0013	0.0557	0.0014	0.0067	0.0002
HD02b-7	0.7142	0.0013	0.7142	0.0013	0.0555	0.0015	0.0066	0.0002
HD02b-8	0.7147	0.0015	0.7147	0.0015	0.0547	0.0011	0.0065	0.0001
HD10a-3	0.7178	0.0020	0.7178	0.0020	0.0558	0.0023	0.0067	0.0003
HD10a-4	0.7129	0.0017	0.7129	0.0017	0.0537	0.0020	0.0064	0.0002
HD10a-5	0.7152	0.0023	0.7152	0.0023	0.0547	0.0023	0.0065	0.0003
HD10a-6	0.7137	0.0025	0.7137	0.0025	0.0529	0.0025	0.0063	0.0003
HD10a-8	0.7175	0.0018	0.7175	0.0018	0.0582	0.0015	0.0070	0.0002
HD10b-2	0.7123	0.0020	0.7123	0.0020	0.0523	0.0018	0.0062	0.0002
HD10b-3	0.7033	0.0027	0.7033	0.0027	0.0501	0.0034	0.0060	0.0004
HD10b-4	0.7081	0.0022	0.7081	0.0022	0.0561	0.0012	0.0067	0.0001
HD10b-5	0.7176	0.0020	0.7176	0.0020	0.0517	0.0020	0.0062	0.0002
HD10b-6	0.7089	0.0025	0.7089	0.0025	0.0512	0.0031	0.0061	0.0004
HD10b-7	0.7097	0.0025	0.7097	0.0025	0.0527	0.0030	0.0063	0.0004
HD10b-9	0.7076	0.0019	0.7076	0.0019	0.0530	0.0018	0.0063	0.0002

6.5 Discussion

6.5.1 Mineral REE redistribution as an indicator of fluid-assisted interactions

Interpretations of the trace elements and REE chondrite-normalised pattern of garnet and accessory minerals are key to constraining distinct metamorphic processes and fluid/rock interactions. Previous studies have proposed that understanding the mineral geochemistry and REE patterns is key to investigating the circumstances and processes experienced in distinct geological events (e.g. Bea and Montero, 1999; Hermann and Rubatto, 2003; Buick et al., 2010; Mottram et al., 2014; Janot et al., 2018; Gillespie et al., 2022). Here we make a case for an intriguing REE redistribution between garnet,

monazite and apatite in parts of the SMZ that experienced fluid-assisted amphibolite-facies retrogression (e.g., Fig. 6.12).

6.5.1.1 Peritectic garnet Grt1 and monazite as co-genetic phases

Petrography shows two distinct garnet generations in the hydrated zone of the SMZ represented by primary garnet (Grt1) containing rim with retrogressed features (Grt2) and small idioblastic garnets (Grt2) dispersed in the matrix (Fig. 6.2). Garnet REE chondrite-normalised diagram for all samples analysed is represented by a depletion in the LREE ($(\text{La}/\text{Gd})_N = 0.01\text{--}0.07$) and a smooth variable pattern for the HREE ($(\text{Gd}/\text{Lu})_N = 0.14\text{--}0.33$), showing a strong negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.26\text{--}0.36$) for Grt1. A significant enrichment in the MREE is observed for garnet Grt2, exhibiting a positive Eu anomaly ($\text{Eu}/\text{Eu}^* = 1.51\text{--}1.69$) (Fig. 6.3; Electronic Supplement 2 - Table S1).

The REE pattern for all monazite samples investigated contains a slightly decreasing uniform LREE pattern ($(\text{La}/\text{Gd})_N = 7.2\text{--}9.5$) with negative Eu anomaly ($(\text{Eu}/\text{Eu}^* = 0.20\text{--}0.38$; Fig. 6.4). Some variations are observed in the monazite HREE pattern ($(\text{Gd}/\text{Lu})_N = 447.1\text{--}930.6$) showing a similar fractionated distribution for all the samples investigated (Fig. 6.4). Considering the monazite HREE depletion in the chondrite-normalised diagram (Fig. 6.4), this indicates that these mineral phases crystallised in the presence of garnet (e.g. Xia et al., 2017). Similar negative Eu anomalies are noticeable for garnet Grt1 ($\text{Eu}/\text{Eu}^* = 0.26\text{--}0.36$) and monazite ($\text{Eu}/\text{Eu}^* = 0.20\text{--}0.38$) but are slightly distinct for apatite ($\text{Eu}/\text{Eu}^* = 0.34\text{--}0.67$) (Fig. 6.11). Akin magnitudes of Eu anomaly in monazite and garnet usually indicate they are co-genetic phases (e.g. Bea, 1996; Hermann and Rubatto, 2003; Buick et al., 2010; Mottram et al., 2014). Thus the REE patterns from the monazite and garnet Grt1 are consistent with the petrographic relationships and geological context that garnet Grt1 with monazite (Fig. 6.11) crystallised during the prograde metamorphic reactions of the SMZ in granulite-facies conditions (Fig. 6.12).

The monazite trace element compositions yielded Th/U ratios ranging from 0.9 to 11.5 (excluding two outlier values of ~ 40.0) and Y contents varying from 821 to 15857 ppm. Overall, the very consistent REE pattern behaviour for all the monazite samples suggests that the crystals were not completely affected by fluid interaction, despite the petrographic evidence of crystallisation in the presence of melt (e.g. Stevens, 1997; Nicoli et al., 2015; Vezinet et al., 2018; Madlakana et al., 2020). We believe that the fluid-crystal

interaction was minimised due to the low solubility of monazite in the presence of the peraluminous melt (Bea and Montero, 1999; Wolf and London, 1995). Indeed, experimental results acquired for the initial melt composition of the SMZ rocks indicate a peraluminous melt composition (Stevens, 1997).

It is important to highlight that some monazite grains exhibit slight scatter zoning with darker heterogeneous areas in BSE images (Fig. 6.7a) which, together with some minor chemical composition variations in them (e.g. U, Th, Y and HREE), might indicate a metasomatically induced dissolution-reprecipitation process (Harlov et al., 2007), which probably occurred in the presence of melt during increasing metamorphism (Bea and Montero, 1999) and crust exhumation (Xia et al., 2017) as reported for the granulite facies event of the SMZ (e.g. Stevens, 1997; Nicoli et al., 2015; Vezinet et al., 2018; Madlakana et al., 2020). The chemical variations observed in U, Th, Y and HREE are consistent with the fact that these elements are less compatible with monazite (Seidou-Guillaume et al., 2002) and were probably removed during the monazite crystallisation in the presence of melt/fluid interactions. Thus, these facts possibly indicate that the melt composition controls the U, Th, Y and REE redistribution between the accessory phases (Bea and Montero, 1999) where the mineral/fluid surface dynamics will rule the dissolution-reprecipitation processes of the preexisting crystal (Seidou-Guillaume et al., 2002).

6.5.1.2 Retrogressed garnet Grt2 crystallisation during apatite breakdown

While garnet Grt1 and monazite are co-genetic phases, additional chemical composition evidence attests to a disequilibrium between garnet Grt1 and garnet Grt2 (rim/small garnets). Garnet Grt2 exhibits positive Eu anomalies ($\text{Eu}/\text{Eu}^* = 1.55\text{--}1.69$; Fig. 6.3), indicating a different crystallisation stage as observed in Figures 6.11 and 6.12. Garnet Grt2 ($\text{Alm}_{65}\text{Pyr}_{30}\text{Grs}_1\text{Sps}_1$) shows a slight Mn decrease that did not affect the spessartine average composition compared to Grt1 ($\text{Alm}_{63}\text{Pyr}_{32}\text{Grs}_3\text{Sps}_1$), indicating that its growth was probably caused by processes related to dissolution-reprecipitation and recrystallisation (Kohn, 2003; Cheng et al., 2007, 2009a; Xia et al., 2012, 2016, 2017). The MREE enrichment noticed in garnet Grt2 can be related to a breakdown of an MREE-enriched phase (e.g. Zhou et al., 2011; Mottram et al., 2014; Xia et al., 2017). Considering the chemical composition disequilibrium observed in the two apatite mineral generations (e.g. REE-enriched and -depleted; Fig. 6.5), we suggest that the REE-depleted apatite

experienced breakdown contributing to a MREE-enrichment for garnet Grt2 crystallisation during fluid reactions (Fig. 6.12). These chemical implications together with the retrogressed mineral assemblage contained in garnet Grt2 (e.g. orthoamphiboles, quartz, biotite) suggest a fluid-enhanced overgrowth episode instead of a continuation of the prograde growth of garnet Grt1 (Cheng et al., 2009b). Given that the REE mobility in apatite is slow, the main factor influencing the REE migration from apatite to melt is related to apatite dissolution-reprecipitation processes, rather than an equilibrium between apatite and melt (Beard et al., 1994). This is consistent with findings from experiments that included two generations of apatite in the presence of melt (Beard et al., 1994).

6.5.1.3 REE-enriched apatite crystallised via dissolution-precipitation of REE-depleted apatite

Trace element compositions indicate two distinct apatite generations (Fig. 6.5). The REE-depleted apatite is mainly observed in samples HD10a and HD10b. This group is characterised by lower Sm, Nd, Y and U contents (consequently higher Th/U ratios), which reflect a metamorphic origin for these apatite populations that presented a tendency to U partitioning when crystallising in the presence of melt (Bea and Montero, 1999). The REE-depleted apatite also contains lower Dy_N/Lu_N ratios (0.50-2.74) compared to the REE-enriched apatite (Fig. 6.11).

The REE-enriched apatite is marked by higher Sm, Nd, Y and U chemical compositions and higher Dy_N/Lu_N ratios (4.01-44.25; Fig. 6.11). We suggest that while interacting with the melt, the newly formed anatectic REE-enriched apatite group (HD10a and HD10b) incorporated U (9-96 ppm), Y (254-1081 ppm) and REE contents (Electronic Supplement 2 - Table S3). In the case of HD02b, we suggest that all apatite analysed for trace elements is represented by the newly formed anatectic crystals, as their U contents and Th/U ratios are similar to the REE-enriched groups from samples HD10a and HD10b. Thus, chemical composition variations observed in the different apatite REE patterns from each sample investigated suggest distinct apatite phases that likely underwent metasomatic induced partial dissolution-reprecipitation processes through fluid-assisted interaction (e.g., Bea and Montero, 1999; Putnis, 2009; Harlov, 2007; Janot et al., 2018).

Experimental work of Peiffert et al. (1996) reported that in the presence of partial melting, U solubility is enhanced into the melt through the formation of complexes in its

+4 oxidation state with halides (Keppler and Wyllie, 1990, 1991), wherein chloride combines with U and Th and fluoride with U to produce stable complexes (Keppler and Wyllie, 1990, 1991; Peiffert et al. 1996). Bea and Montero (1999) revealed that this explanation is consistent with the presence of stable graphite, ilmenite, and pyrite, which were also observed in our samples and represent low oxygen fugacity in the rocks. Regarding the concentration of F (1.16-3.73 wt%) observed in the apatite of all samples and of Cl (0.67-2.35 wt%) contained in the apatite of the HD02b sample, we suggest that there was an enhancement of U partitioning into the melt compared to Th (e.g. Bea and Montero, 1999). This can be observed for all the apatite from HD02b that are enriched in U. This process also had an influence on apatite from HD10a and HD10b, wherein the apatite grains contain negligible Cl contents but also presented U-enriched and depleted apatite populations.

The incorporation of Y and REE in all samples probably occurred through coupled substitution via reaction (1) $\text{Si}^{4+} + (\text{Y}+\text{REE})^{3+} = \text{P}^{5+} + \text{Ca}^{2+}$ or (2) $\text{Na}^{+} + (\text{Y}+\text{REE})^{3+} = 2 \text{Ca}^{2+}$ (Harlov, 2007), although it is unclear which element (Si or Na) prompted the reaction in this study. In addition, the partial dissolution observed in HD10a crystals instead of the complete dissolution observed in HD10b grains might be related to the fluid composition at the reaction interface instead of the bulk fluid composition (Xia et al., 2017), which did not change completely the REE contents within the same and/or distinct grains. Therefore, comparing the behaviour of monazite-apatite accessory minerals together with garnet distinct populations during fluid interactions gives insights into the U, Th, Y and REE mobility related to partial melting processes. These interpretations contribute to a better understanding of fluid reactivity during the granulite facies and amphibolite retrogression in the metapelites of the SMZ.

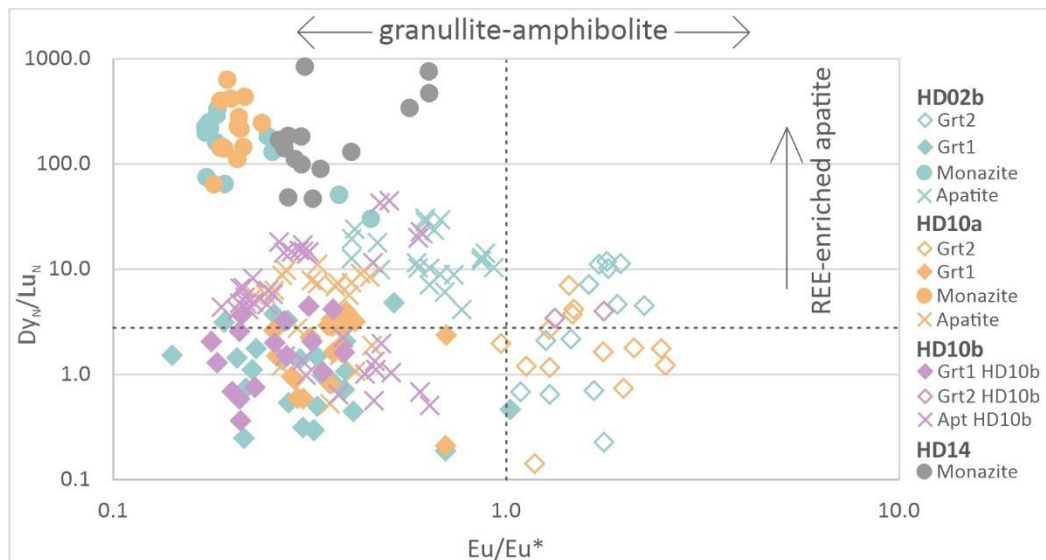


Figure 6.11: Dy_N/Lu_N versus Eu/Eu^* diagram for all the mineral phases investigated in this study. The Eu/Eu^* anomaly separates the distinct garnet generations. The Dy_N/Lu_N ratio separates the REE-depleted and -enriched apatite populations.

6.5.2 *Significance and geological interpretations of the poly-metamorphic evolution in the hydrated zone of the SMZ based on U-Pb dating and Sm-Nd and Sr-Sr isotope compositions*

6.5.2.1 Archean and Paleoproterozoic evolution – Sm-Nd and U-Pb isotopic system behaviour

U-Pb geochronology and Sm-Nd isotope compositions of apatite and monazite samples investigated from the hydrated zone of the SMZ present distinct isotopic opened and- closed system behaviour during the melt/fluid interactions and geological events experienced in the SMZ. Whereas monazite U-Pb ages are consistent with the Sm-Nd isochron age, the apatite U-Pb ages are systematically younger. The amphibole results followed the same evolution trend in the Sm-Nd isochron compared to these mineral phases.

Considering the apatite population aligned in the Sm-Nd isochron and the ones that plotted slightly below (Fig. 6.10), both present an $Nd-Nd_i$ signature that is consistent with the monazite $Nd-Nd_i$ values, indicating that apatite followed the same evolution trend that monazite and crystallised at ca. 2.7 Ga during the granulite facies event from the SMZ (e.g. Kreissig et al., 2001; Nicoli et al., 2015). The amphibole aliquots aligned in both isochron spreadings indicate that the hydration event of amphibolite-facies conditions of the former granulites from the SMZ occurred at ca. 2.7 Ga. The small slope variation suggests that the apatite and amphibole group plotted below the main isochron probably experienced some small isotope disturbance during fluid interactions and/or

protracted post-tectonic re-heating geological events in the SMZ (Laurent et al., 2013; Zeh et al., 2015) but did not affect the consistency between the initial $^{143}\text{Nd}/^{144}\text{Nd}$ isochron values of both isochron populations. This could be related to the granitoid intrusions at ~2685 Ma close to the Hout River shear zone in the SMZ (Fig. 6.1) during the exhumation of the crust under granulite-facies (Matok Igneous Complex) and lower temperatures (<600°C) and pressure (<6 kbar) conditions (Mashashane, Moletsi and Matlala plutons) (Fig. 6.1; Laurent et al., 2013). Previous studies have shown that due to the low mobility of rare earth elements under hydrothermal conditions (White, 2014), the Sm-Nd isotopic system can preserve the primary signature even after experiencing alteration by hydrothermal fluids (Chen and Zhang, 2018; Huang et al., 2019; Zhang et al., 2020). This can be observed in the Sm-Nd isotope signatures of the REE-enriched anatectic apatites, which crystallised after interacting with the fluids contained in the melt and agree with monazite Nd-Nd_i values, preserving the primary signature at ca. 2.7 Ga.

The obtained U-Pb ages for apatite (ca. 2.05 Ga) and monazite (ca. 2.7 Ga) reveal distinct isotopic re-equilibration related to the different closure temperatures for the U-Pb system between apatite ($T_c = 450\text{--}550^\circ\text{C}$; Cherniak et al., 1991; Nemchin and Pidgeon 1999; Chamberlain and Bowring 2001) and monazite ($T_c = 900^\circ\text{C}$; Cherniak et al., 2004). Due to the slow Pb-volume diffusion in monazite in natural conditions, Pb loss by diffusion tends to have less effect on the U-Pb discordancy (Seydoux-Guillaume, 2002). Neoarchean monazite U-Pb ages (Fig. 6.8) are consistent with the Sm-Nd isochron age (2685 ± 50 Ma; Fig. 6.10) and with previous monazite ages from the SMZ reported by Kreissig et al. (2001; 2691 ± 7 Ma) for the granulite-facies zone. These ages are also consistent with U-Pb zircon ages of ca. 2712 Ma from anatectic leucosomes that occur in the metapelites of the Bandelierkop Formation in the granulite zone (Taylor et al., 2014; Nicoli et al., 2015).

In contrast, the systematically younger apatite U-Pb ages of ca. 2.05 Ga (Fig. 6.9) obtained in this study compared to the ca. 2.7 Ga Sm-Nd isochron values (Fig. 6.10) suggest that a U-Pb opening system (e.g. Cherniak et al., 1991; Cherniak, 2000; Schoene and Bowring, 2007) occurred during cooling below the closure temperature in the Paleoproterozoic re-heating event but did not affect the Neoarchean Sm-Nd isotopic signature. This younger event is probably related to a solid-state diffusion process that caused isotopic re-equilibrium promoting the diffusion of Pb in apatite (Cherniak et al., 1991; Cherniak, 2000) under suitable thermal conditions (Gillespie et al., 2022). It is

important to note that in a process in which fluid was involved causing the reset in the U-Pb system by dissolution-precipitation (e.g. Mezger and Krogstad, 1997; Putnis, 2009), the Sm-Nd isotopic system should at least present some disturbance (Gillespie et al., 2022), which in this study there is no evidence for a Sm-Nd disturbance related to the younger Paleoproterozoic apatite ages. Previous studies showed that in the absence of significant amounts of fluid, events in amphibolite facies (<600 °C) are unable to induce an isotopic re-equilibration (e.g. Janot et al., 2018) for the Sm-Nd system (~700 °C; Cherniak, 2010). This is consistent with the younger Paleoproterozoic U-Pb apatite ages compared to the Neoarchean Sm-Nd isochron age preserved for all the mineral assemblages investigated in this study. Thus, the distinct apatite ages for U-Pb isotopic systems register distinct events besides the ca. 2.7 Ga granulite facies metamorphism recorded in the SMZ (e.g. Kreissig et al., 2001; Nicoli et al., 2015).

Previous studies have presented evidence of thermal events around the SMZ region postdating the ca. 2.7 Ga granulite-facies event. The apatite age of ca. 2.05 Ga is consistent with previously published rutile ages (2058 ± 96 Ma to 2135 ± 90 Ma; Madlakana et al., 2020) for the partially retrogressed granulite-facies metapelites from the SMZ. Madlakana et al. (2020) proposed an explanation to interpret the rutile cooling age ($T_c = \sim 600$ °C; Cherniak, 2000) of ca. 2.1 Ga suggesting a thermal source possibly associated with the formation of mantle-derived volcanic rocks at 2.32 to 2.06 Ga in the Pretoria Group of the Transvaal Supergroup (Lenhardt et al., 2012). As the apatite in this study has a younger age of 2.05 Ga, but is consistent within uncertainties with the rutile ages (Madrakana et al., 2020), a possible alternative explanation is associated with the crystallisation of the Bushveld Complex and igneous intrusions in the northwest of the Kaapvaal craton between 2.05 Ga and 2.06 Ga (Scoates and Friedman, 2008; Olsson et al., 2010; Zeh et al., 2015) (Fig. 6.12). The Bushveld Complex was emplaced and cooled in a short period of less than one million years based on zircon ages of 2056-2055 Ma (Zeh et al., 2015). The thermal modelling conditions for the region indicate a rapid magma accumulation that crystallised and cooled below 700 °C (Zeh et al., 2015). This temperature is higher than the closure temperature for Pb in apatites, agreeing with the conditions for disturbing the U-Pb system ($T_c = 450-550$ °C; Cherniak et al. 1991; Nemchin and Pidgeon 1999; Chamberlain and Bowring 2001) without affecting the Sm-Nd system (~700 °C; Cherniak, 2010) in the absence of fluid (Janot et al., 2018) during the Paleoproterozoic as observed in this study.

Based on phase equilibrium modelling of the metapelites from the SMZ, the area experienced granulite facies peak metamorphic conditions of ~850 °C and ~11 kbar (Van Reenen, 1983; Van Reenen et al., 1987; Roering et al., 1992a; Stevens & Van Reenen, 1992b; Taylor et al., 2014; Nicoli et al., 2015), resulting in fluid-absent melting reactions during a period of prograde heating (Stevens & Van Reenen, 1992). Following the peak metamorphism the metapelites experienced an isothermal decompression and isobaric cooling to amphibolite facies conditions of 660-600 °C and 5-6 kbar (e.g. Stevens, 1997; Nicoli et al., 2015). Madlakana et al. (2020) proposed that the metapelites from the granulite and amphibolite zones experienced similar amphibolite metamorphic conditions due to the same orthoamphibole assemblages found in both zones, which only the amount of fluid available to prompt the reactions was different. Considering that the metapelites from the hydrated zone recorded the granulite facies event at ca. 2.7 Ga according to monazite U-Pb ages and Sm-Nd isochron age (this study) and that apatite reacted with an internally derived fluid (Stevens, 1997) available during partial melting reactions (section 5.1) during the Neoproterozoic (Fig. 6.12), we suggest that the equilibration in amphibolite facies occurred on the final stage of the P-T loop where the granulite mineral assemblages were intensely rehydrated in the kyanite stability field under conditions of 660-600 °C and 5-6 kbar (e.g. Stevens, 1997; Nicoli et al., 2015) at ca. 2.7 Ga (Fig. 6.12). The orthoamphibole Sm-Nd isotope compositions also support this interpretation as it represents one of the retrogressed hydrated phases aligned with the ca. 2.7 Ga Sm-Nd isochron. In addition, previously published Sm-Nd bulk-rock composition for both hydrated and granulite-facies zone from the SMZ (Kreissig et al., 2001) follows the same evolution trend in the Sm-Nd isochron (Fig. 6.10), reinforcing that there was no externally derived fluid interacting with the mineral assemblages. Additionally, Madlakana et al. (2020) have reported that the metapelites that record retrogressed mineral assemblages in the granulite zone (e.g. Diener et al., 2008) exhibit preserved earlier second-generation orthopyroxene and garnet, indicating a localised hydration reaction that excludes an externally buffered $a_{\text{H}_2\text{O}}$ activity.

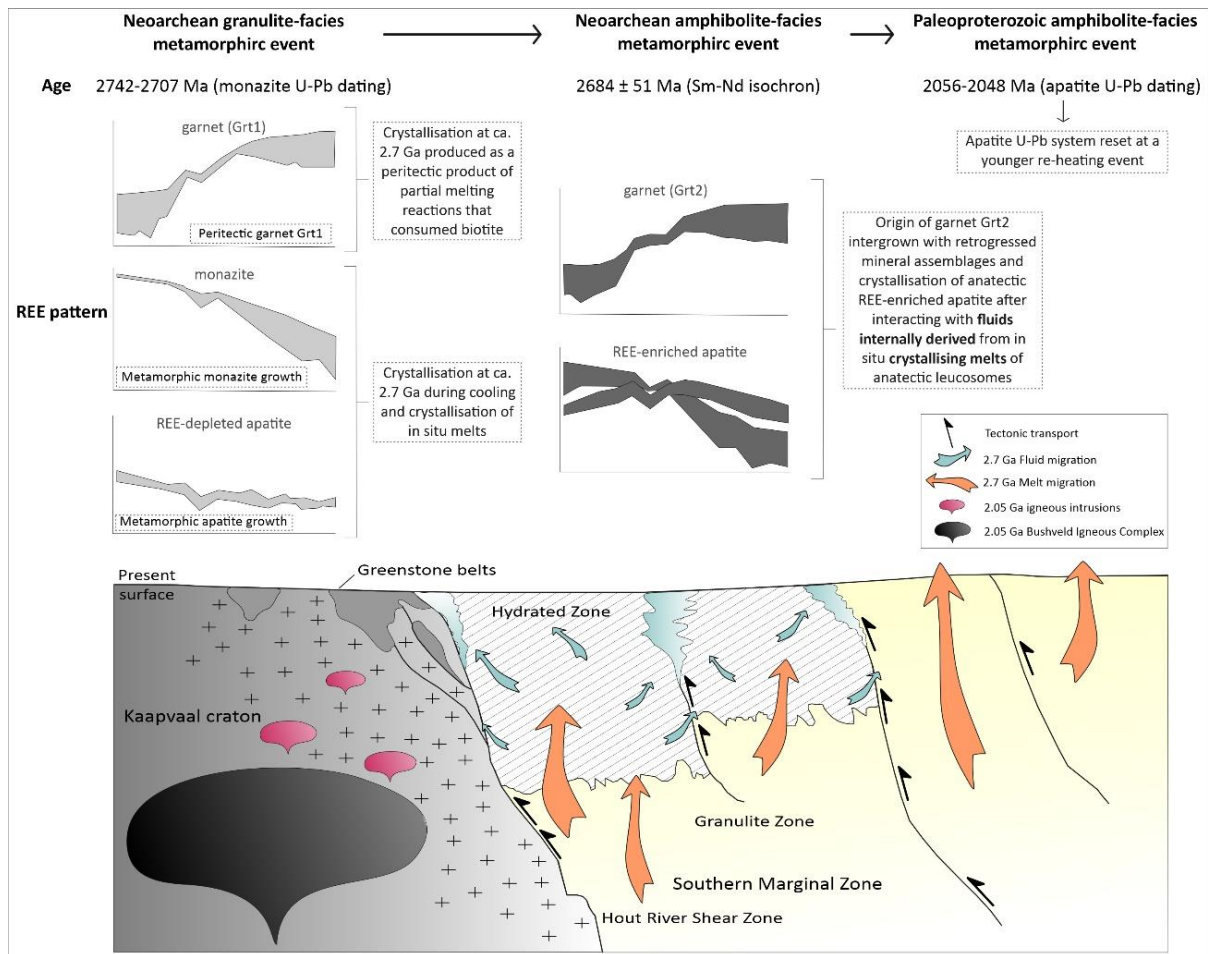


Figure 6.12: Summary of the metamorphic events in the SMZ (modified from Stevens, 1997), where the metapelites experienced granulite facies conditions with partial melting. The melt crystallisation produced internally derived fluids that hydrated the former granulites at amphibolite facies conditions during the Neoarchean. The reset of U-Pb apatite ages in the region records a later re-heating Paleoproterozoic event probably caused by the emplacement of the Bushveld Igneous Complex and igneous intrusions.

6.5.2.2 ϵNd and Sr-Sr isotopes as indicative of fluid sources

The ϵNd and Sr-Sr data in apatite is consistent with a fluid of crustal composition (Fig. 6.13), excluding the possibility of a mantle-derived fluid that infiltrated the SMZ (e.g. Touret and Huizenga, 2011, 2012). The Sr-Sr values indicate a significant variation that can be interpreted by two possibilities: 1) the Sr-Sr system reached equilibrium during the metamorphic peak of the granulite-facies event and 2) this equilibrium was compromised during the retrogression in amphibolite-facies conditions. Previous studies suggest similar processes for the isotopic equilibrium of the Sm-Nd and Rb-Sr systems experienced by early formed phases in peak eclogite-facies metamorphism retrogressed under amphibolite-facies conditions (Xie et al. 2004). The disequilibrium observed in the $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 6.13) may be attributed to notable variations in the Sr isotopic

composition of the fluids that interacted with the apatites or some disturbances that compromised the closed-system conditions (Richardson et al., 1990).

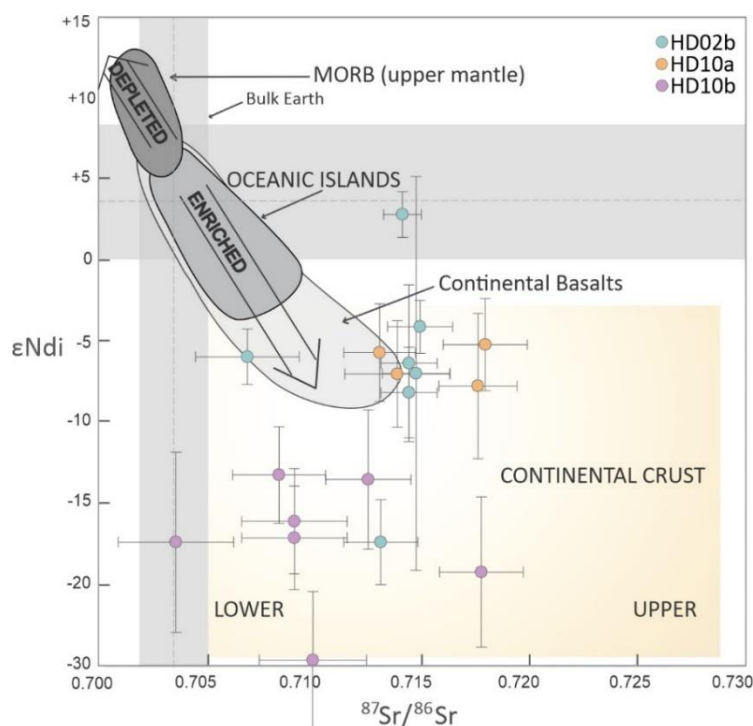


Figure 6.13: ϵNd versus $^{87}\text{Sr}/^{86}\text{Sr}$ diagram (Modified from White, 2015) for the apatite samples analysed in this study indicating a crustal signature.

6.6 Conclusion

In the broader context of the poly-metamorphic evolution of the SMZ, we interpret that this terrain experienced a Neoarchean granulite-facies metamorphism at ca. 2.7 Ga based on the Sm-Nd data and monazite U-Pb dating. The mineral assemblages investigated in this study and the bulk-rock composition (Kreissig et al., 2001) indicate that the metapelites from the retrogressed hydrated zone interacted with an internally derived fluid from crystallising leucosomes as proposed by Stevens (1997) during the Neoarchean. If a fluid externally derived interacted with the metapelites, the bulk rock compositions and the mineral assemblages that interacted with the fluids (e.g. apatite, amphiboles) would likely plot in a distinct region in the Sm-Nd isochron, presenting a distinct Sm-Nd isotopic signature. The Paleoproterozoic younger age recorded at ca. 2.05 Ga suggests retrograde evolution in the amphibolite-facies caused by a re-heating event that reset the U-Pb system for mineral phases with lower closure temperature (e.g. apatite, rutile).

CAPÍTULO 7

CONCLUSÕES

7.1 Conclusões

Com base nos estudos realizados e nas microanálises de alta resolução espacial, apresentamos dois novos materiais de referência potenciais de titanita para métodos analíticos de alta resolução espacial. A titanita Khan River apresenta homogeneidade isotópica de Nd consistente, mas apresenta as razões de Sm-Nd variáveis. Além disso, possui altos teores de U, Th, Pb radiogênico e ETR, e contém Pb_c relativamente baixo e ligeiramente variável. A técnica de abrasão química produziu fragmentos livres de áreas danificadas e o tratamento químico auxiliou a identificar as porções do cristal que são adequadas para microanálises. Vale ressaltar que os fragmentos e porções a serem analisados devem ser escolhidos criteriosamente, evitando inclusões, bem como áreas altamente heterogêneas (por exemplo, zoneamento, porção danificada) e fraturadas. Os valores recomendados para este material de referência são (1) média ponderada não corrigida para Pb_c da razão $^{206}Pb/^{238}U$ de 0.08381 ± 0.00027 (2s); (2) média ponderada corrigida para Pb_c da razão $^{206}Pb/^{238}U$ de 0.08328 ± 0.00026 (2s), e da razão $^{207}Pb/^{206}Pb$ de 0.05760 ± 0.00007 (2s), e (3) média ponderada da razão $^{143}Nd/^{144}Nd$ de 0.511587 ± 0.00027 (2s). Sugerimos que a titanita Khan River é adequada como material de referência secundário para geocronologia U-Pb e análises de isótopos Nd-Nd.

A titanita Bear Lake é homogênea e mais translúcida que a titanita Khan River e não apresenta inclusões minerais. Possui alto grau de homogeneidade isotópica e química, apresentando relações isotópicas Sm-Nd consistentes, altas concentrações de REE, U, Th e Pb radiogênico, porém contém níveis relativamente altos de Pb_c . O Pb_c é relativamente homogêneo, produzindo variações mínimas nas relações $^{207}Pb/^{206}Pb$ e $^{206}Pb/^{204}Pb$. Os valores recomendados para este material de referência são (1) média ponderada não corrigida para Pb_c da razão $^{206}Pb/^{238}U$ de 0.18774 ± 0.00012 (2s); (2) média ponderada corrigida para Pb_c da razão $^{206}Pb/^{238}U$ de 0.17867 ± 0.00054 (2s), e da razão $^{207}Pb/^{206}Pb$ de 0.07433 ± 0.00029 (2s), e (3) média ponderada da razão $^{143}Nd/^{144}Nd$ de 0.512321 ± 0.000004 (2s) e razões médias de $^{147}Sm/^{144}Nd$ de 0.1327 ± 0.0003 . A titanita Bear Lake pode ser usada como material de referência para microanálise de elementos traços in situ e análise de isótopos Sm-Nd e datação U-Pb. As titanitas Bear Lake e Khan River estão disponíveis em grandes quantidades para serem distribuídos à comunidade científica mediante solicitação.

A monazita Vermilion é homogênea em termos de U-Pb, Sm-Nd e elementos traços. Nós a propomos para ser utilizada como um material de referência primário para análises de

U-Pb LA-ICP-MS, conforme confirmado pelos resultados de round-robin, utilizando a monazita Vermilion para reproduzir as idades dos materiais de referência e amostras desconhecidas. Além disso, também propomos a monazita Vermilion como um material de referência secundário para estudos de Sm-Nd. Todos os resultados obtidos por solução MC-ICP-MS e LA-ICP-MS estão de acordo com os dados de ID-TIMS e SHRIMP. As médias ponderadas da idade $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ obtida por ID-TIMS de 2666.5 ± 3.0 Ma (2σ ; MSWD = 4.5; $n = 3$) e da razão 0.1815 ± 0.0003 (2σ ; MSWD = 4.4; $n = 3$); e da idade $^{206}\text{Pb}^*/^{238}\text{U}$ de 2668.4 ± 2.6 (2σ ; $n = 3$; MSWD = 0.36) e da razão de 0.5128 ± 0.0006 (2σ ; $n = 3$; MSWD = 0.36); e a idade $^{207}\text{Pb}^*/^{235}\text{U}$ de 2667.3 ± 1.3 (2σ ; $n = 3$; MSWD = 0.9) e razão de 12.8310 ± 0.0180 (2σ ; $n = 3$; MSWD = 0.89), são os valores recomendados para o material de referência da monazita Vermilion. Existem grandes quantidades deste material de referência a serem distribuídos.

Por último, utilizando a monazita Vermilion no estudo de circulação e proveniência de fluidos realizado no Cinturão Limpopo, na Zona Marginal Sul (SMZ), foi possível investigar o tempo a fonte de fluidos que causaram a retrogressão de antigos granulitos da SMZ em fácies anfibolito causada durante a colisão dos crátons Kaapvaal e Zimbabwe em ca. 2.7 Ga. A partir de análises isotópicas de U-Pb em monazitas e apatitas e de Sm-Nd nestes minerais e em anfibólios, foi possível restringir as possíveis interpretações relacionadas aos processos de hidratação dos metapelitos. Análises de elementos traços em apatita, monazita e duas gerações distintas de granadas permitiram interpretar as fases minerais e sua evolução durante os eventos metamórficos. A partir destas interpretações e das análises de rocha total de Sm-Nd da literatura e dos valores de Sr-Sr em apatitas, foi possível concluir que o fluido era internamente derivado proveniente da cristalização do *melt* dos leucossomas originados durante o evento de fácies granulito em ca. 2.7Ga. As assinaturas de ϵNd e Sr-Sr apoiam esta interpretação de fluidos com origem continentais e descartam a possibilidade de uma fonte mantélica conforme proposto anteriormente.

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1.1 Garnet major element compositions

Sample	Garnet	Area	Na2O	MgO	Al2O3	Si2O	K2O	CaO	Ti2O	Cr2O3	MnO	FeO	Total	Almandine	Grossular	Pyrope	Spessartine
HD02B	A1	core	0.10	7.71	21.47	38.86	0.08	1.26	0.00	0.20	0.57	30.81	101.07	65.47	1.85	29.78	1.25
		core	0.09	7.96	21.43	38.37	0.00	1.36	0.00	0.00	0.55	30.72	100.50	64.03	1.50	30.94	1.22
		rim	0.00	6.87	21.24	38.63	0.00	2.36	0.00	0.16	0.44	31.23	100.93	65.85	4.20	26.60	0.97
		rim	0.00	6.53	21.01	38.43	0.00	2.52	0.00	0.00	0.41	31.45	100.35	66.41	4.77	25.57	0.91
	A2	small garnet	0.00	7.08	21.20	38.22	0.00	1.40	0.00	0.07	0.51	32.18	100.66	67.32	1.14	27.61	1.14
			0.00	7.36	21.38	38.34	0.00	1.51	0.00	0.10	0.41	32.18	101.27	66.23	1.04	28.63	0.91
			0.00	6.79	21.27	38.26	0.05	2.63	0.00	0.11	0.45	31.49	101.04	65.19	4.27	26.44	0.99
	A3	core	0.00	7.23	20.98	38.04	0.00	1.40	0.00	0.00	0.52	31.40	99.57	66.57	1.46	28.32	1.17
		core	0.00	7.22	21.07	38.27	0.00	1.53	0.00	0.13	0.55	31.25	100.02	66.31	1.85	28.17	1.22
		rim	0.00	6.82	21.09	38.19	0.00	1.49	0.14	0.15	0.61	31.59	100.08	67.70	2.24	26.73	1.36
		rim	0.00	6.70	21.18	38.07	0.00	2.46	0.00	0.09	0.44	31.18	100.12	65.85	4.48	26.24	0.99
HD10A	A2	new garnet	0.00	9.06	21.12	38.14	0.00	1.82	0.00	0.08	0.41	27.72	98.37	58.55	2.94	35.41	0.92
			0.12	8.77	20.84	37.95	0.00	1.76	0.00	0.15	0.43	28.00	98.01	59.41	2.58	34.64	0.96
	A4	small garnet	0.00	9.60	20.99	38.55	0.00	1.56	0.00	0.24	0.34	27.56	98.84	57.32	1.70	37.54	0.76
			0.00	8.98	21.08	37.77	0.00	1.59	0.00	0.17	0.46	28.26	98.32	59.00	1.79	35.45	1.03
	A6	small garnet	0.00	8.06	21.13	38.64	0.00	2.21	0.09	0.23	0.58	29.16	100.09	61.09	3.98	31.43	1.29
			0.00	7.76	20.65	38.20	0.00	2.02	0.00	0.17	0.56	28.79	98.14	61.83	3.98	31.09	1.27
	A9	rim	0.14	8.76	21.11	38.35	0.00	1.78	0.00	0.21	0.57	28.44	99.36	59.62	2.54	34.13	1.27
		rim	0.00	9.42	21.33	38.71	0.00	1.84	0.00	0.22	0.52	27.76	99.79	57.48	2.58	36.28	1.13
	A10	core	0.00	8.87	21.03	37.34	0.04	1.32	0.08	0.23	0.64	27.97	97.52	59.35	1.62	35.41	1.45
		core	0.00	9.13	21.05	37.77	0.00	1.31	0.00	0.14	0.68	27.40	97.49	58.73	1.97	36.03	1.52
		core	0.00	8.75	21.46	38.36	0.06	1.36	0.00	0.00	0.87	28.22	99.08	60.27	2.60	34.01	1.92
	A11	core	0.00	9.12	21.01	38.64	0.00	1.43	0.00	0.17	0.70	28.06	99.12	58.68	1.66	35.74	1.55
		core	0.00	8.83	20.97	38.82	0.04	1.46	0.00	0.14	0.62	27.93	98.82	59.41	2.76	35.02	1.40
HD14	A1	core	0.00	7.26	20.75	37.62	0.00	0.90	0.00	0.00	0.44	30.61	97.58	67.23	1.41	29.15	1.01
		core	0.09	6.73	20.55	37.33	0.00	1.18	0.08	0.07	0.64	31.67	98.34	68.26	0.75	26.90	1.45

	A2	core	0.11	6.57	20.77	37.21	0.00	1.03	0.00	0.15	0.65	31.87	98.36	69.22	0.96	26.33	1.48
		core	0.00	5.97	20.58	37.56	0.04	1.38	0.00	0.00	0.47	32.90	98.89	71.10	1.57	23.86	1.06
	A3	core	0.11	7.03	20.57	37.57	0.00	1.18	0.00	0.00	0.55	31.92	98.93	67.48	0.00	27.90	1.24
		core	0.00	6.72	20.78	37.61	0.00	1.05	0.00	0.00	0.74	31.95	98.85	68.72	0.66	26.62	1.67
		core	0.00	6.96	20.59	37.45	0.04	1.04	0.00	0.09	0.56	31.89	98.64	68.04	0.00	27.72	1.28
	A4	core	0.00	6.84	20.72	38.05	0.00	1.09	0.00	0.07	0.43	32.15	99.35	68.73	0.75	27.19	0.97
		small grt	0.00	6.55	20.79	38.09	0.00	1.15	0.00	0.11	0.50	32.54	99.73	69.65	1.05	25.96	1.12
		core	0.00	6.07	20.86	38.00	0.05	1.22	0.00	0.00	0.48	32.89	99.58	71.27	1.92	24.15	1.08

1.2 Amphiboles major element compositions

Sample	Na2O	MgO	Al2O3	Si2O	K2O	CaO	Ti2O	Cr2O3	MnO	FeO	Total	Group	Subgroup of (OH,F,Cl)	Species	Mg#
HD02B - 1	0.42	20.06	3.87	53.21	0.08	0.27	0.11	0.12	0.00	19.23	97.36	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.07
HD02B - 2	0.32	20.14	3.27	53.81	0.00	0.19	0.00	0.07	0.00	19.34	97.12	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.04
HD02B - 3	0.18	20.58	2.18	54.20	0.00	0.29	0.00	0.08	0.12	19.57	97.18	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.26
HD02B - 4	0.23	20.85	2.03	54.71	0.00	0.26	0.00	0.11	0.00	19.86	98.05	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.22
HD02B - 5	0.29	20.00	3.90	52.90	0.00	0.27	0.08	0.20	0.00	19.05	96.70	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.22
HD02B - 6	0.25	20.47	2.68	54.45	0.00	0.21	0.12	0.00	0.11	19.12	97.42	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.67
HD02B - 7	0.33	20.70	3.31	54.35	0.00	0.26	0.13	0.09	0.07	19.30	98.52	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.70
HD02B - 8	0.34	20.27	3.74	53.32	0.00	0.33	0.18	0.11	0.11	18.86	97.26	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.75
HD10A - 1	0.00	22.43	3.06	50.93	0.00	0.09	0.29	0.11	0.15	20.88	97.94	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.74
HD10A - 2	0.00	22.43	2.31	51.62	0.00	0.19	0.00	0.09	0.17	21.35	98.16	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.23
HD10A - 3	0.15	21.48	1.59	53.95	0.00	0.12	0.00	0.10	0.09	17.26	94.73	OH,F,Cl	Mg-Fe-Mn	anthophyllite	68.98
HD10A - 4	0.17	20.45	2.61	52.57	0.04	0.23	0.07	0.13	0.00	17.23	93.49	OH,F,Cl	Mg-Fe-Mn	anthophyllite	67.95
HD10A - 5	0.00	20.40	2.58	50.49	0.00	0.12	0.00	0.13	0.31	23.41	97.44	OH,F,Cl	Mg-Fe-Mn	anthophyllite	60.88
HD10A - 6	0.13	20.04	2.70	50.03	0.00	0.13	0.00	0.10	0.15	23.52	96.80	OH,F,Cl	Mg-Fe-Mn	anthophyllite	60.35
HD10A - 7	0.00	20.93	3.00	50.61	0.00	0.10	0.00	0.00	0.34	22.71	97.69	OH,F,Cl	Mg-Fe-Mn	anthophyllite	62.21
HD10A - 8	0.24	20.52	2.45	53.70	0.00	0.20	0.08	0.15	0.16	18.35	95.84	OH,F,Cl	Mg-Fe-Mn	anthophyllite	66.64
HD10A - 9	0.12	21.42	2.97	51.12	0.00	0.15	0.00	0.00	0.08	22.35	98.21	OH,F,Cl	Mg-Fe-Mn	anthophyllite	63.12
HD10B - 1	0.00	21.42	2.48	51.02	0.00	0.07	0.00	0.00	0.15	22.75	97.89	OH,F,Cl	Mg-Fe-Mn	anthophyllite	62.71
HD10B - 2	0.00	20.92	2.46	50.44	0.00	0.07	0.00	0.12	0.25	22.80	97.05	OH,F,Cl	Mg-Fe-Mn	anthophyllite	62.10
HD10B - 3	0.15	20.47	2.81	49.42	0.00	0.12	0.00	0.11	0.18	22.44	95.69	OH,F,Cl	Mg-Fe-Mn	anthophyllite	61.97
HD10B - 4	0.24	21.28	2.55	54.35	0.00	0.18	0.14	0.09	0.09	18.08	97.00	OH,F,Cl	Mg-Fe-Mn	anthophyllite	67.77
HD10B - 5	0.19	21.62	1.87	54.32	0.00	0.15	0.00	0.07	0.00	17.98	96.20	OH,F,Cl	Mg-Fe-Mn	anthophyllite	68.24
HD10B - 6	0.09	22.51	3.20	51.06	0.00	0.16	0.07	0.21	0.19	20.36	97.86	OH,F,Cl	Mg-Fe-Mn	anthophyllite	66.39
HD10B - 7	0.22	21.07	2.28	53.91	0.04	0.21	0.00	0.11	0.15	17.76	95.74	OH,F,Cl	Mg-Fe-Mn	anthophyllite	67.93
HD10B - 8	1.32	17.19	12.89	45.90	0.00	0.18	0.14	0.00	0.10	18.04	95.76	OH,F,Cl	Mg-Fe-Mn	gedrite	62.98

HD10B - 9	1.13	18.15	9.92	47.53	0.00	0.26	0.14	0.00	0.28	18.05	95.45	OH,F,Cl	Mg-Fe-Mn	gedrite	64.23
HD10B - 10	0.17	20.47	2.13	53.26	0.00	0.18	0.00	0.00	0.24	18.43	94.89	OH,F,Cl	Mg-Fe-Mn	anthophyllite	66.48
HD10B - 11	0.15	21.76	2.24	54.95	0.05	0.27	0.00	0.00	0.22	17.40	97.04	OH,F,Cl	Mg-Fe-Mn	anthophyllite	69.07
HD10B - 12	0.86	19.14	8.06	49.94	0.00	0.27	0.14	0.07	0.20	18.13	96.79	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.35
HD10B - 13	1.52	16.50	14.81	45.08	0.07	0.22	0.09	0.00	0.20	17.93	96.42	OH,F,Cl	Mg-Fe-Mn	gedrite	62.18
HD10B - 14	1.53	16.46	14.18	45.68	0.00	0.23	0.11	0.00	0.12	18.27	96.59	OH,F,Cl	Mg-Fe-Mn	gedrite	61.67
HD10B - 15	0.25	20.55	3.03	54.07	0.00	0.24	0.00	0.13	0.16	19.36	97.79	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.47
HD10B - 16	0.30	20.51	2.66	53.98	0.00	0.28	0.00	0.00	0.15	18.66	96.54	OH,F,Cl	Mg-Fe-Mn	anthophyllite	66.26
HD10B - 17	0.12	21.14	2.47	51.46	0.00	0.08	0.00	0.00	0.25	23.05	98.58	OH,F,Cl	Mg-Fe-Mn	anthophyllite	62.09
HD10B - 18	0.08	20.69	2.83	50.32	0.05	0.11	0.09	0.00	0.38	23.17	97.72	OH,F,Cl	Mg-Fe-Mn	anthophyllite	61.47
HD10B - 19	0.00	21.42	3.00	50.99	0.00	0.10	0.00	0.09	0.16	22.68	98.46	OH,F,Cl	Mg-Fe-Mn	anthophyllite	62.78
HD10B - 20	0.30	20.75	2.61	53.81	0.00	0.09	0.00	0.00	0.18	18.05	95.80	OH,F,Cl	Mg-Fe-Mn	anthophyllite	67.25
HD10B - 21	0.00	22.06	2.91	51.60	0.07	0.00	0.00	0.00	0.14	22.35	99.14	OH,F,Cl	Mg-Fe-Mn	anthophyllite	63.81
HD10B - 22	0.11	21.21	3.06	50.85	0.00	0.08	0.00	0.09	0.26	22.59	98.26	OH,F,Cl	Mg-Fe-Mn	anthophyllite	62.65
HD10B - 23	0.11	20.73	2.61	53.26	0.00	0.18	0.00	0.10	0.20	17.89	95.08	OH,F,Cl	Mg-Fe-Mn	anthophyllite	67.43
HD10B - 24	0.30	21.53	2.85	53.79	0.04	0.16	0.07	0.23	0.18	17.92	97.08	OH,F,Cl	Mg-Fe-Mn	anthophyllite	68.22
HD10B - 25	0.84	19.10	8.48	49.40	0.00	0.24	0.20	0.33	0.14	17.10	95.81	OH,F,Cl	Mg-Fe-Mn	anthophyllite	66.62
HD10B - 26	0.18	22.62	2.51	51.20	0.00	0.11	0.00	0.14	0.00	21.14	97.90	OH,F,Cl	Mg-Fe-Mn	anthophyllite	65.65

1.2 Continued.

Si	Ti	Al	Cr	Fe+3	Fe+2	Mn	Mg	Ca	Na	K	Total
7.63	0.01	0.66	0.01	0.00	2.31	0.00	4.29	0.04	0.12	0.01	15.08
7.73	0.00	0.55	0.01	0.00	2.32	0.00	4.31	0.03	0.09	0.00	15.04
7.79	0.00	0.37	0.01	0.00	2.35	0.01	4.41	0.04	0.05	0.00	15.04
7.80	0.00	0.34	0.01	0.00	2.37	0.00	4.43	0.04	0.06	0.00	15.05
7.63	0.01	0.66	0.02	0.00	2.30	0.00	4.30	0.04	0.08	0.00	15.05
7.78	0.01	0.45	0.00	0.00	2.29	0.01	4.36	0.03	0.07	0.00	15.01
7.69	0.01	0.55	0.01	0.00	2.29	0.01	4.37	0.04	0.09	0.00	15.06
7.64	0.02	0.63	0.01	0.00	2.26	0.01	4.33	0.05	0.09	0.00	15.06
7.37	0.03	0.52	0.01	0.00	2.53	0.02	4.84	0.01	0.00	0.00	15.33
7.46	0.00	0.39	0.01	0.00	2.58	0.02	4.83	0.03	0.00	0.00	15.33
7.87	0.00	0.27	0.01	0.00	2.11	0.01	4.67	0.02	0.04	0.00	15.01
7.78	0.01	0.46	0.01	0.00	2.13	0.00	4.51	0.04	0.05	0.01	15.00
7.44	0.00	0.45	0.01	0.00	2.89	0.04	4.48	0.02	0.00	0.00	15.33
7.43	0.00	0.47	0.01	0.00	2.92	0.02	4.44	0.02	0.04	0.00	15.35
7.41	0.00	0.52	0.00	0.00	2.78	0.04	4.57	0.02	0.00	0.00	15.33
7.79	0.01	0.42	0.02	0.00	2.23	0.02	4.44	0.03	0.07	0.00	15.02
7.42	0.00	0.51	0.00	0.00	2.71	0.01	4.63	0.02	0.03	0.00	15.34
7.45	0.00	0.43	0.00	0.00	2.78	0.02	4.66	0.01	0.00	0.00	15.34
7.44	0.00	0.43	0.01	0.00	2.81	0.03	4.60	0.01	0.00	0.00	15.34
7.40	0.00	0.50	0.01	0.00	2.81	0.02	4.57	0.02	0.04	0.00	15.37
7.77	0.01	0.43	0.01	0.00	2.16	0.01	4.54	0.03	0.07	0.00	15.03
7.83	0.00	0.32	0.01	0.00	2.17	0.00	4.64	0.02	0.05	0.00	15.04
7.38	0.01	0.55	0.02	0.00	2.46	0.02	4.85	0.03	0.03	0.00	15.34
7.81	0.00	0.39	0.01	0.00	2.15	0.02	4.55	0.03	0.06	0.01	15.03
6.72	0.02	2.22	0.00	0.00	2.21	0.01	3.75	0.03	0.37	0.00	15.34
6.98	0.02	1.72	0.00	0.00	2.22	0.04	3.97	0.04	0.32	0.00	15.30

7.81	0.00	0.37	0.00	0.00	2.26	0.03	4.48	0.03	0.05	0.00	15.03
7.83	0.00	0.38	0.00	0.00	2.07	0.03	4.62	0.04	0.04	0.01	15.01
7.21	0.02	1.37	0.01	0.00	2.19	0.02	4.12	0.04	0.24	0.00	15.21
6.56	0.01	2.54	0.00	0.00	2.18	0.02	3.58	0.03	0.43	0.01	15.38
6.64	0.01	2.43	0.00	0.00	2.22	0.02	3.57	0.04	0.43	0.00	15.35
7.72	0.00	0.51	0.01	0.00	2.31	0.02	4.37	0.04	0.07	0.00	15.05
7.78	0.00	0.45	0.00	0.00	2.25	0.02	4.41	0.04	0.08	0.00	15.03
7.47	0.00	0.42	0.00	0.00	2.80	0.03	4.57	0.01	0.03	0.00	15.34
7.39	0.01	0.49	0.00	0.00	2.85	0.05	4.53	0.02	0.02	0.01	15.37
7.40	0.00	0.51	0.01	0.00	2.75	0.02	4.63	0.02	0.00	0.00	15.34
7.79	0.00	0.45	0.00	0.00	2.19	0.02	4.48	0.01	0.08	0.00	15.03
7.41	0.00	0.49	0.00	0.00	2.69	0.02	4.73	0.00	0.00	0.01	15.35
7.40	0.00	0.52	0.01	0.00	2.75	0.03	4.60	0.01	0.03	0.00	15.35
7.77	0.00	0.45	0.01	0.00	2.18	0.03	4.51	0.03	0.03	0.00	15.01
7.70	0.01	0.48	0.03	0.00	2.15	0.02	4.59	0.03	0.08	0.01	15.09
7.17	0.02	1.45	0.04	0.00	2.08	0.02	4.13	0.04	0.24	0.00	15.18
7.42	0.00	0.43	0.02	0.00	2.56	0.00	4.89	0.02	0.05	0.00	15.38

1.3 Monazite major element compositions

Spectrum	SiO2	P2O5	CaO	Y2O3	La2O3	Ce2O3	Pr2O3	Nd2O3	Sm2O3	Gd2O3	Tb2O3	Dy2O3	PbO	ThO2	UO2	Total
HD02B - 1	0.00	30.93	0.37	0.00	17.83	37.68	4.54	8.29	1.06	0.00	0.00	0.00	0.00	0.91	0.00	101.60
HD02B - 2	0.38	30.48	0.87	0.00	14.51	34.56	4.95	11.22	1.62	1.21	0.00	0.00	0.00	3.87	0.00	103.66
HD02B - 3	0.00	30.14	0.64	0.00	13.22	34.32	4.55	12.47	2.11	1.43	0.00	0.00	0.00	3.54	0.00	102.42
HD02B - 4	0.00	30.41	0.74	0.00	13.82	34.31	4.27	12.59	2.18	1.68	0.00	0.00	0.00	3.11	0.00	103.13
HD02B - 5	0.54	31.50	0.57	0.00	16.09	35.89	4.23	9.53	0.00	0.00	0.00	0.00	0.00	3.12	0.00	101.46
HD02B - 6	0.54	31.29	0.81	0.00	15.65	35.01	3.80	9.06	1.19	1.10	0.00	0.00	0.00	3.92	0.00	102.37
HD10A - 1	0.00	30.74	1.11	0.00	13.72	34.24	4.52	11.73	1.75	1.26	0.00	0.00	0.00	4.55	0.00	103.63
HD10A - 2	0.49	30.93	0.76	0.00	14.22	34.08	3.27	10.37	1.69	2.46	0.00	1.31	0.00	3.29	0.94	103.80
HD10A - 3	0.57	31.37	0.69	0.00	14.13	34.29	4.04	10.90	1.58	1.89	0.00	0.00	0.00	2.90	0.00	102.36
HD10A - 4	0.52	31.42	0.59	0.00	14.59	35.42	4.45	11.63	2.05	1.73	0.00	1.29	0.00	2.55	0.00	106.23
HD10A - 5	0.00	29.68	0.85	0.00	13.26	32.81	4.54	11.68	1.82	1.05	0.00	0.00	0.00	4.17	0.73	100.58
HD10A - 6	0.42	28.98	0.87	0.00	13.35	32.91	5.54	11.55	1.92	1.07	0.00	0.00	0.00	3.73	0.00	100.34
HD10A - 7	0.00	30.28	0.92	0.00	13.47	33.22	4.09	11.59	1.72	1.34	0.00	0.00	0.00	4.12	0.72	101.47
HD10A - 8	0.47	30.89	0.72	0.00	14.32	34.65	5.31	11.19	1.89	1.50	0.00	0.93	0.00	3.08	0.00	104.93
HD10A - 9	0.46	29.90	0.86	0.00	13.69	33.76	4.82	11.89	2.00	1.99	0.00	0.00	0.00	3.73	0.00	103.09
HD10A - 10	0.00	30.32	0.98	0.00	14.09	34.49	5.21	12.19	1.61	1.14	0.00	0.00	0.00	3.74	0.00	103.76
HD10A - 11	0.47	30.20	0.84	0.00	13.82	33.24	4.30	10.66	1.83	1.44	0.00	0.97	0.00	3.80	0.72	102.29
HD10A - 12	0.00	29.72	0.86	0.00	13.49	33.22	4.55	11.27	1.40	1.02	0.00	0.00	0.00	3.70	0.00	99.25
HD10B - 1	0.45	32.19	1.07	0.00	13.86	33.22	4.76	11.35	1.72	1.43	0.00	0.00	0.00	3.49	0.74	104.28
HD10B - 2	0.56	30.95	0.79	0.00	14.07	33.39	3.96	11.14	1.88	1.33	0.00	0.00	0.00	3.22	0.00	101.28
HD10B - 3	0.72	31.45	0.56	0.00	14.38	34.55	4.90	11.57	1.92	1.86	0.00	0.00	0.00	1.69	0.96	104.55
HD10B - 4	0.00	32.44	0.90	0.00	13.25	33.15	4.35	11.28	1.41	1.30	0.00	0.00	0.00	2.82	0.77	101.68
HD10B - 5	0.00	31.01	0.97	0.00	14.47	33.84	5.03	11.54	1.85	0.00	0.00	0.00	0.00	4.19	0.00	102.89
HD10B - 6	0.50	30.83	0.92	0.00	13.79	34.38	5.19	12.20	1.81	1.25	0.00	0.00	0.00	3.34	0.00	104.22
HD10B - 7	0.41	32.07	1.28	0.00	13.79	33.08	4.29	10.88	1.62	1.28	0.00	0.00	0.00	4.31	0.00	103.01
HD14 - 1	0.00	30.04	0.82	0.00	13.40	34.22	4.35	13.17	1.96	1.53	0.00	0.00	0.00	3.48	0.00	102.98
HD14 - 2	0.68	29.06	0.91	0.00	12.27	31.85	3.60	12.45	1.68	1.93	0.00	0.00	0.00	3.41	0.00	97.85

HD14 - 3	0.50	30.59	0.61	0.00	12.71	33.19	4.01	12.81	2.22	2.43	0.00	0.00	0.00	2.53	0.69	102.28
HD14 - 4	1.07	29.76	0.59	0.00	12.62	32.95	4.42	12.95	1.80	1.91	0.00	0.00	0.00	2.63	0.00	100.71
HD14 - 5	0.42	30.18	0.72	0.00	13.29	33.62	4.49	13.38	2.48	2.29	0.00	0.00	0.00	2.67	0.70	104.23
HD14 - 6	0.89	30.41	0.71	0.00	12.77	32.84	3.96	13.14	2.35	2.19	0.00	0.00	0.00	2.68	0.00	101.95
HD14 - 7	0.63	29.69	0.77	0.00	13.25	33.77	4.13	13.11	1.80	1.65	0.00	0.00	0.00	3.42	0.00	102.22
HD14 - 8	3.12	28.18	0.74	0.00	12.31	32.38	3.59	12.34	0.00	1.09	0.00	0.00	0.00	3.66	0.00	97.41
HD14 - 9	10.78	26.57	1.26	0.00	12.02	30.02	3.70	10.48	1.37	1.26	0.00	0.00	0.00	2.58	0.00	100.03
HD14 - 10	0.84	29.88	0.60	0.00	12.47	33.10	4.46	13.13	2.39	2.38	0.00	1.26	0.00	2.59	0.00	103.12
HD14 - 11	2.76	28.57	0.73	0.00	12.40	30.71	3.31	11.44	1.73	1.94	0.00	0.90	0.00	3.09	0.00	97.58

1.3 Continued.

ThSiO ₄	(La-Sm)PO ₄	(Th, Ca, U, Pb)(PO ₄) ₂	Y(Gd-Lu)PO ₄	Sum
0.01	0.98	0.01	0.00	1.00
0.04	0.92	0.02	0.02	1.00
0.04	0.92	0.02	0.02	1.00
0.03	0.92	0.02	0.02	1.00
0.04	0.95	0.02	0.00	1.00
0.04	0.92	0.02	0.02	1.00
0.05	0.91	0.03	0.02	1.00
0.05	0.88	0.02	0.05	1.00
0.03	0.92	0.02	0.03	1.00
0.03	0.92	0.02	0.04	1.00
0.06	0.90	0.02	0.01	1.00
0.04	0.92	0.02	0.02	1.00
0.06	0.90	0.03	0.02	1.00
0.03	0.92	0.02	0.03	1.00
0.04	0.91	0.02	0.03	1.00
0.04	0.92	0.03	0.02	1.00
0.05	0.89	0.02	0.03	1.00
0.04	0.92	0.02	0.01	1.00
0.04	0.91	0.03	0.02	1.00
0.03	0.92	0.02	0.02	1.00
0.03	0.93	0.02	0.03	1.00
0.04	0.92	0.03	0.02	1.00
0.04	0.93	0.03	0.00	1.00
0.03	0.92	0.03	0.02	1.00
0.04	0.90	0.04	0.02	1.00
0.04	0.92	0.02	0.02	1.00

0.04	0.91	0.03	0.03	1.00
0.04	0.91	0.02	0.03	1.00
0.03	0.93	0.02	0.03	1.00
0.04	0.91	0.02	0.03	1.00
0.03	0.92	0.02	0.03	1.00
0.04	0.92	0.02	0.02	1.00
0.04	0.92	0.02	0.02	1.00
0.02	0.92	0.04	0.02	1.00
0.03	0.91	0.02	0.05	1.00
0.04	0.90	0.02	0.04	1.00

1.4 Apatite major element compositions

Sample	CaO	P2O5	Na2O	SiO2	FeO	F	Cl	O=F,Cl	Total
HD02B - 1	53.57	42.86	0.00	0.00	0.00	2.78	1.56	1.52	100.77
HD02B - 2	52.75	42.09	0.00	0.00	0.00	2.64	0.67	1.26	98.15
HD02B - 3	52.76	42.23	0.00	0.00	0.34	1.16	2.23	0.99	98.73
HD02B - 4	53.44	42.31	0.00	0.00	0.32	1.37	2.35	1.11	99.79
HD02B - 5	54.10	42.85	0.00	0.34	0.00	2.58	0.68	1.24	100.56
HD02B - 6	53.00	42.36	0.00	0.00	0.00	1.26	2.25	1.04	98.87
HD10A - 1	55.49	43.31	0.00	0.00	0.00	1.88	0.00	0.79	100.68
HD10A - 2	54.62	42.67	0.28	0.00	0.00	1.56	0.00	0.66	99.13
HD10A - 3	53.35	42.11	0.00	0.00	0.30	2.51	0.00	1.06	98.27
HD10A - 4	53.61	42.59	0.00	0.00	0.29	2.25	0.00	0.95	98.74
HD10A - 5	50.51	41.83	0.00	0.00	0.00	2.83	0.00	1.19	95.16
HD10A - 6	54.24	42.97	0.00	0.00	0.22	1.73	0.00	0.73	99.16
HD10A - 7	54.15	43.18	0.00	0.00	0.00	1.53	0.00	0.64	98.85
HD10A - 8	53.51	42.69	0.00	0.00	0.00	2.25	0.00	0.95	98.45
HD10A - 9	52.59	41.81	0.00	0.00	0.00	1.72	0.00	0.72	96.12
HD10B - 1	54.13	43.22	0.00	0.00	0.00	3.72	0.00	1.57	101.07
HD10B - 2	53.05	43.08	0.00	0.00	0.64	2.08	0.00	0.88	98.84
HD10B - 3	52.85	43.17	0.00	0.00	0.65	1.87	0.00	0.79	98.55
HD10B - 4	53.34	42.84	0.00	0.26	0.47	1.39	0.00	0.59	98.29
HD10B - 5	54.17	43.01	0.00	0.00	0.00	2.07	0.00	0.87	99.25
HD10B - 6	53.90	42.44	0.00	0.00	0.00	2.28	0.00	0.96	98.62
HD10B - 7	51.91	42.46	0.87	0.28	0.61	2.02	0.00	0.85	98.15
HD10B - 8	52.29	42.75	0.25	0.00	0.88	2.59	0.00	1.09	98.76
HD10B - 9	54.27	42.92	0.00	0.40	0.00	2.00	0.00	0.84	99.59
HD10B - 10	52.92	42.66	0.00	0.26	0.00	2.49	0.00	1.05	98.33
HD10B - 11	53.59	42.39	0.00	0.00	0.00	1.99	0.00	0.84	97.98
HD10B - 12	53.84	42.95	0.00	0.00	0.00	2.36	0.00	0.99	99.15

2.1 Table S1 – Garnet trace element compositions – HD02b

Garnet crystals	Identifier	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc	Mg	Mn	Area analysed	Comments
A1	A1-1	0.02	0.00	0.01	0.05	1.04	0.91	3.25	1.14	4.95	0.60	1.10	0.20	1.22	0.24	17	53	35101	3343	rim	positive Eu anomaly
	A1-2	0.01	0.01	0.00	0.23	1.80	1.80	3.15	0.84	3.04	0.35	0.61	0.09	0.57	0.07	10	32	33148	2530		
	A1-3	0.02	0.02	0.00	0.03	0.70	0.64	3.28	1.83	10.67	1.77	3.75	0.48	3.37	0.54	44	62	32131	3384		
	A1-4	0.00	0.01	0.00	0.07	0.77	1.04	4.70	2.18	11.82	1.55	2.29	0.26	1.51	0.17	43	50	34108	3158		
	A1-5	0.01	0.00	0.00	0.02	1.51	1.45	3.35	0.87	3.04	0.36	0.58	0.08	0.41	0.07	10	37	32024	2403		
	A1-6	0.01	0.00	0.00	0.03	0.19	0.07	1.99	1.94	33.06	13.28	52.69	9.59	72.25	11.91	235	218	38030	3844	core	negative Eu anomaly
	A1-7	0.01	0.01	0.01	0.08	0.25	0.05	2.04	2.28	33.10	14.46	55.00	9.84	78.35	14.14	263	197	37316	3702		
	A1-8	0.00	0.01	0.00	0.16	0.20	0.07	2.18	1.99	28.29	12.09	43.22	7.83	58.33	9.98	228	215	38613	4023		
	A1-9	0.00	0.00	0.00	0.02	0.22	0.07	2.41	2.37	33.98	12.50	36.98	6.18	45.81	6.68	245	215	38079	4235		
	A1-10	0.00	0.00	0.01	0.05	0.15	0.05	1.67	1.58	22.76	9.19	33.77	5.76	45.95	7.69	184	200	38221	3860		
A2	A2-1	0.14	0.42	0.06	0.30	0.41	0.20	1.73	0.89	7.08	1.65	6.13	1.58	19.05	3.97	47	95	34629	3132	small idioblastic garnet	negative Eu anomaly
	A2-2	0.01	0.00	0.00	0.07	0.20	0.06	1.07	0.66	4.69	0.82	2.11	0.41	3.16	0.56	29	105	34762	2808		positive Eu anomaly
	A2-3	0.01	0.05	0.01	0.10	0.60	0.51	2.31	0.79	3.89	0.70	1.95	0.39	3.77	0.63	25	66	30442	3172		
	A2-4	0.28	0.83	0.12	0.61	0.61	0.45	2.44	0.98	6.57	1.26	3.65	0.75	6.71	1.01	39	81	33008	2806		
	A2-5	0.03	0.09	0.01	0.09	0.23	0.07	1.29	1.05	12.43	3.91	12.45	2.31	17.55	2.96	107	103	33106	3248		negative Eu anomaly
A3	A3-1	0.39	0.76	0.15	0.74	0.40	0.13	1.34	0.66	3.13	0.41	0.57	0.07	0.48	0.07	11	69	33856	4396	core	negative Eu anomaly
	A3-2	0.00	0.00	0.00	0.05	0.23	0.07	1.26	0.70	3.57	0.49	0.96	0.13	0.80	0.10	16	79	33485	3900		
	A3-3	0.01	0.00	0.01	0.02	0.21	0.03	1.08	0.40	2.25	0.23	0.52	0.05	0.47	0.08	8	60	31550	3905		
	A3-4	0.01	0.02	0.01	0.11	0.90	0.88	2.70	0.65	2.83	0.55	1.64	0.30	2.52	0.43	13	85	33554	2811	rim	positive Eu anomaly
	A3-5	0.02	0.01	0.00	0.06	0.48	0.58	1.98	0.65	4.76	1.31	4.87	1.06	10.89	2.21	24	87	32350	2949		
	A3-6	0.01	0.02	0.00	0.06	0.75	0.27	5.80	2.24	13.26	2.23	5.14	0.68	4.92	0.68	59	156	36104	3570	core	negative Eu anomaly
	A3-7	0.00	0.00	0.00	0.13	0.84	0.27	6.68	2.79	18.37	3.50	9.13	1.46	11.94	1.99	74	162	35902	3517		
	A3-8	0.01	0.03	0.00	0.09	0.44	0.11	3.47	1.21	5.99	1.02	2.57	0.38	2.80	0.46	19	97	37229	3899		
	A3-9	0.01	0.01	0.01	0.12	0.36	0.16	4.12	1.49	8.92	1.75	4.39	0.70	6.16	1.32	32	139	33129	4005		

A4	A4-1	0.01	0.00	0.00	0.01	0.25	0.07	1.16	0.78	6.41	1.22	3.00	0.47	4.75	0.63	44	104	32494	3414	core	negative Eu anomaly
	A4-2	0.01	0.00	0.00	0.05	0.36	0.29	1.90	1.17	10.26	2.22	7.01	1.35	13.72	2.33	69	116	35095	3486		
	A4-3	0.02	0.00	0.01	0.06	0.32	0.11	2.67	1.63	15.33	3.36	9.04	1.52	11.98	1.92	82	120	33254	4468		
	A4-4	0.02	0.00	0.00	0.06	0.19	0.04	1.93	1.00	7.17	1.55	4.19	0.74	7.17	1.03	50	109	36121	3538		
	A4-5	0.03	0.05	0.01	0.01	0.25	0.07	1.70	1.17	12.64	3.39	11.26	1.87	15.90	2.68	94	108	35007	3593		
A5	A5-1	0.01	0.01	0.00	0.12	1.24	1.29	3.56	0.82	2.82	0.26	0.27	0.05	0.23	0.03	9	64	31083	2808	rim	positive Eu anomaly
	A5-2	0.02	0.01	0.00	0.25	1.79	1.68	4.27	0.77	2.40	0.23	0.37	0.04	0.18	0.02	7	60	31786	2956		
	A5-3	0.00	0.03	0.03	0.22	0.67	0.76	2.00	0.41	1.50	0.12	0.16	0.03	0.18	0.01	3	44	29674	2234		
	A5-4	0.00	0.01	0.01	0.20	1.29	1.31	3.94	0.49	1.35	0.09	0.11	0.00	0.04	0.01	3	35	31984	2573	core	negative Eu anomaly
	A5-5	0.01	0.00	0.01	0.02	0.23	0.07	1.82	1.37	15.25	4.17	10.67	1.30	8.89	1.14	103	85	35626	4523		
	A5-6	0.03	0.01	0.00	0.03	0.12	0.04	1.74	1.08	11.02	2.98	7.76	1.03	7.56	1.05	78	86	34470	4696		
	A5-7	0.01	0.01	0.01	0.07	0.16	0.03	1.47	1.01	11.08	2.56	6.17	0.87	5.91	0.81	64	85	32586	5112		
	A5-8	0.02	0.00	0.01	0.03	0.32	0.04	2.17	1.42	15.87	3.81	9.82	1.25	8.26	1.10	98	86	32737	5106		
A6	A6-1	0.00	0.01	0.00	0.07	0.30	0.09	2.13	1.28	14.30	3.33	8.80	1.10	7.38	1.02	89	86	35955	5441	core	negative Eu anomaly
	A6-2	0.01	0.01	0.00	0.03	0.34	0.08	3.16	1.58	11.43	2.02	4.04	0.58	4.36	0.68	57	83	35429	6894		
	A6-3	0.00	0.01	0.00	0.08	0.86	0.28	10.05	3.90	25.68	4.48	9.56	1.33	8.74	0.83	171	115	38822	9392		
	A6-4	0.00	0.01	0.01	0.06	1.04	0.32	13.40	5.14	34.07	5.72	11.02	1.34	8.51	0.96	147	122	40100	9784		

2.2 Table S1 – Garnet trace element compositions – HD10a

Garnet crystals	Identifier	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc	Mg	Mn	Area analysed	Comments
A1	A1-1	0.01	0.01	0.00	0.03	0.33	0.06	1.32	0.99	7.45	1.42	3.00	0.48	3.57	0.52	39	97	45259	4590	core	negative Eu anomaly
	A1-2	0.00	0.00	0.00	0.12	0.44	0.10	1.43	1.17	8.45	1.53	3.32	0.51	3.88	0.55	41	112	44013	4210		
	A1-3	0.01	0.02	0.00	0.10	0.33	0.08	1.23	0.91	6.55	1.17	2.31	0.37	2.49	0.38	32	98	43018	4168		
	A1-4	0.00	0.00	0.00	0.12	0.42	0.09	1.27	0.81	4.82	0.70	1.29	0.20	1.29	0.18	19	97	43301	4699		
	A1-5	0.01	0.01	0.01	0.19	0.59	0.12	1.41	0.96	4.87	0.63	1.35	0.16	0.97	0.13	18	94	44377	5909		
A2	A2-1	0.01	0.01	0.00	0.00	0.27	0.27	1.13	0.68	4.34	0.63	1.14	0.12	0.58	0.07	15	38	40692	2980	small idioblastic garnet	positive Eu anomaly
	A2-2	0.04	0.10	0.01	0.11	0.18	0.14	0.54	0.42	4.31	1.14	3.21	0.48	2.93	0.39	27	35	39996	2644		
A3	A3-1	0.05	0.15	0.02	0.13	0.17	0.12	0.51	0.56	8.23	3.36	14.16	3.40	31.82	6.13	67	63	40594	3303	small idioblastic garnet	positive Eu anomaly
A4	A4-1	0.01	0.00	0.00	0.02	0.25	0.22	1.40	0.99	8.31	2.21	5.90	0.83	4.94	0.73	49	86	47507	2903	small idioblastic garnet	positive Eu anomaly
	A4-2	0.01	0.01	0.01	0.07	0.39	0.31	1.27	0.76	5.51	1.04	2.11	0.29	1.43	0.22	26	50	44100	2637		
	A4-3	0.00	0.01	0.00	0.08	0.39	0.24	1.37	0.83	5.74	1.07	2.75	0.35	2.53	0.31	30	64	41613	3289		
A5	A5-1	0.01	0.02	0.00	0.06	0.46	0.09	1.77	1.83	26.25	9.58	28.81	4.54	31.28	4.68	216	165	43086	4685	core	negative Eu anomaly
	A5-2	0.01	0.02	0.00	0.01	0.19	0.10	0.90	1.00	14.86	5.94	24.71	4.98	44.68	7.48	134	123	43572	4283		
	A5-3	0.02	0.01	0.01	0.06	0.32	0.07	1.51	1.53	22.92	7.85	24.63	4.15	27.89	4.12	182	130	42982	5134		
A6	A6-1	0.00	0.02	0.00	0.09	0.26	0.39	0.85	0.57	4.50	0.93	2.28	0.32	2.13	0.27	22	112	39438	3809	small idioblastic garnet	positive Eu anomaly
	A6-2	0.01	0.00	0.00	0.09	0.21	0.20	0.44	0.44	4.06	1.08	3.05	0.54	4.46	0.58	26	94	40185	3679		
	A6-3	0.01	0.00	0.00	0.02	0.21	0.31	0.64	0.35	2.54	0.45	1.04	0.20	1.50	0.22	11	104	39528	3630		
	A6-4	0.01	0.01	0.00	0.08	0.23	0.28	0.68	0.35	2.40	0.49	1.09	0.14	0.99	0.14	13	71	40963	3367		
A7	A7-1	0.00	0.00	0.00	0.17	0.36	0.10	1.43	0.90	6.86	1.18	2.48	0.31	1.78	0.23	35	91	40470	4958	core	negative Eu anomaly
	A7-2	0.00	0.00	0.01	0.10	0.39	0.09	1.32	1.01	7.83	1.38	3.02	0.35	2.05	0.29	41	94	44056	5354		
	A7-3	0.00	0.00	0.00	0.18	0.41	0.11	1.86	1.15	9.04	1.54	3.00	0.39	2.46	0.29	42	94	39070	5474		
A8	A8-1	0.02	0.03	0.01	0.05	0.29	0.08	1.48	1.05	9.40	2.40	5.41	0.71	4.77	0.61	57	124	40857	5259	core	negative Eu anomaly
	A8-2	0.06	0.19	0.03	0.21	0.27	0.15	1.41	0.91	6.54	1.18	2.39	0.34	2.01	0.29	33	114	40056	4862		
A9/A10	A9/A10-1	0.01	0.03	0.01	0.01	0.37	0.29	0.92	0.30	2.00	0.29	0.71	0.08	0.41	0.06	9	22	39655	2745	rim	

	A9/A10-2	0.07	0.11	0.02	0.15	0.40	0.35	0.87	0.38	2.58	0.49	1.38	0.21	1.36	0.17	14	26	39725	2603		positive Eu anomaly
	A9/A10-3	0.00	0.03	0.00	0.10	0.27	0.24	0.82	0.40	2.31	0.31	0.64	0.07	0.58	0.06	9	57	41883	3849		
	A9/A10-4	0.01	0.00	0.01	0.07	0.30	0.09	1.49	0.89	5.96	0.93	1.80	0.22	1.60	0.23	26	116	43373	4335		
A10/A9	A9/A10-5	0.00	0.01	0.00	0.10	0.30	0.07	1.61	0.89	5.56	0.98	1.90	0.22	1.63	0.26	25	126	47390	4721	core	negative Eu anomaly
	A9/A10-6	0.00	0.01	0.00	0.06	0.42	0.07	1.75	1.01	7.39	1.22	2.55	0.32	2.09	0.30	31	126	44746	4615		
A11	A11-1	0.01	0.01	0.01	0.07	0.39	0.08	1.70	1.54	16.05	4.31	12.57	1.77	12.74	1.77	114	85	41866	4046	core	negative Eu anomaly
	A11-2	0.00	0.00	0.01	0.11	0.37	0.10	1.95	1.54	18.13	5.07	15.69	2.26	15.74	2.35	107	90	43568	4038		
	A11-3	0.02	0.01	0.00	0.13	0.42	0.09	2.04	1.38	16.61	4.45	12.32	1.81	12.51	1.95	118	89	44042	4481		

2.3 Table S1 – Garnet trace element compositions – HD10b

Garnet crystals	Identifier	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc	Mg	Mn	Area analysed	Comments
A1	A1-1	0.17	0.41	0.04	0.19	0.31	0.06	2.11	1.60	26.35	7.68	34.40	5.66	57.59	7.68	242	100	36202	2456	core	negative Eu anomaly
	A1-2	0.12	0.25	0.02	0.11	0.18	0.27	1.17	0.63	5.57	1.00	2.82	0.25	1.74	0.15	27	39	33248	2463	small idioblastic garnet	positive Eu anomaly
	A1-3	0.05	0.15	0.02	0.20	0.31	0.27	1.21	0.56	6.25	1.14	3.27	0.30	1.90	0.19	28	40	33296	2533		
	A1-4	0.20	0.40	0.05	0.15	0.28	0.05	2.34	1.43	16.34	3.44	11.01	1.21	9.09	0.84	105	80	34934	2894	core	negative Eu anomaly
	A1-5	0.12	0.36	0.04	0.28	0.35	0.06	2.40	1.32	15.79	3.67	15.38	2.25	19.23	2.43	100	105	35715	3622		
	A1-6	0.12	0.22	0.03	0.30	0.56	0.09	3.20	1.44	14.49	3.76	15.40	2.33	20.36	2.62	95	117	36497	3737		
A2	A2-1	0.16	0.33	0.02	0.31	0.31	0.06	2.18	0.98	8.87	1.51	4.04	0.46	3.74	0.36	47	71	35516	3767	core	negative Eu anomaly
	A2-2	0.27	0.56	0.06	0.42	0.42	0.13	2.20	1.00	11.25	2.45	7.74	0.85	6.48	0.74	61	77	32429	3337		
	A2-3	0.01	0.17	0.01	0.18	0.30	0.05	2.58	1.37	14.81	3.14	10.54	1.32	11.74	1.22	93	84	39392	3344		
A3	A3-1	0.18	0.39	0.04	0.30	0.61	0.14	2.41	0.99	10.47	2.27	8.42	1.12	8.59	1.05	62	68	34614	4126	core	negative Eu anomaly
	A3-2	0.17	0.36	0.05	0.29	0.33	0.09	2.58	1.00	10.45	2.14	6.95	0.82	6.70	0.73	55	51	34251	3966		
	A3-4	0.25	0.55	0.06	0.30	0.43	0.10	1.85	0.91	7.18	1.20	3.45	0.37	3.31	0.37	36	74	33252	3803		
	A3-5	0.19	0.36	0.04	0.31	0.41	0.08	2.08	0.89	8.25	1.32	3.86	0.42	3.55	0.44	36	81	36475	3713		
	A3-6	0.23	0.43	0.05	0.30	0.26	0.07	1.54	0.72	3.88	0.46	1.03	0.14	0.96	0.09	15	76	35738	3178		
	A3-7	0.15	0.33	0.03	0.09	0.42	0.07	1.72	0.85	8.56	1.55	5.62	1.01	10.73	1.21	66	62	37548	3285		
A4	A4-1	0.37	0.81	0.07	0.28	0.42	0.10	1.73	0.53	3.44	0.40	0.95	0.11	0.77	0.09	11	53	36553	3376	core	negative Eu anomaly
	A4-2	0.25	0.40	0.11	0.46	0.50	0.07	1.72	0.51	3.13	0.36	0.97	0.09	0.74	0.09	10	48	36933	3510		
	A4-3	0.23	0.46	0.04	0.21	0.52	0.08	1.49	0.49	3.30	0.44	0.92	0.10	0.90	0.11	12	49	37786	3390		

2.4 Table S2 – Monazite trace element compositions

Identifier	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Th	U	Th/U
HD02B - 1	143486	297000	34834	134768	24714	1086	14319	789	1485	76.47	64.19	2.99	16.27	0.70	1650	28531	6725	4.2
HD02B - 2	142780	297000	35699	140546	27252	1460	18676	1648	5372	595.73	779.39	47.81	152.75	8.80	10822	27247	4406	6.2
HD02B - 3	143469	297000	35175	137086	25819	1228	17258	1348	3844	373.34	463.82	28.06	90.33	5.42	7495	27533	5560	5.0
HD02B - 4	144528	297000	34839	134056	24436	1066	13887	773	1482	78.25	66.92	3.24	16.74	0.79	1696	25808	6600	3.9
HD02B - 5	146522	297000	34520	132259	23741	1110	13621	788	1641	86.97	68.60	3.04	14.45	0.59	1969	28183	6058	4.7
HD02B - 6	153999	297000	31810	107729	16150	2040	11078	1285	5502	665.28	1196.49	83.86	277.71	19.36	15563	16820	5628	3.0
HD02B - 7	146152	297000	34516	132132	23678	1093	13122	671	1073	44.77	33.02	1.47	10.87	0.34	1027	25355	6152	4.1
HD02B - 8	146021	297000	34760	132495	23875	1050	13276	706	1186	55.15	43.67	2.09	12.75	0.51	1231	26385	6811	3.9
HD02B - 9	154818	297000	32697	117992	17890	1151	10097	645	1556	113.50	118.99	5.95	19.86	1.27	2343	9400	5578	1.7
HD02B - 10	152768	297000	33057	119405	18657	1163	10447	657	1537	108.36	111.42	5.35	18.00	0.88	2287	13475	5179	2.6
HD02B - 11	168561	297000	31146	106707	17591	1959	13611	1586	6464	720.23	1162.61	72.86	216.72	13.41	15857	3172	3480	0.9
HD02B - 12	147625	297000	34109	129119	23110	1032	13045	713	1307	64.52	53.95	2.59	14.13	0.63	1434	25675	6902	3.7
HD02B - 13	146732	297000	34571	132712	23577	1046	13427	753	1476	77.47	65.62	3.10	16.27	0.75	1724	28715	6484	4.4
HD02B - 14	142967	297000	34878	135101	24947	1219	15717	1077	2771	177.70	173.25	8.88	33.92	1.83	3791	23254	5199	4.5
HD10a - 1	148615	289000	32423	119434	20267	1116	12679	926	2731	227.40	261.98	13.89	43.11	2.59	5126	31983	4112	7.8
HD10a - 2	145907	289000	33025	124636	21975	1145	14288	1093	3257	289.34	310.49	15.44	41.79	2.45	6420	28606	6749	4.2
HD10a - 3	145710	289000	33167	125323	21835	1062	11977	594	942	41.50	29.15	1.22	9.32	0.16	954	32462	6908	4.7
HD10a - 4	145405	289000	33677	128726	23925	1283	16837	1552	5096	514.99	541.36	25.83	64.66	3.71	10902	20937	7183	2.9
HD10a - 5	144494	289000	33071	125664	22633	1156	16026	1486	5096	599.56	784.19	43.02	123.25	8.41	13472	35570	5046	7.0
HD10a - 6	148366	289000	32415	118777	20268	1104	11356	640	1100	45.80	30.09	1.21	8.72	0.27	1069	25470	6154	4.1
HD10a - 7	143873	289000	33011	124148	21822	1149	12015	647	1206	68.19	59.33	2.89	13.63	0.59	1521	25106	7359	3.4
HD10a - 8	147930	289000	32307	119872	20063	1240	11823	923	2745	175.97	151.92	6.86	21.19	1.18	4682	13821	5911	2.3
HD10a - 9	146911	289000	32382	120459	20979	1116	14931	1352	4423	445.50	469.71	22.55	57.88	3.28	10158	17793	7523	2.4
HD10a - 10	144135	289000	33161	125176	21673	1085	12023	616	1038	43.81	30.07	1.23	9.32	0.26	1042	28662	6813	4.2
HD10a - 11	147059	289000	32700	121763	20968	1121	11506	629	1218	68.34	64.47	3.62	16.87	0.89	1643	27040	6603	4.1
HD10a - 12	146285	289000	32806	122534	21096	1081	11347	614	1180	73.14	67.65	3.22	13.42	0.55	1593	27934	6514	4.3
HD10a - 13	146210	289000	32683	121557	20329	970	11568	679	1246	55.18	40.34	1.76	9.88	0.33	1412	35482	6822	5.2

HD10a - 14	141404	289000	33381	127203	22321	1150	12003	596	846	35.97	27.49	1.33	9.32	0.32	821	34281	6811	5.0
HD14 - 1	133327	278000	32750	127249	22642	2077	14803	1234	3826	376.10	422.58	21.85	68.17	4.49	8127	30569	5321	5.7
HD14 - 2	136105	278000	32638	125467	24775	4753	19901	1670	3417	159.13	95.75	3.47	18.01	0.48	4006	18584	7048	2.6
HD14 - 3	135355	278000	32652	125390	22921	1931	15174	1037	2224	101.26	61.96	2.15	11.32	0.28	2336	27529	4201	6.6
HD14 - 4	133562	278000	33198	131144	21924	1524	10292	524	966	58.50	54.61	2.71	12.15	0.56	1237	32621	806	40.5
HD14 - 5	132882	278000	32900	128773	22791	1823	14148	1116	3385	324.41	365.15	18.53	56.40	3.62	7073	34195	4274	8.0
HD14 - 6	137384	278000	32805	127103	25396	4313	20049	1825	4257	251.43	191.17	8.39	28.65	1.33	5972	11488	6432	1.8
HD14 - 7	132568	278000	33244	130022	24737	1916	16861	1379	3927	351.87	338.36	14.88	42.88	2.25	7561	30931	5057	6.1
HD14 - 8	133526	278000	32568	126746	23101	1624	14442	1097	3231	265.54	263.47	12.58	37.37	2.03	5804	38219	3322	11.5
HD14 - 9	133275	278000	32907	128223	23875	1802	16130	1378	4234	405.55	417.77	19.38	53.87	3.17	8892	39458	5728	6.9
HD14 - 10	134269	278000	33110	128536	24420	4294	16387	1083	2070	91.94	66.37	2.77	14.21	0.47	2229	8864	4195	2.1
HD14 - 11	133872	278000	32917	129004	23553	2102	15925	1470	5511	658.49	1002.09	59.15	170.79	12.46	15345	35853	7933	4.5
HD14 - 12	133540	278000	33324	132141	25032	1980	17751	1561	5379	610.28	861.88	50.25	156.28	11.85	13549	31180	7494	4.2
HD14 - 13	135113	278000	32658	126890	24282	2780	17215	1463	3945	330.93	338.46	16.26	52.21	3.21	7478	19361	6438	3.0
HD14 - 14	134457	278000	33225	131408	21698	1476	10528	604	1457	109.91	119.00	6.36	22.39	1.38	2272	30612	758	40.4

2.5 Table S3 – Apatite trace element compositions

Sample	Identifier	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Pb	Th	U	Mn	Sr	Y	Th/U	Comments
HD02b (in situ)	AP1-1	377	1215	148	595	156	43	135	8	10	1	2	0	1	0	17	3	27	261	479	17	0.1	REE-enriched apatite
	AP1-2	356	1121	143	613	169	44	134	8	11	1	2	0	1	0	17	2	23	240	471	17	0.1	
	AP1-3	381	1232	164	665	181	48	150	9	12	1	2	0	1	0	18	3	23	244	461	16	0.1	
	AP1-4	550	1686	233	897	231	66	192	11	14	1	3	0	1	0	28	5	34	286	747	19	0.1	
	AP2-1	1403	3059	363	1470	348	55	330	32	89	9	18	1	7	1	30	3	30	355	537	222	0.1	
	AP2-2	153	629	96	479	176	39	182	23	68	7	12	1	6	1	15	0	19	279	389	163	0.0	
	AP2-3	234	860	141	678	235	47	231	27	72	8	13	1	6	1	18	0	27	292	458	167	0.0	
	AP2-4	214	804	128	623	225	44	221	26	74	8	13	1	6	1	18	0	26	309	514	194	0.0	
	AP3-1	347	1112	162	709	227	47	218	22	49	4	6	0	1	0	19	4	20	262	503	81	0.2	
	AP3-2	363	1118	149	679	214	42	191	20	42	4	5	0	1	0	18	4	32	287	521	92	0.1	
	AP3-3	297	969	132	620	193	38	176	18	41	3	5	0	1	0	15	1	18	276	495	84	0.1	
	AP3-4	290	1040	145	640	217	45	195	21	49	4	7	0	2	0	20	3	27	273	577	106	0.1	
	AP3-5	261	857	120	521	178	40	170	18	44	4	6	0	1	0	17	2	21	236	477	92	0.1	
HD02b (mount)	AP4-1	195	545	89	513	208	42	161	20	55	6	10	1	8	1	15	1	25	222	367	145	0.1	REE-enriched apatite
	AP4-2	201	704	108	536	199	45	165	19	55	5	10	1	7	1	15	1	31	226	405	124	0.0	
	AP5-1	128	262	64	409	192	37	284	45	145	14	21	2	9	1	10	13	25	110	321	429	0.5	
	AP6-1	171	470	85	542	225	33	249	35	91	7	7	0	5	0	14	2	25	253	377	183	0.1	
	AP6-2	183	477	87	559	227	32	236	32	79	6	7	0	4	0	15	2	20	275	398	162	0.1	
	AP7-1	80	313	49	377	182	27	216	28	114	8	14	1	11	1	7	2	18	435	474	342	0.1	
	AP8-1	265	712	117	636	219	43	156	14	32	3	6	0	6	1	14	2	28	496	383	69	0.1	
	AP8-2	246	632	103	576	209	39	160	16	34	3	6	1	5	1	10	1	22	449	358	80	0.0	
	AP8-3	359	980	144	690	214	46	147	12	23	2	6	1	3	1	18	7	26	258	431	45	0.3	
HD10a (in situ)	AP1-1	30	55	6	21	8	1	8	1	5	1	3	0	2	0	31	16	4	361	189	29	4.22	REE-depleted apatite
	AP2-1	21	42	5	22	5	1	4	1	3	1	3	0	3	1	43	15	4	313	186	21	4.28	REE-depleted apatite
	AP2-2	33	53	7	18	9	1	7	1	6	1	4	0	2	1	59	17	4	436	343	29	3.78	
	AP2-3	37	61	7	27	8	1	9	1	6	1	4	1	3	1	49	16	7	493	280	37	2.44	

	AP3-1	34	93	17	106	64	9	92	19	95	15	26	2	12	1	62	17	16	422	274	304	1.10	REE-enriched apatite
	AP3-2	24	100	23	166	105	12	115	32	155	24	40	4	15	1	25	7	20	278	241	470	0.32	
	AP3-3	31	68	6	30	8	1	9	1	9	1	4	0	2	0	33	14	5	384	183	37	2.80	REE-depleted apatite
	AP4-1	37	222	55	339	192	26	202	55	293	50	99	11	51	5	5	0	26	179	301	975	0.00	
	AP4-2	51	208	39	250	128	16	134	36	189	29	60	5	28	3	46	12	25	325	311	546	0.49	REE-enriched apatite
	AP4-3	50	88	8	31	11	1	8	1	11	1	5	0	2	1	56	14	8	510	305	40	1.70	
HD10a (mount)	AP5-1	19	98	26	207	113	19	148	35	196	31	61	5	22	2	3	0.0	17	151	155	648	0.00	REE-enriched apatite
	AP5-2	25	116	29	226	120	19	158	36	200	31	58	5	25	3	4	0.1	19	124	167	678	0.00	
	AP5-3	17	96	24	174	100	17	134	31	174	29	51	5	23	2	6	0.1	16	165	183	624	0.01	
	AP6-1	21	131	34	270	167	15	223	42	199	31	58	6	31	4	4	0.0	30	159	213	636	0.00	
	AP6-2	17	111	30	235	157	15	213	41	209	34	71	7	36	4	4	0.0	28	186	209	690	0.00	
	AP7-1	18	115	31	231	148	19	198	38	175	24	45	4	23	3	5	<b.d.l	40	164	189	554	0.00	
	AP7-2	23	102	29	270	186	19	267	50	210	29	52	5	30	4	4	<b.d.l	34	167	235	719	0.00	
	AP7-3	43	169	40	308	174	22	231	40	180	24	38	4	20	2	3	0.1	32	148	207	612	0.00	
	AP8-1	21	108	31	278	185	21	277	56	243	36	64	6	32	3	8	0.1	28	153	270	1018	0.00	
	AP8-2	36	149	36	292	173	18	227	45	200	26	48	5	21	2	2	0.1	27	149	193	656	0.00	
HD10b (in situ)	AP1-1	40	226	36	261	119	29	178	39	248	31	57	4	15	1	5	0.2	16	111	302	685	0.02	REE-enriched apatite
	AP1-2	36	221	30	199	100	25	150	32	185	23	41	2	11	1	6	0.3	17	98	230	530	0.02	
	AP2-1	70	266	41	267	125	24	165	33	206	21	35	2	6	0	6	0.5	25	122	276	527	0.02	REE-enriched apatite
	AP2-2	43	253	37	240	124	23	167	35	196	22	35	2	6	0	5	0.0	24	127	280	484	0.00	
	AP3-1	22	183	37	287	178	20	212	42	240	26	53	4	20	2	5	0.8	33	175	308	567	0.03	REE-enriched apatite
	AP3-2	21	191	37	285	170	20	215	45	249	28	57	4	22	2	6	0.0	36	197	283	558	0.00	
	AP3-3	25	208	41	314	185	20	214	46	259	28	59	4	21	2	6	0.1	36	176	282	581	0.00	
	AP3-4	68	329	60	387	199	19	224	44	252	27	56	4	20	2	5	0.4	36	194	297	599	0.01	
	AP3-5	22	189	37	290	172	20	217	45	249	27	53	4	19	2	5	0.0	33	213	304	596	0.00	
	AP3-6	23	186	37	281	166	18	203	42	237	25	52	4	20	2	5	0.0	32	183	287	571	0.00	
	AP4-1	28	59	5	25	7	1	5	1	6	1	3	0	2	0	45	15	5	433	215	35	3.02	REE-depleted apatite
	AP4-2	28	60	6	28	6	1	6	1	7	1	3	0	3	0	38	14	12	364	201	26	1.20	

	AP4-3	28	56	5	28	7	1	7	0	5	1	2	1	3	0	39	16	4	404	195	25	4.44	
	AP4-4	28	57	6	28	8	1	4	1	6	1	4	0	3	1	42	17	5	409	204	27	3.48	
	AP4-5	26	50	5	23	7	1	3	1	5	1	3	0	3	0	32	14	3	381	182	23	4.52	
	AP4-6	27	59	6	30	6	1	4	0	3	1	3	0	2	0	36	14	4	385	194	23	3.90	
	AP5-1	27	57	6	25	6	1	8	0	6	1	3	0	4	0	44	16	5	444	193	23	3.44	REE-depleted apatite
	AP5-2	28	59	5	27	6	1	5	0	3	1	2	0	2	0	38	27	4	418	194	21	6.87	
	AP6-1	39	318	65	502	257	18	223	27	106	13	28	2	17	1	10	0.7	86	2444	330	299	0.01	REE-enriched apatite
	AP7-1	22	47	5	24	5	1	3	1	2	1	2	0	2	0	34	13	3	330	154	17	4.12	REE-depleted apatite
	AP7-2	32	64	6	33	5	1	5	1	4	1	3	0	2	1	39	16	4	383	182	22	4.08	
	AP8-1	47	451	89	591	261	26	248	36	169	17	32	2	12	1	9	0.7	96	1518	323	485	0.01	REE-enriched apatite
	AP8-2	39	372	76	525	253	23	255	37	160	17	32	2	11	1	9	0.4	76	659	292	464	0.00	
	AP9-1	35	67	8	38	9	1	6	1	5	1	1	1	3	0	46	14	4	343	168	21	3.65	REE-depleted apatite
	AP9-2	28	50	5	27	5	1	4	1	4	1	2	0	3	1	37	14	3	317	156	21	4.10	
	AP9-3	25	46	5	17	3	1	3	0	5	1	3	1	3	1	37	14	3	323	160	21	4.56	
HD10b (mount)	AP10-1	19	123	33	245	169	16	212	37	169	25	53	6	26	3	3	0	45	153	249	642	0.00	
	AP10-2	22	116	32	276	203	17	263	45	203	34	70	7	35	4	3	0	48	114	250	799	0.00	
	AP10-3	20	129	34	270	165	16	216	37	166	25	53	5	28	3	5	0	49	142	231	605	0.01	
	AP11-1	17	164	43	324	201	16	239	32	101	10	19	2	20	2	6	0	64	319	263	278	0.00	
	AP11-2	17	147	40	319	207	16	243	32	93	10	19	2	20	2	5	0	64	310	231	267	0.00	
	AP11-3	17	132	38	309	203	14	240	32	97	11	20	2	18	2	5	<b.d.l	61	299	235	288	0.00	REE-enriched apatite
	AP11-4	16	151	41	301	197	15	224	32	97	11	19	3	18	2	6	0	64	309	253	254	0.00	
	AP12-1	35	154	32	234	166	14	227	38	154	21	40	4	27	2	4	0	31	159	199	525	0.01	
	AP12-2	11	87	21	191	146	12	204	33	140	18	35	4	21	2	4	0	33	153	212	516	0.00	
	AP13-1	17	134	37	298	201	17	256	38	145	19	38	4	31	3	5	<b.d.l	60	115	223	528	0.00	
	AP13-2	20	119	35	321	227	20	310	46	183	27	49	7	39	5	7	0	53	170	222	637	0.00	
	AP13-3	16	122	34	254	174	17	229	35	128	17	32	4	26	3	4	0	52	128	206	461	0.00	

Note: <b.d.l = below detection limit

3.1 Table S4 – U-Pb data for monazite samples

PRIMARY REFERENCE MATERIAL

Vermilion monazite	U (ppm)	Th (ppm)	Th/U	²⁰⁷ Pb(cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s (abs)	²⁰⁷ Pb/ ²³⁵ U	2s (abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s (abs)
VERM-1	693	57101	82.4	41363	0.1813	1.0840	12.8943	1.4132	0.5158	0.9066	0.64	2681	20	2672	16	2665	18
VERM-2	627	54457	86.9	37270	0.1812	1.0714	12.8745	1.3464	0.5154	0.8154	0.61	2680	18	2671	15	2664	18
VERM-3	718	57350	79.9	42473	0.1815	1.0763	12.8140	1.4287	0.5119	0.9397	0.66	2665	21	2666	16	2667	18
VERM-4	456	41587	91.2	27094	0.1820	1.1462	12.9379	1.5161	0.5157	0.9924	0.65	2681	22	2675	17	2671	19
VERM-5	656	54247	82.7	38531	0.1803	1.2029	12.7731	1.4632	0.5139	0.8331	0.57	2673	18	2663	16	2655	20
VERM-6	597	50646	84.9	35359	0.1833	1.2025	12.9550	1.4710	0.5126	0.8473	0.58	2668	19	2676	16	2683	20
VERM-7	521	45661	87.7	30437	0.1811	1.0949	12.7915	1.4348	0.5124	0.9274	0.65	2667	20	2664	16	2663	18
VERM-8	589	50111	85.1	34352	0.1810	0.8878	12.8300	1.2108	0.5142	0.8233	0.68	2674	18	2667	14	2662	15
VERM-9	606	49864	82.3	35437	0.1813	1.1670	12.8760	1.4573	0.5152	0.8729	0.60	2679	19	2671	16	2665	19
VERM-10	606	50693	83.6	35343	0.1818	0.9727	12.9254	1.2913	0.5158	0.8494	0.66	2681	19	2674	15	2669	16
VERM-11	633	51622	81.6	36459	0.1815	1.1807	12.7801	1.4360	0.5106	0.8173	0.57	2659	18	2664	16	2667	20
VERM-12	471	42360	90.0	27389	0.1832	1.2813	12.9865	1.5585	0.5142	0.8872	0.57	2675	19	2679	17	2682	21
VERM-13	498	44171	88.7	28477	0.1807	1.0997	12.7502	1.4070	0.5118	0.8778	0.62	2664	19	2661	16	2659	18

SECONDARY REFERENCE MATERIAL

Thompson Mine monazite	U(ppm)	Th(ppm)	Th/U	²⁰⁷ Pb(cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s (abs)	²⁰⁷ Pb/ ²³⁵ U	2s (abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s (abs)
TM-1	2732	109479	40.1	62108	0.1078	0.9970	4.6874	1.5294	0.3154	1.1598	0.76	1767	18	1765	14	1763	18
TM-2	3234	129433	40.0	73278	0.1076	1.2095	4.6765	1.8590	0.3152	1.4118	0.76	1766	22	1763	17	1759	22
TM-3	776	59376	76.5	17872	0.1091	2.3563	4.7567	4.3676	0.3163	3.6775	0.84	1772	57	1777	39	1784	44
TM-4	3568	149197	41.8	80475	0.1068	1.3863	4.6614	2.6660	0.3166	2.2772	0.85	1773	35	1760	24	1745	26
TM-5	3061	140997	46.1	68457	0.1064	1.8682	4.6245	4.0256	0.3153	3.5658	0.89	1767	55	1754	36	1738	35
Steenkam- pskraal monazite	U(ppm)	Th(ppm)	Th / U	²⁰⁷ Pb(cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s (abs)	²⁰⁷ Pb/ ²³⁵ U	2s (abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s (abs)
STK-1	1578	72992	46.3	13595	0.0738	1.1373	1.7747	1.6802	0.1745	1.2368	0.74	1037	12	1036	12	1035	23

STK-2	1684	79353	47.1	14510	0.0738	1.3252	1.7759	2.0347	0.1745	1.5439	0.76	1037	15	1037	14	1036	27
STK-3	1472	68142	46.3	12375	0.0739	1.2160	1.7774	1.9618	0.1744	1.5395	0.78	1036	15	1037	14	1039	25
STK-4	1357	63024	46.4	11306	0.0736	0.9963	1.7621	1.5247	0.1737	1.1541	0.76	1032	11	1032	11	1030	20
STK-5	1124	52063	46.3	9457	0.0740	0.9817	1.7821	1.6458	0.1746	1.3209	0.80	1037	13	1039	12	1042	20
STK-6	1337	62292	46.6	11251	0.0741	0.9749	1.7824	1.7344	0.1745	1.4345	0.83	1037	14	1039	12	1043	20
STK-7	1451	68484	47.2	12289	0.0747	1.0774	1.7949	1.8366	0.1743	1.4873	0.81	1036	14	1044	13	1060	22

SAMPLES

HD02b monazite	U (ppm)	Th (ppm)	Th/U	²⁰⁷ Pb(cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s (abs)	²⁰⁷ Pb/ ²³⁵ U	2s (abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s (abs)
HD02b-1	2008	11814	5.9	124477	0.1855	2.2434	12.8350	2.9150	0.5017	1.8612	0.64	2621	40	2668	30	2703	38
HD02b-2	2053	12174	5.9	127080	0.1853	1.8349	12.8261	2.9422	0.5020	2.3000	0.78	2622	50	2667	31	2701	31
HD02b-3	2055	12472	6.1	128133	0.1859	1.7487	12.9212	2.2434	0.5040	1.4053	0.63	2631	30	2674	24	2707	29
HD02b-4	2487	15092	6.1	161145	0.1875	1.0584	13.4351	1.7331	0.5197	1.3723	0.79	2698	30	2711	19	2720	18
HD02b-5	3389	17229	5.1	215655	0.1869	1.1156	13.2010	2.8020	0.5122	2.5703	0.92	2666	56	2694	29	2715	19
HD02b-6	2966	20270	6.8	187330	0.1863	1.0968	13.1087	2.7087	0.5103	2.4767	0.91	2658	54	2688	28	2710	18
HD02b-7	2574	15262	5.9	159853	0.1852	1.1507	12.8893	1.4541	0.5046	0.8890	0.61	2634	19	2672	16	2700	19
HD02b-8	2273	16870	7.4	142122	0.1861	0.8230	12.9898	1.1974	0.5064	0.8697	0.73	2641	19	2679	14	2708	14
HD02b-9	2240	17651	7.9	141119	0.1858	0.8600	13.1021	1.3753	0.5115	1.0732	0.78	2663	23	2687	15	2705	14
HD02b-10	3077	20989	6.8	191272	0.1854	1.0812	12.9372	1.5139	0.5061	1.0597	0.70	2640	23	2675	17	2702	18
HD02b-11	2770	15492	5.6	175089	0.1863	1.3708	13.1613	1.8565	0.5124	1.2520	0.67	2667	27	2691	20	2710	23
HD02b-12	2930	15809	5.4	184422	0.1862	1.5377	13.1106	1.8577	0.5106	1.0424	0.56	2659	23	2688	20	2709	26
HD02b-13	3318	17021	5.1	211201	0.1867	1.0759	13.2682	1.6126	0.5155	1.2013	0.74	2680	26	2699	18	2713	18
HD02b-14	2378	15742	6.6	147630	0.1856	0.8713	12.9527	1.2121	0.5062	0.8427	0.70	2640	18	2676	14	2704	14
HD02b-15	2740	14968	5.5	168896	0.1854	2.3112	12.8627	2.5029	0.5031	0.9607	0.38	2627	21	2670	26	2702	39
HD02b-16	3590	22533	6.3	218624	0.1849	1.5003	12.7182	1.7506	0.4990	0.9020	0.52	2609	19	2659	19	2697	25
HD02b-17	3218	19028	5.9	197536	0.1851	0.8918	12.8475	1.2857	0.5033	0.9262	0.72	2628	20	2669	15	2699	15
HD02b-18	2752	17472	6.3	170256	0.1855	1.2417	12.9596	1.5298	0.5068	0.8936	0.58	2643	19	2677	17	2702	21
HD02b-19	2863	16483	5.8	176127	0.1854	0.9448	12.8945	1.3332	0.5043	0.9406	0.71	2632	20	2672	15	2702	16
HD02b-20	2783	18005	6.5	170383	0.1856	0.9585	12.8449	1.2994	0.5019	0.8774	0.68	2622	19	2668	15	2704	16

HD02b-21	2636	16162	6.1	161605	0.1856	0.8594	12.8688	1.2397	0.5028	0.8934	0.72	2626	19	2670	14	2704	14
HD02b-22	1964	5686	2.9	123079	0.1860	1.2069	13.1674	1.7161	0.5135	1.2200	0.71	2671	27	2692	19	2707	20
HD02b-23	1536	7263	4.7	97974	0.1880	1.4043	13.4142	1.7474	0.5175	1.0398	0.60	2689	23	2709	19	2725	23
HD02b-24	1935	5146	2.7	122911	0.1870	1.2541	13.3643	1.6784	0.5182	1.1155	0.66	2692	25	2706	18	2716	21
HD02b-25	2988	19504	6.5	186440	0.1865	0.8702	13.1599	1.1931	0.5118	0.8163	0.68	2664	18	2691	14	2711	14
HD02b-26	2993	17846	6.0	185886	0.1865	0.9594	13.1093	1.4489	0.5099	1.0858	0.75	2656	24	2688	16	2711	16
HD02b-27	2741	18532	6.8	170915	0.1865	1.0773	13.1742	1.4189	0.5123	0.9234	0.65	2666	20	2692	16	2712	18

3.2 Table S5 – U-Pb data for monazite samples

PRIMARY REFERENCE MATERIAL

Vermilion monazite	U (ppm)	Th (ppm)	Th / U	²⁰⁷ Pb (cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s (%)	²⁰⁷ Pb/ ²³⁵ U	2s (%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s (abs)	²⁰⁷ Pb/ ²³⁵ U	2s (abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s (abs)
VERM-1	614	53545	87.2	28924	0.1811	2.7435	12.8617	3.2157	0.5151	1.6776	0.52	2678	37	2670	33	2663	46
VERM-2	526	50265	95.5	24455	0.1811	0.7541	12.6967	1.7811	0.5085	1.6135	0.91	2650	35	2657	19	2663	13
VERM-3	625	54222	86.8	29435	0.1817	0.8344	12.8852	1.9199	0.5143	1.7291	0.90	2675	38	2671	21	2669	14
VERM-4	523	49607	94.9	24442	0.1812	0.8354	12.7834	2.1297	0.5117	1.9590	0.92	2664	43	2664	23	2664	14
VERM-5	525	50069	95.3	24464	0.1811	0.7434	12.7209	1.8305	0.5095	1.6727	0.91	2655	37	2659	20	2663	12
VERM-6	779	56104	72.1	36554	0.1814	0.7422	12.8356	1.8904	0.5131	1.7387	0.92	2670	38	2668	20	2666	12
VERM-7	555	50003	90.1	26509	0.1825	1.6656	13.0920	2.8807	0.5202	2.3504	0.82	2700	52	2686	30	2676	28
VERM-8	637	53654	84.2	30805	0.1826	1.1986	13.2488	2.9156	0.5261	2.6578	0.91	2725	59	2698	30	2677	20
VERM-9	637	52874	83.0	30464	0.1822	0.7607	13.0924	1.9276	0.5212	1.7712	0.92	2704	39	2686	21	2673	13
VERM-10	706	53577	75.8	33049	0.1817	0.6801	12.8278	1.7580	0.5120	1.6211	0.92	2665	35	2667	19	2669	11
VERM-11	536	48450	90.4	24813	0.1818	0.9328	12.7033	1.9191	0.5068	1.6772	0.87	2643	36	2658	21	2669	16
VERM-12	489	46769	95.6	22578	0.1812	0.8123	12.6887	2.0299	0.5079	1.8603	0.92	2648	41	2657	22	2664	14
VERM-13	594	47957	80.8	25634	0.1817	2.0654	11.8877	3.7617	0.4744	3.1440	0.84	2503	66	2596	38	2669	35
VERM-14	683	53069	77.7	31832	0.1807	0.8105	12.8290	2.1618	0.5150	2.0041	0.93	2678	44	2667	23	2659	13
VERM-15	596	49392	82.9	29381	0.1825	0.9564	13.5942	2.4327	0.5402	2.2368	0.92	2784	51	2722	26	2676	16
VERM-16	636	49345	77.6	30499	0.1806	0.6612	13.2126	2.0014	0.5305	1.8890	0.94	2744	42	2695	22	2659	11
VERM-17	640	49875	77.9	30168	0.1809	0.8023	13.0082	1.7809	0.5215	1.5900	0.89	2706	35	2680	19	2661	13
VERM-18	721	53651	74.4	32382	0.1807	0.7911	12.4030	2.3958	0.4978	2.2614	0.94	2604	49	2635	25	2659	13
VERM-19	509	46270	91.0	23423	0.1818	0.7277	12.7325	1.6722	0.5079	1.5055	0.90	2648	33	2660	18	2670	12
VERM-20	470	45262	96.3	21545	0.1814	0.7560	12.6407	1.9522	0.5055	1.7999	0.92	2637	39	2653	21	2665	13
VERM-21	581	49793	85.7	27247	0.1812	0.8332	12.9528	1.6669	0.5184	1.4437	0.87	2693	32	2676	18	2664	14
VERM-22	633	49275	77.9	30171	0.1805	0.7586	13.1968	2.2743	0.5301	2.1440	0.94	2742	48	2694	24	2658	13
VERM-23	509	45572	89.6	23589	0.1827	0.9212	12.8623	1.8874	0.5107	1.6473	0.87	2660	36	2670	20	2677	15
VERM-24	437	41158	94.3	20076	0.1823	0.9107	12.7301	1.8503	0.5066	1.6107	0.87	2642	35	2660	20	2674	15

SECONDARY REFERENCE MATERIAL

Steenkamps kraal monazite	U (ppm)	Th (ppm)	Th/U	²⁰⁷ Pb (cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s (%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s (%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s (abs)	²⁰⁷ Pb/ ²³⁵ U	2s (abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s (abs)
STK-1	1361	60020	44.1	8228	0.0731	1.3646	1.7503	1.9290	0.1737	1.3634	0.71	1033	13	1027	13	1016	28
STK-2	1792	78238	43.7	10997	0.0742	1.1994	1.7771	1.7190	0.1736	1.2315	0.72	1032	12	1037	12	1048	24
STK-3	1478	64699	43.8	9115	0.0745	1.2731	1.7858	1.7943	0.1739	1.2645	0.70	1034	12	1040	13	1054	26
STK-4	1935	83205	43.0	11874	0.0743	1.7869	1.7769	2.1933	0.1734	1.2718	0.58	1031	12	1037	15	1050	36
STK-5	1630	73939	45.4	10019	0.0746	1.8807	1.7794	2.2596	0.1729	1.2524	0.55	1028	12	1038	16	1058	38
STK-6	1493	65474	43.8	9135	0.0737	1.2620	1.7723	1.8074	0.1745	1.2939	0.72	1037	12	1035	13	1032	26
STK-7	1421	61914	43.6	8642	0.0737	1.2887	1.7616	1.8451	0.1734	1.3205	0.72	1031	13	1031	13	1033	26
STK-8	1705	74694	43.8	10478	0.0743	1.0889	1.7801	1.5901	0.1739	1.1588	0.73	1033	11	1038	11	1048	22
STK-9	1655	72889	44.0	10017	0.0747	1.6471	1.7734	2.1178	0.1723	1.3313	0.63	1025	13	1036	15	1059	34
STK-10	1413	64808	45.9	8497	0.0741	1.5198	1.7628	2.0007	0.1725	1.3012	0.65	1026	12	1032	14	1044	31
STK-11	1530	68029	44.5	9202	0.0739	1.7644	1.7634	2.1861	0.1731	1.2908	0.59	1029	12	1032	15	1039	36
STK-12	1538	69039	44.9	9368	0.0746	1.9804	1.7867	2.3019	0.1737	1.1733	0.51	1033	11	1041	16	1057	40
STK-13	1652	72894	44.1	9822	0.0736	1.7310	1.7424	2.1333	0.1718	1.2470	0.58	1022	12	1024	15	1030	35
STK-14	1377	60633	44.0	8286	0.0741	1.0268	1.7661	1.6044	0.1728	1.2327	0.77	1027	12	1033	11	1045	21
STK-15	1626	72584	44.6	9810	0.0740	1.6153	1.7702	2.0551	0.1734	1.2705	0.62	1031	12	1035	14	1042	33
STK-16	1861	83170	44.7	11347	0.0746	1.5317	1.7896	1.9519	0.1740	1.2098	0.62	1034	12	1042	14	1058	31
Thompson Mine monazite	U (ppm)	Th (ppm)	Th/U	²⁰⁷ Pb (cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s(abs)	²⁰⁷ Pb/ ²³⁵ U	2s (abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(abs)
TM-1	4936	169545	34.3	77850	0.1082	1.5056	4.5715	2.0895	0.3064	1.4489	0.69	1723	22	1744	19	1769	28
TM-2	3743	138393	37.0	63189	0.1087	1.0142	4.8933	1.7195	0.3266	1.3886	0.81	1822	22	1801	16	1777	19
TM-3	4105	145656	35.5	67694	0.1086	1.1908	4.7811	2.1519	0.3194	1.7924	0.83	1787	28	1782	20	1775	22
TM-4	1974	110752	56.1	31052	0.1080	2.8169	4.5597	6.2456	0.3063	5.5743	0.89	1723	85	1742	55	1765	52
TM-5	4472	158236	35.4	75209	0.1088	1.3085	4.8766	2.2478	0.3250	1.8277	0.81	1814	29	1798	21	1780	24

TM-6	1614	61593	38.2	25792	0.1070	2.1200	4.6327	4.5099	0.3141	3.9805	0.88	1761	62	1755	40	1749	39
TM-7	3154	122187	38.7	52668	0.1076	1.4883	4.8421	2.7448	0.3263	2.3063	0.84	1821	37	1792	25	1759	27
TM-8	3657	158129	43.2	59652	0.1081	2.5060	4.7891	3.7955	0.3214	2.8506	0.75	1797	45	1783	34	1767	46
TM-9	~~2653~~	~~126939~~	~~47.8~~	~~46929~~	~~0.1152~~	~~1.8641~~	~~5.1955~~	~~3.5289~~	~~0.3272~~	~~2.9964~~	~~0.85~~	~~1825~~	~~48~~	~~1852~~	~~32~~	~~1883~~	~~34~~
TM-10	2825	120652	42.7	48201	0.1105	1.6564	5.0124	2.4161	0.3289	1.7589	0.73	1833	28	1821	22	1808	30
TM-11	3785	135743	35.9	62383	0.1076	1.4668	4.8432	2.1437	0.3266	1.5633	0.73	1822	25	1792	20	1758	27
TM-12	3726	148133	39.8	59826	0.1079	2.1266	4.7186	13.7963	0.3170	13.6315	0.99	1775	215	1771	124	1765	39
TM-13	3993	147604	37.0	65191	0.1089	1.8799	4.7981	2.4801	0.3195	1.6178	0.65	1787	25	1785	23	1781	35
TM-14	1968	59416	30.2	32470	0.1078	1.4951	4.8490	6.4183	0.3262	6.2417	0.97	1820	100	1793	57	1763	28

SAMPLES

HD10a monazite	U (ppm)	Th (ppm)	Th/U	²⁰⁷ Pb(cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s(abs)	²⁰⁷ Pb/ ²³⁵ U	2s(abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(abs)
HD10a-1	1932	30229	15.6	95102	0.1913	1.7637	14.0789	2.2347	0.5338	1.3724	0.61	2758	31	2755	24	2753	29
HD10a-2	2664	26935	10.1	130961	0.1911	1.2744	14.0615	1.6840	0.5337	1.1008	0.65	2757	25	2754	19	2752	21
HD10a-3	2290	21849	9.5	110902	0.1898	0.8647	13.8517	1.4981	0.5294	1.2234	0.82	2739	27	2740	17	2740	14
HD10a-4	3056	22562	7.4	148339	0.1895	0.7923	13.8854	1.5890	0.5314	1.3773	0.87	2747	31	2742	18	2738	13
HD10a-5	3324	33604	10.1	158262	0.1878	2.1571	13.6266	2.5214	0.5263	1.3056	0.52	2726	29	2724	27	2723	36
HD10a-6	3017	20377	6.8	146939	0.1902	0.8903	13.9376	1.6776	0.5315	1.4219	0.85	2748	32	2745	19	2744	15
HD10a-7	2817	21573	7.7	136836	0.1899	0.7877	13.9019	1.5564	0.5310	1.3424	0.86	2746	30	2743	17	2741	13
HD10a-8	3214	7267	2.3	157631	0.1908	0.9579	14.0410	1.7906	0.5337	1.5128	0.84	2757	34	2752	20	2749	16
HD10a-9	4519	31444	7.0	213324	0.1879	1.2693	13.5175	1.8619	0.5217	1.3622	0.73	2706	30	2717	20	2724	21
HD10a-10	3719	26616	7.2	177790	0.1877	1.2806	13.6898	1.7354	0.5291	1.1711	0.67	2738	26	2728	19	2722	21
HD10a-11	4301	13035	3.0	212433	0.1915	1.1044	14.1462	1.5846	0.5358	1.1363	0.72	2766	26	2760	18	2755	18
HD10a-12	4616	23900	5.2	212323	0.1856	1.3642	13.1768	1.9040	0.5150	1.3282	0.70	2678	29	2692	21	2703	23
HD10a-13	3931	11768	3.0	190899	0.1900	0.7405	13.9142	1.5108	0.5312	1.3169	0.87	2747	30	2744	17	2742	12
HD10a-14	3019	19240	6.4	144385	0.1885	3.3773	13.7016	3.6824	0.5272	1.4677	0.40	2730	33	2729	38	2729	57
HD10a-15	4488	18837	4.2	213867	0.1881	0.8232	13.6513	1.5243	0.5264	1.2829	0.84	2726	29	2726	17	2726	14
HD10a-16	3993	28214	7.1	191338	0.1886	2.0338	13.7356	2.3384	0.5282	1.1541	0.49	2734	26	2732	25	2730	34
HD10a-17	3587	24561	6.8	172858	0.1892	3.1885	13.8149	3.4393	0.5296	1.2893	0.37	2740	29	2737	36	2735	53

HD10a-18	3220	21537	6.7	156621	0.1899	0.8434	13.9447	1.6054	0.5325	1.3660	0.85	2752	31	2746	18	2742	14
HD10a-19	3524	21723	6.2	169161	0.1894	0.9838	13.7638	1.5147	0.5269	1.1516	0.76	2729	26	2734	17	2737	16
HD10a-20	2877	21154	7.4	139966	0.1901	0.4668	13.9491	1.4012	0.5321	1.3212	0.94	2750	30	2746	16	2743	8
HD10a-21	3821	29775	7.8	178980	0.1873	0.7350	13.4364	2.0399	0.5203	1.9029	0.93	2700	42	2711	22	2719	12
HD10a-22	4663	15337	3.3	228598	0.1909	2.2710	14.0618	2.6340	0.5342	1.3343	0.51	2759	30	2754	28	2750	38
HD10a-23	3646	20339	5.6	177707	0.1904	0.5038	13.9804	1.3971	0.5325	1.3031	0.93	2752	29	2748	16	2746	8
HD10a-24	3990	16744	4.2	198643	0.1925	2.4737	14.2861	2.7851	0.5382	1.2797	0.46	2776	29	2769	29	2764	41
HD10a-25	3021	20648	6.8	146600	0.1903	0.4240	13.9293	1.4239	0.5310	1.3593	0.95	2746	30	2745	16	2744	7
HD10a-26	3310	22331	6.7	160490	0.1902	1.4288	13.9177	1.9797	0.5306	1.3703	0.69	2744	31	2744	21	2744	24
HD10a-27	4084	23203	5.7	197180	0.1895	1.9821	13.8620	2.3659	0.5306	1.2917	0.55	2744	29	2740	25	2738	33
HD10a-28	4335	25571	5.9	208637	0.1897	0.5274	13.8200	1.3345	0.5283	1.2258	0.92	2734	27	2737	15	2740	9
HD10a-29	4656	27374	5.9	223721	0.1894	2.2856	13.7973	2.6286	0.5282	1.2982	0.49	2734	29	2736	28	2737	38
HD10a-30	4389	7849	1.8	215393	0.1913	0.7380	14.0956	1.5025	0.5344	1.3087	0.87	2760	29	2756	17	2753	12
HD10a-31	4113	10534	2.6	201866	0.1913	0.5671	14.0973	1.4280	0.5345	1.3106	0.92	2760	29	2756	16	2753	9
HD14 monazite	U (ppm)	Th (ppm)	Th/U	²⁰⁷Pb (cps)	²⁰⁷Pb/ ²⁰⁶Pb	2s(%)	²⁰⁷Pb/ ²³⁵U	2s(%)	²⁰⁶Pb/ ²³⁸U	2s(%)	ρ	²⁰⁶Pb/ ²³⁸U	2s (abs)	²⁰⁷Pb/ ²³⁵U	2s (abs)	²⁰⁷Pb/ ²⁰⁶Pb	2s (abs)
HD14-1	3981	14638	3.7	192589	0.1879	0.6804	13.9029	1.6034	0.5366	1.4519	0.91	2769	33	2743	18	2724	11
HD14-2	2979	11272	3.8	146008	0.1900	1.3445	14.0868	2.2804	0.5377	1.8418	0.81	2774	42	2756	24	2742	22
HD14-3	306	17758	58.0	14355	0.1868	0.8975	13.4694	1.8034	0.5231	1.5642	0.87	2712	35	2713	20	2714	15
HD14-4	2303	26009	11.3	107939	0.1863	0.7428	13.4711	1.8006	0.5245	1.6402	0.91	2718	36	2713	20	2709	12
HD14-5	326	20120	61.8	15542	0.1880	1.0022	13.7170	1.8999	0.5292	1.6141	0.85	2738	36	2730	21	2725	17
HD14-6	1084	8847	8.2	57282	0.1894	2.1743	15.1846	4.3249	0.5815	3.7386	0.86	2955	89	2827	45	2737	36
HD14-7	854	23930	28.0	41638	0.1869	0.8727	14.0171	1.6497	0.5439	1.3999	0.85	2800	32	2751	18	2715	14
HD14-8	1906	20601	10.8	91042	0.1877	0.8125	13.7390	1.6519	0.5308	1.4383	0.87	2745	32	2732	18	2722	13
HD14-9	1775	20016	11.3	84622	0.1882	0.7918	13.7158	1.5221	0.5285	1.2999	0.85	2735	29	2730	17	2727	13
HD14-10	215	18730	87.2	10511	0.1889	1.2234	14.0843	2.6124	0.5409	2.3083	0.88	2787	52	2755	28	2732	20
HD14-11	149	21295	143.0	6981	0.1856	1.3953	13.4832	2.6647	0.5268	2.2702	0.85	2728	51	2714	28	2704	23
HD14-12	2679	3471	1.3	133747	0.1910	0.9721	14.3717	1.8626	0.5458	1.5888	0.85	2807	36	2775	20	2751	16
HD14-13	2163	5778	2.7	112005	0.1900	1.2485	14.9112	2.1890	0.5692	1.7981	0.82	2905	42	2810	24	2742	21

HD14-14	1015	25961	25.6	47636	0.1859	0.7096	13.5125	1.5451	0.5271	1.3724	0.89	2729	31	2716	17	2707	0.5
HD14-15	1961	29200	14.9	91724	0.1859	0.7320	13.4662	1.5273	0.5253	1.3405	0.88	2722	30	2713	17	2706	12
HD14-16	1394	27815	20.0	66654	0.1858	0.8314	13.7757	1.5447	0.5376	1.3018	0.84	2774	29	2734	17	2706	14
HD14-17	2602	23257	8.9	124310	0.1857	0.7603	13.7668	1.6765	0.5376	1.4942	0.89	2773	34	2734	18	2705	13
HD14-18	2813	22855	8.1	134287	0.1871	0.9300	13.7601	1.7867	0.5335	1.5256	0.85	2756	34	2733	20	2717	15
HD14-19	2087	14832	7.1	105212	0.1890	1.1696	14.5280	2.4542	0.5576	2.1576	0.88	2857	50	2785	26	2733	19
HD14-20	2374	7202	3.0	116210	0.1889	1.5376	14.1121	2.3425	0.5419	1.7673	0.75	2791	40	2757	25	2732	26
HD14-21	~~1486~~	~~2596~~	~~1.7~~	~~74342~~	~~0.1887~~	~~1.2501~~	~~14.4310~~	~~5.3490~~	~~0.5547~~	~~5.2008~~	~~0.97~~	~~2845~~	~~121~~	~~2778~~	~~55~~	~~2731~~	~~21~~
HD14-22	3257	5502	1.7	160673	0.1885	1.2893	14.2282	2.0927	0.5474	1.6484	0.79	2814	38	2765	23	2729	21
HD14-23	2355	26557	11.3	113068	0.1872	0.9241	13.8402	1.8617	0.5363	1.6161	0.87	2768	36	2739	20	2717	15
HD14-24	3345	27993	8.4	158597	0.1855	0.8311	13.6811	2.2466	0.5350	2.0872	0.93	2763	47	2728	24	2702	14
HD14-25	6878	24310	3.5	319170	0.1851	1.3063	13.3904	1.7565	0.5247	1.1743	0.67	2719	26	2708	19	2699	22
HD14-26	1285	19284	15.0	60829	0.1845	1.1403	13.6553	2.5111	0.5367	2.2372	0.89	2770	51	2726	27	2694	19
HD14-27	1577	13834	8.8	76054	0.1860	1.5109	13.9301	2.9213	0.5432	2.5003	0.86	2797	57	2745	31	2707	25
HD14-28	4315	22105	5.1	203721	0.1869	0.7662	13.6319	1.5518	0.5291	1.3494	0.87	2737	30	2724	17	2715	13
HD14-29	2487	20394	8.2	116228	0.1855	0.8168	13.4990	1.6467	0.5277	1.4299	0.87	2732	32	2715	18	2703	14
HD14-30	5154	29555	5.7	244072	0.1867	1.1555	13.6774	1.7489	0.5312	1.3128	0.75	2747	29	2728	19	2714	19

3.3 Table S6 – U-Pb data for apatite samples

PRIMARY REFERENCE MATERIAL

NIST 612 glass	U (ppm)	Th (ppm)	Th/ U	²⁰⁷ Pb (cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s (abs)	²⁰⁷ Pb/ ²³⁵ U	2s(abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(abs)
NIST-1	25	25	1.01	46526	0.9053	1.0047	35.9680	1.4637	0.2882	1.0644	0.73	1632	15	3666	18	5097	14
NIST-2	27	27	1.00	51047	0.9066	1.0063	36.3591	1.4726	0.2909	1.0751	0.73	1646	16	3676	18	5099	14
NIST-3	26	26	1.00	49092	0.9096	1.0043	36.3253	1.4447	0.2896	1.0385	0.72	1640	15	3675	18	5104	14
NIST-4	25	26	1.01	48877	0.9077	1.0044	36.4049	1.4489	0.2909	1.0443	0.72	1646	15	3678	18	5101	14
NIST-5	29	29	1.01	54523	0.9067	1.0068	36.2656	1.4671	0.2901	1.0671	0.73	1642	15	3674	18	5099	14
NIST-6	27	27	1.01	51096	0.9078	1.0045	36.3797	1.4558	0.2906	1.0536	0.72	1645	15	3677	18	5101	14
NIST-7	28	28	1.00	52789	0.9069	1.0062	36.2097	1.4764	0.2896	1.0805	0.73	1639	16	3672	18	5100	14
NIST-8	28	28	1.01	53528	0.9075	1.0060	36.2591	1.4555	0.2898	1.0518	0.72	1641	15	3674	18	5101	14
NIST-9	28	28	1.01	52984	0.9055	1.0035	35.8748	1.4599	0.2873	1.0603	0.73	1628	15	3663	18	5097	14
NIST-10	28	29	1.00	54304	0.9063	1.0046	36.5457	1.4757	0.2925	1.0809	0.73	1654	16	3681	18	5099	14
NIST-11	32	33	1.01	61487	0.9059	1.0063	36.4433	1.4782	0.2918	1.0828	0.73	1650	16	3679	18	5098	14
NIST-12	29	28	0.99	54022	0.9083	1.0046	36.3323	1.4757	0.2901	1.0809	0.73	1642	16	3676	18	5102	14
NIST-13	29	29	0.99	54583	0.9079	1.0042	36.1593	1.4623	0.2889	1.0629	0.73	1636	15	3671	18	5101	14
NIST-14	28	28	1.00	53445	0.9076	1.0050	36.3705	1.4650	0.2906	1.0659	0.73	1645	15	3677	18	5101	14
NIST-15	32	32	0.99	60132	0.9059	1.0092	35.9141	1.4734	0.2875	1.0735	0.73	1629	15	3664	18	5098	14
NIST-16	29	29	1.00	55799	0.9084	1.0044	36.3327	1.4415	0.2901	1.0340	0.72	1642	15	3676	18	5102	14
NIST-17	29	29	0.99	54316	0.9082	1.0058	36.3397	1.4485	0.2902	1.0423	0.72	1642	15	3676	18	5102	14
NIST-18	29	29	1.01	55436	0.9064	1.0055	36.3645	1.4452	0.2910	1.0380	0.72	1646	15	3676	18	5099	14
NIST-19	29	29	0.99	54700	0.9075	1.0036	36.4668	1.4668	0.2914	1.0696	0.73	1649	16	3679	18	5101	14
NIST-20	30	29	0.99	56031	0.9071	1.0034	36.1684	1.4470	0.2892	1.0426	0.72	1637	15	3671	18	5100	14
NIST-21	30	29	0.99	56117	0.9078	1.0042	36.1721	1.4337	0.2890	1.0233	0.71	1636	15	3671	18	5101	14
NIST-22	33	33	1.01	62042	0.9080	1.0095	36.4088	1.5998	0.2908	1.2411	0.78	1646	18	3678	19	5101	14
NIST-23	28	28	1.00	53838	0.9102	1.0046	36.2389	1.4595	0.2888	1.0587	0.73	1635	15	3673	18	5105	14
NIST-24	30	30	1.00	56892	0.9082	1.0037	36.4254	1.4608	0.2909	1.0613	0.73	1646	15	3678	18	5102	14
NIST-25	29	29	1.00	54587	0.9072	1.0053	36.4029	1.4272	0.2910	1.0131	0.71	1647	15	3677	18	5100	14
NIST-26	31	31	0.99	59005	0.9046	1.0055	36.2325	1.4447	0.2905	1.0374	0.72	1644	15	3673	18	5096	14

NIST-27	32	32	0.99	60868	0.9047	1.0098	35.9158	1.4550	0.2879	1.0476	0.72	1631	15	3664	18	5096	14
NIST-28	29	29	1.00	55007	0.9081	1.0053	36.4315	1.4470	0.2910	1.0407	0.72	1646	15	3678	18	5102	14
NIST-29	30	30	1.00	56813	0.9064	1.0038	36.3020	1.4418	0.2905	1.0350	0.72	1644	15	3675	18	5099	14
NIST-30	29	30	1.01	56359	0.9061	1.0046	36.4639	1.4456	0.2919	1.0394	0.72	1651	15	3679	18	5098	14
NIST-31	29	29	1.00	54873	0.9059	1.0049	36.3690	1.4383	0.2912	1.0291	0.72	1647	15	3677	18	5098	14
NIST-32	33	32	0.99	61328	0.9080	1.0055	35.9867	1.4500	0.2875	1.0447	0.72	1629	15	3666	18	5101	14
NIST-33	31	31	0.99	58206	0.9083	1.0039	36.1597	1.4282	0.2887	1.0159	0.71	1635	15	3671	18	5102	14
NIST-34	32	32	1.00	60295	0.9066	1.0077	35.9066	1.5825	0.2873	1.2202	0.77	1628	18	3664	19	5099	14
NIST-35	32	32	1.00	61180	0.9085	1.0043	36.2487	1.4387	0.2894	1.0301	0.72	1638	15	3673	18	5102	14
NIST-36	32	32	1.00	61050	0.9085	1.0045	36.0856	1.4236	0.2881	1.0088	0.71	1632	15	3669	18	5102	14
NIST-37	32	32	1.00	60976	0.9065	1.0039	36.4764	1.4527	0.2918	1.0500	0.72	1651	15	3679	18	5099	14
NIST-38	31	31	1.01	59572	0.9068	1.0033	36.4826	1.4233	0.2918	1.0096	0.71	1651	15	3680	18	5099	14
NIST-39	31	31	1.01	58636	0.9061	1.0042	36.4568	1.4513	0.2918	1.0479	0.72	1651	15	3679	18	5098	14
NIST-40	32	32	1.00	60380	0.9095	1.0065	36.5268	1.4265	0.2913	1.0110	0.71	1648	15	3681	18	5104	14
NIST-41	32	32	0.99	60902	0.9079	1.0041	36.3319	1.4318	0.2902	1.0207	0.71	1643	15	3676	18	5101	14
NIST-42	36	36	1.00	67739	0.9057	1.0061	36.4718	1.4400	0.2920	1.0303	0.72	1652	15	3679	18	5098	14
NIST-43	33	32	0.99	61238	0.9064	1.0034	36.0517	1.4361	0.2885	1.0274	0.72	1634	15	3668	18	5099	14
NIST-44	32	32	0.99	59531	0.9075	1.0061	35.9549	1.4510	0.2874	1.0456	0.72	1628	15	3665	18	5101	14
NIST-45	35	35	1.01	66553	0.9081	1.0049	36.6389	1.4450	0.2926	1.0384	0.72	1655	15	3684	18	5101	14
NIST-46	31	31	1.00	59073	0.9073	1.0045	36.0155	1.4474	0.2879	1.0422	0.72	1631	15	3667	18	5100	14

SECONDARY REFERENCE MATERIAL

401 apatite	U (ppm)	Th (ppm)	Th/ U	²⁰⁷ Pb (cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s (abs)	²⁰⁷ Pb/ ²³⁵ U	2s(abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(abs)
401-1	13	126	9.48	493	0.0691	1.9284	0.8161	2.5087	0.0857	1.6045	0.64	530	8	606	12	901	40
401-2	12	121	9.84	487	0.0698	1.5731	0.8278	2.3765	0.0860	1.7813	0.75	532	9	612	12	923	33
401-3	13	124	9.84	492	0.0701	1.9275	0.8314	2.5226	0.0861	1.6274	0.65	532	8	614	12	930	40
401-4	14	135	9.84	564	0.0732	2.5426	0.8669	2.9244	0.0858	1.4449	0.49	531	7	634	14	1021	52
401-5	14	130	9.13	518	0.0674	2.4036	0.7849	2.7881	0.0845	1.4129	0.51	523	7	588	13	850	51
401-6	14	132	9.63	512	0.0679	2.0390	0.7945	2.4520	0.0848	1.3620	0.56	525	7	594	12	866	43

401-7	14	137	9.82	526	0.0685	1.9878	0.8126	2.5653	0.0861	1.6216	0.63	532	8	604	12	883	42
401-8	14	131	9.61	521	0.0691	2.1141	0.8044	2.6121	0.0844	1.5342	0.59	523	8	599	12	901	44
401-9	14	134	9.52	623	0.0734	1.7977	0.8634	2.1978	0.0854	1.2644	0.58	528	6	632	11	1024	37
401-10	13	126	9.69	559	0.0700	2.3702	0.8220	2.7587	0.0852	1.4116	0.51	527	7	609	13	929	49
401-11	14	131	9.58	577	0.0694	2.8092	0.8174	3.1814	0.0854	1.4932	0.47	529	8	607	15	910	59
401-12	14	130	9.49	566	0.0680	1.6824	0.7966	2.1873	0.0850	1.3978	0.64	526	7	595	10	868	35
401-13	13	127	9.42	556	0.0687	1.9551	0.8048	2.3788	0.0850	1.3551	0.57	526	7	600	11	890	41
401-14	13	128	9.55	575	0.0698	3.2728	0.8195	3.5457	0.0851	1.3642	0.38	527	7	608	17	923	69
Durango apatite	U (ppm)	Th (ppm)	Th/ U	²⁰⁷ Pb (cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s (abs)	²⁰⁷ Pb/ ²³⁵ U	2s(abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(abs)
DUR-1	14	273	18.88	135	0.1910	3.3240	0.1637	3.7504	0.0062	1.7368	0.46	40	1	154	6	2751	56
DUR-2	14	266	18.68	150	0.2097	2.6880	0.1835	3.1501	0.0063	1.6425	0.52	41	1	171	5	2903	44
DUR-3	14	265	18.92	133	0.1911	3.7079	0.1671	4.1385	0.0063	1.8381	0.44	41	1	157	6	2752	62
DUR-4	15	271	18.37	133	0.1876	3.1118	0.1592	3.4739	0.0062	1.5443	0.44	40	1	150	5	2722	52
DUR-5	15	276	19.00	140	0.1966	3.2612	0.1653	3.7977	0.0061	1.9460	0.51	39	1	155	6	2798	54
DUR-6	15	272	18.66	140	0.1948	3.6620	0.1686	4.0625	0.0063	1.7590	0.43	40	1	158	6	2784	61
DUR-7	16	292	18.36	145	0.1896	5.5595	0.1628	6.1581	0.0062	2.6485	0.43	40	1	153	9	2739	95
DUR-8	14	274	18.96	140	0.1975	3.2493	0.1693	3.7337	0.0062	1.8393	0.49	40	1	159	6	2805	54
DUR-9	14	274	19.98	142	0.2078	2.9866	0.1803	3.4457	0.0063	1.7183	0.50	40	1	168	6	2888	49
DUR-10	14	280	19.56	150	0.2103	3.4014	0.1841	4.0068	0.0063	2.1177	0.53	41	1	172	6	2908	56
DUR-11	14	269	19.50	144	0.2059	3.8297	0.1821	4.4187	0.0064	2.2042	0.50	41	1	170	7	2873	64
DUR-12	14	265	19.01	139	0.2043	2.8554	0.1765	3.3776	0.0063	1.8041	0.53	40	1	165	5	2861	47
DUR-13	14	258	18.91	134	0.1996	3.6777	0.1752	4.1813	0.0064	1.9895	0.48	41	1	164	6	2823	61
DUR-14	14	267	19.04	130	0.1887	3.2904	0.1590	3.7304	0.0061	1.7576	0.47	39	1	150	5	2731	55
DUR-15	14	273	18.86	136	0.1952	2.1158	0.1659	3.3068	0.0062	2.5414	0.77	40	1	156	5	2786	35
DUR-16	14	271	18.95	133	0.1918	3.8281	0.1622	4.2781	0.0061	1.9099	0.45	39	1	153	6	2758	64
DUR-17	14	268	18.94	130	0.1923	2.8745	0.1624	3.3009	0.0061	1.6227	0.49	39	1	153	5	2762	48
DUR-18	14	262	19.11	131	0.1988	2.6453	0.1685	3.0108	0.0061	1.4379	0.48	39	1	158	5	2816	44
Ipirá apatite	U (ppm)	Th (ppm)	Th/ U	²⁰⁷ Pb (cps)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(%)	²⁰⁷ Pb/ ²³⁵ U	2s(%)	²⁰⁶ Pb/ ²³⁸ U	2s(%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2s (abs)	²⁰⁷ Pb/ ²³⁵ U	2s(abs)	²⁰⁷ Pb/ ²⁰⁶ Pb	2s(abs)

IPIRA-1	70	991	14.07	32379	0.1931	1.0097	10.7361	1.5207	0.4033	1.1372	0.75	2184	21	2501	16	2769	17
IPIRA-2	65	901	13.93	29522	0.1904	1.0234	10.6025	1.4509	0.4040	1.0285	0.71	2187	19	2489	16	2745	17
IPIRA-3	77	1025	13.38	34181	0.1866	1.0117	10.3768	1.4974	0.4033	1.1039	0.74	2184	20	2469	16	2713	17
IPIRA-4	71	971	13.74	31632	0.1863	1.0162	10.3177	1.5157	0.4018	1.1245	0.74	2177	21	2464	16	2709	17
IPIRA-5	73	1036	14.14	31403	0.1795	1.0231	9.9129	1.5733	0.4006	1.1952	0.76	2172	22	2427	17	2648	17
IPIRA-6	67	945	14.03	31945	0.1954	1.0233	10.9113	1.5137	0.4050	1.1154	0.74	2192	21	2516	16	2788	17
IPIRA-7	71	967	13.67	32388	0.1897	1.0057	10.4926	1.4493	0.4011	1.0436	0.72	2174	19	2479	16	2740	17
IPIRA-8	67	938	13.99	31192	0.1911	1.0065	10.6435	1.4652	0.4040	1.0647	0.73	2187	20	2493	16	2751	17
IPIRA-9	80	1081	13.47	37405	0.1763	2.4143	9.6484	2.7097	0.3969	1.2303	0.45	2155	23	2402	27	2618	41
IPIRA-10	80	1085	13.61	37495	0.1786	1.0043	9.6859	1.4276	0.3933	1.0145	0.71	2138	18	2405	15	2640	17
IPIRA-11	77	1047	13.63	36113	0.1759	1.0137	9.6822	1.7234	0.3992	1.3937	0.81	2165	26	2405	18	2615	17
IPIRA-12	77	1036	13.48	36511	0.1787	1.0094	9.7651	1.4896	0.3964	1.0955	0.74	2152	20	2413	16	2641	17
IPIRA-13	78	1079	13.86	36676	0.1766	1.0116	9.6034	1.6793	0.3945	1.3405	0.80	2144	24	2397	18	2621	17
IPIRA-14	74	1022	13.79	35700	0.1797	1.0059	9.9013	1.5113	0.3996	1.1279	0.75	2167	21	2426	16	2650	17
IPIRA-15	71	968	13.55	35216	0.1829	1.0070	10.0310	1.4614	0.3977	1.0590	0.72	2158	19	2438	16	2680	17
IPIRA-16	75	978	13.06	36788	0.1809	2.4268	10.0083	2.8507	0.4012	1.4956	0.52	2174	28	2436	29	2661	41
IPIRA-17	69	953	13.87	35932	0.1897	1.0064	10.5404	1.5758	0.4029	1.2126	0.77	2182	22	2483	17	2740	17
IPIRA-18	70	976	13.88	36995	0.1902	1.0092	10.5535	1.4284	0.4024	1.0109	0.71	2180	19	2485	16	2744	17
IPIRA-19	74	1017	13.72	37604	0.1858	1.0048	10.1721	1.4501	0.3970	1.0455	0.72	2155	19	2451	16	2706	17
IPIRA-20	73	1011	13.92	37314	0.1867	1.0081	10.3151	1.7042	0.4007	1.3741	0.81	2172	25	2463	18	2713	17
IPIRA-21	78	1115	14.35	36897	0.1750	1.0511	9.5070	1.7455	0.3941	1.3936	0.80	2142	25	2388	18	2606	18
IPIRA-22	67	926	13.84	35895	0.1938	1.0106	10.7793	1.4558	0.4033	1.0479	0.72	2184	19	2504	16	2775	17
IPIRA-23	69	955	13.74	36580	0.1901	1.0071	10.5579	1.4931	0.4028	1.1022	0.74	2182	20	2485	16	2743	17
IPIRA-24	71	975	13.75	36635	0.1875	1.0054	10.3793	1.4031	0.4015	0.9786	0.70	2176	18	2469	15	2720	17
IPIRA-25	71	984	13.93	39551	0.1901	1.0040	10.4934	1.5767	0.4004	1.2157	0.77	2171	22	2479	17	2743	17
IPIRA-26	64	983	15.31	36799	0.1935	1.2025	10.7014	1.5649	0.4010	1.0015	0.64	2174	19	2498	17	2773	20
IPIRA-27	64	894	14.00	36976	0.1942	1.0082	10.8015	1.4162	0.4034	0.9946	0.70	2185	18	2506	16	2778	17
IPIRA-28	61	867	14.15	35558	0.1947	1.0087	10.7981	1.4157	0.4023	0.9933	0.70	2179	18	2506	16	2782	17
IPIRA-29	67	935	13.99	37956	0.1916	1.0107	10.5762	1.4625	0.4004	1.0571	0.72	2171	20	2487	16	2756	17

IPIRA-30	63	880	14.02	36438	0.1938	1.0067	10.7910	1.5356	0.4039	1.1596	0.76	2187	22	2505	17	2774	17
IPIRA-31	62	874	14.11	35990	0.1937	1.0073	10.7751	1.9832	0.4035	1.7083	0.86	2185	32	2504	21	2774	17
IPIRA-32	61	857	14.01	35334	0.1934	1.0047	10.7558	1.4841	0.4034	1.0923	0.74	2185	20	2502	16	2771	17
IPIRA-33	70	946	13.56	40070	0.1895	1.0054	10.5166	1.5626	0.4026	1.1962	0.77	2181	22	2481	17	2738	17
IPIRA-34	65	901	13.76	37706	0.1903	1.0049	10.5551	1.4530	0.4023	1.0495	0.72	2180	19	2485	16	2745	17
IPIRA-35	70	974	13.92	38544	0.1825	2.4122	10.0634	2.8397	0.3999	1.4984	0.53	2168	28	2441	29	2676	40
IPIRA-36	66	898	13.63	36697	0.1845	1.0065	10.2039	1.4396	0.4010	1.0293	0.71	2174	19	2453	16	2694	17
IPIRA-37	69	927	13.40	39517	0.1898	1.0459	10.4861	1.5683	0.4007	1.1686	0.75	2172	22	2479	17	2740	17
IPIRA-38	69	922	13.32	38188	0.1826	1.0091	10.1180	1.5283	0.4018	1.1478	0.75	2177	21	2446	16	2677	17
IPIRA-39	70	970	13.89	39606	0.1871	1.0080	10.3585	1.8261	0.4015	1.5228	0.83	2176	28	2467	19	2717	17
IPIRA-40	72	1001	13.93	40740	0.1880	1.0124	10.3875	1.4587	0.4007	1.0501	0.72	2172	19	2470	16	2725	17
Madagascar blue apatite	U (ppm)	Th (ppm)	Th/ U	²⁰⁷Pb (cps)	²⁰⁷Pb/ ²⁰⁶Pb	2s(%)	²⁰⁷Pb/ ²³⁵U	2s(%)	²⁰⁶Pb/ ²³⁸U	2s(%)	ρ	²⁰⁶Pb/ ²³⁸U	2s (abs)	²⁰⁷Pb/ ²³⁵U	2s(abs)	²⁰⁷Pb/ ²⁰⁶Pb	2s(abs)
MAD B-1	18	570	30.95	1038	0.1098	1.3886	1.1986	1.8652	0.0791	1.2452	0.67	491	6	800	11	1797	25
MAD B-2	17	513	31.02	949	0.1084	1.7488	1.1800	2.3212	0.0790	1.5263	0.66	490	7	791	14	1773	32
MAD B-3	15	480	32.30	871	0.1083	1.9255	1.1833	2.4824	0.0792	1.5668	0.63	492	7	793	14	1771	36
MAD B-4	17	569	33.52	919	0.1021	1.4257	1.1219	1.9662	0.0797	1.3541	0.69	494	6	764	11	1663	27
MAD B-5	16	504	31.99	908	0.1088	1.3733	1.1909	1.9023	0.0794	1.3164	0.69	493	6	796	11	1779	25
MAD B-6	16	533	33.26	869	0.1032	1.7720	1.1264	2.2329	0.0792	1.3585	0.61	491	6	766	13	1682	33
MAD B-7	16	547	33.62	857	0.1000	1.7687	1.0862	2.3301	0.0788	1.5168	0.65	489	7	747	13	1624	33
MAD B-8	16	535	32.51	934	0.1044	2.7816	1.1381	3.2156	0.0791	1.6133	0.50	491	8	772	18	1703	52
MAD B-9	16	487	30.48	1053	0.1074	1.1935	1.1799	1.7635	0.0797	1.2983	0.74	494	6	791	10	1755	22
MAD B-10	16	490	30.51	1023	0.1047	1.2349	1.1522	1.8381	0.0798	1.3615	0.74	495	6	778	11	1710	23
MAD B-11	16	495	31.11	1051	0.1081	1.1943	1.1879	1.7875	0.0797	1.3299	0.74	494	6	795	11	1768	22
MAD B-12	16	502	30.92	1074	0.1075	1.2204	1.1933	1.7681	0.0805	1.2793	0.72	499	6	797	11	1758	22
MAD B-13	16	489	30.79	1013	0.1041	1.1682	1.1484	1.8347	0.0800	1.4146	0.77	496	7	776	11	1698	22
MAD B-14	16	491	31.20	1057	0.1069	1.2317	1.1849	1.8048	0.0804	1.3191	0.73	498	6	794	11	1747	23
MAD B-15	16	483	30.01	984	0.1020	1.2562	1.1079	1.8295	0.0788	1.3301	0.73	489	6	757	10	1661	23
MAD B-16	16	470	30.30	997	0.1018	1.2419	1.1161	1.9305	0.0795	1.4781	0.77	493	7	761	11	1657	23

Madagascar green apatite	U (ppm)	Th (ppm)	Th/ U	²⁰⁷Pb (cps)	²⁰⁷Pb/ ²⁰⁶Pb	2s(%)	²⁰⁷Pb/ ²³⁵U	2s(%)	²⁰⁶Pb/ ²³⁸U	2s(%)	ρ	²⁰⁶Pb/ ²³⁸U	2s (abs)	²⁰⁷Pb/ ²³⁵U	2s(abs)	²⁰⁷Pb/ ²⁰⁶Pb	2s(abs)
MAD G-1	19	602	31.69	2480	0.2217	1.1840	2.9154	1.7397	0.0954	1.2747	0.73	587	7	1386	14	2993	19
MAD G-2	19	617	32.38	2678	0.2287	1.2479	3.0480	1.7412	0.0967	1.2144	0.70	595	7	1420	15	3043	20
MAD G-3	19	631	32.45	2606	0.2228	1.7957	2.9360	2.2521	0.0956	1.3592	0.60	588	8	1391	18	3001	29
MAD G-4	19	616	32.44	2608	0.2241	2.1927	2.9653	2.5825	0.0960	1.3643	0.53	591	8	1399	21	3011	36
MAD G-5	20	633	32.07	2638	0.2224	1.0951	2.9281	1.6208	0.0955	1.1949	0.74	588	7	1389	14	2998	18
MAD G-6	20	634	32.45	2708	0.2285	1.2361	3.0405	1.7754	0.0965	1.2743	0.72	594	7	1418	15	3041	20
MAD G-7	21	671	32.14	3153	0.2224	1.3868	2.9819	1.8751	0.0972	1.2621	0.67	598	7	1403	16	2998	22
MAD G-8	20	652	31.85	3156	0.2282	1.4820	3.0427	1.9204	0.0967	1.2213	0.64	595	7	1418	16	3039	24
MAD G-9	19	608	31.92	2890	0.2233	1.1222	2.9589	1.6516	0.0961	1.2117	0.73	592	7	1397	14	3004	18
MAD G-10	19	607	32.13	2770	0.2152	1.9348	2.8198	2.3294	0.0950	1.2972	0.56	585	7	1361	19	2945	32
MAD G-11	20	625	31.92	3173	0.2346	1.1534	3.1429	1.6607	0.0971	1.1947	0.72	598	7	1443	14	3084	19
MAD G-12	20	639	31.74	3118	0.2272	1.2698	3.0192	1.7201	0.0964	1.1602	0.67	593	7	1412	14	3032	21
MAD G-13	19	619	31.96	2961	0.2250	1.2247	3.0072	1.7783	0.0969	1.2894	0.73	596	7	1409	15	3017	20
MAD G-14	20	647	31.62	3236	0.2327	1.8007	3.1380	2.3081	0.0978	1.4439	0.63	601	8	1442	19	3071	29
McClure Mountain apatite	U (ppm)	Th (ppm)	Th/ U	²⁰⁷Pb (cps)	²⁰⁷Pb/ ²⁰⁶Pb	2s(%)	²⁰⁷Pb/ ²³⁵U	2s(%)	²⁰⁶Pb/ ²³⁸U	2s(%)	ρ	²⁰⁶Pb/ ²³⁸U	2s (abs)	²⁰⁷Pb/ ²³⁵U	2s(abs)	²⁰⁷Pb/ ²⁰⁶Pb	2s(abs)
McClur-1	12	36	3.00	2343	0.2282	2.4470	3.3123	2.9422	0.1053	1.6336	0.56	645	10	1484	25	3040	40
McClur-2	18	63	3.48	2237	0.1640	1.1499	2.1775	1.6198	0.0963	1.1408	0.70	593	6	1174	12	2498	19
McClur-3	17	53	3.16	2468	0.1860	1.3995	2.5399	1.8808	0.0990	1.2565	0.67	609	7	1284	15	2707	23
McClur-4	17	54	3.20	5162	0.3252	1.7896	5.5198	2.3490	0.1231	1.5217	0.65	748	11	1904	22	3595	28
McClur-5	17	56	3.28	4791	0.3041	2.0380	5.0239	2.4807	0.1198	1.4143	0.57	729	10	1823	23	3491	32
McClur-6	21	52	2.47	3044	0.1967	2.8760	2.6093	3.1168	0.0962	1.2013	0.39	592	7	1303	24	2799	48
McClur-7	18	58	3.27	5164	0.3115	3.2889	5.2293	4.0451	0.1218	2.3550	0.58	741	17	1857	37	3528	52
McClur-8	10	29	3.02	1511	0.1942	2.1297	2.7237	2.7618	0.1017	1.7583	0.64	624	10	1335	22	2778	35
McClur-9	7	20	2.70	1510	0.2360	2.1725	3.4980	3.5570	0.1075	2.8164	0.79	658	18	1527	30	3093	35
McClur-10	9	26	2.92	1600	0.2128	1.2118	3.0501	2.4034	0.1039	2.0756	0.86	637	13	1420	20	2927	20
McClur-11	15	44	3.02	1838	0.1685	2.8869	2.2144	3.1798	0.0953	1.3332	0.42	587	7	1186	24	2543	49

McClur-12	14	40	2.96	1998	0.1880	2.1346	2.5724	2.5170	0.0993	1.3338	0.53	610	8	1293	20	2724	36
McClur-13	5	15	2.87	1801	0.3260	1.4478	5.4716	3.4161	0.1217	3.0941	0.91	741	22	1896	31	3598	22
Sumé apatite	U (ppm)	Th (ppm)	Th/ U	²⁰⁷Pb (cps)	²⁰⁷Pb/ ²⁰⁶Pb	2s(%)	²⁰⁷Pb/ ²³⁵U	2s(%)	²⁰⁶Pb/ ²³⁸U	2s(%)	ρ	²⁰⁶Pb/ ²³⁸U	2s (abs)	²⁰⁷Pb/ ²³⁵U	2s(abs)	²⁰⁷Pb/ ²⁰⁶Pb	2s(abs)
SUME-1	72	2142	29.74	4050	0.0897	1.0574	1.1787	1.4801	0.0953	1.0356	0.70	587	6	791	9	1418	20
SUME-2	72	2138	29.49	3865	0.0848	1.0368	1.1105	1.4611	0.0950	1.0295	0.70	585	6	758	9	1310	20
SUME-3	73	2177	29.97	4291	0.0928	1.0685	1.2230	1.5289	0.0956	1.0936	0.72	589	6	811	9	1483	20
SUME-4	71	2124	29.98	4283	0.0949	1.0675	1.2590	1.5209	0.0962	1.0834	0.71	592	6	827	9	1527	20
SUME-5	73	2202	30.23	4647	0.0992	1.0743	1.3282	1.5716	0.0971	1.1471	0.73	598	7	858	10	1609	20
SUME-6	72	2171	30.10	4467	0.0961	1.0770	1.2821	1.5454	0.0968	1.1083	0.72	596	6	838	10	1549	20
SUME-7	69	2074	30.13	4269	0.0964	1.1641	1.2762	1.6283	0.0960	1.1386	0.70	591	6	835	10	1556	22
SUME-8	71	2143	30.04	4854	0.1037	1.0492	1.4018	1.5134	0.0980	1.0907	0.72	603	6	890	10	1691	19
SUME-9	76	2236	29.48	4000	0.0809	1.0541	1.0509	1.4958	0.0942	1.0613	0.71	581	6	729	8	1219	21
SUME-10	77	2250	29.18	3812	0.0762	1.0464	0.9833	1.4685	0.0936	1.0304	0.70	577	6	695	8	1101	21
SUME-11	73	2138	29.34	3824	0.0794	1.0467	1.0461	1.4833	0.0956	1.0510	0.71	589	6	727	8	1181	21
SUME-12	78	2284	29.40	3897	0.0776	1.0471	1.0024	1.4539	0.0937	1.0087	0.69	577	6	705	8	1137	21
SUME-13	69	2082	30.01	4063	0.0881	1.0431	1.1636	1.4706	0.0957	1.0365	0.70	589	6	784	9	1386	20
SUME-14	75	2226	29.76	4025	0.0818	1.0755	1.0697	1.4793	0.0948	1.0158	0.69	584	6	739	8	1241	21
SUME-15	75	2228	29.56	4025	0.0811	1.0576	1.0619	1.4686	0.0949	1.0191	0.69	585	6	735	8	1225	21
SUME-16	77	2299	29.94	4435	0.0873	1.0644	1.1489	1.5483	0.0955	1.1244	0.73	588	6	777	9	1366	21
SAMPLES																	
HD02b	U (ppm)	Th (ppm)	Th/ U	²⁰⁷Pb (cps)	²⁰⁷Pb/ ²⁰⁶Pb	2s(%)	²⁰⁷Pb/ ²³⁵U	2s(%)	²⁰⁶Pb/ ²³⁸U	2s(%)	ρ	²⁰⁶Pb/ ²³⁸U	2s (abs)	²⁰⁷Pb/ ²³⁵U	2s(abs)	²⁰⁷Pb/ ²⁰⁶Pb	2s(abs)
HD02b-1	36	0	0.01	40363	0.3453	1.0246	22.2681	1.5763	0.4677	1.1979	0.76	2473	25	3195	18	3687	16
HD02b-2	39	0	0.00	32252	0.2789	1.0611	16.7938	1.5615	0.4367	1.1456	0.73	2336	22	2923	18	3357	17
HD02b-3	40	0	0.00	32108	0.2716	1.4348	16.2912	1.9032	0.4351	1.2505	0.66	2329	24	2894	21	3315	23
HD02b-4	29	6	0.22	43715	0.4259	1.0132	30.6359	2.1581	0.5217	1.9055	0.88	2706	42	3507	25	4003	15
HD02b-5	35	2	0.04	42898	0.3707	1.0077	24.7106	1.4654	0.4834	1.0640	0.73	2542	22	3297	17	3794	15
HD02b-6	32	5	0.15	43242	0.3931	1.0067	27.0543	1.4682	0.4991	1.0687	0.73	2610	23	3385	18	3883	15

HD02b-7	37	0	0.00	24270	0.2273	1.0129	13.0183	1.5604	0.4153	1.1870	0.76	2239	22	2681	17	3033	16
HD02b-8	28	0	0.00	22502	0.2690	1.0201	15.9941	1.5158	0.4312	1.1212	0.74	2311	22	2876	17	3300	16
HD02b-9	49	1	0.02	29841	0.2164	1.1511	12.1999	1.5373	0.4089	1.0189	0.66	2210	19	2620	17	2954	19
HD02b-10	40	2	0.04	43918	0.3425	1.0186	21.7592	1.5228	0.4608	1.1320	0.74	2443	23	3173	18	3674	16
HD02b-11	55	1	0.02	32278	0.2104	1.0397	11.7732	1.8997	0.4059	1.5899	0.84	2196	30	2587	20	2908	17
HD02b-12	34	3	0.08	42567	0.3703	1.0039	24.5897	1.4613	0.4816	1.0619	0.73	2534	22	3292	17	3793	15
HD02b-13	33	1	0.04	39597	0.3624	1.0157	23.7205	1.6615	0.4747	1.3149	0.79	2504	27	3257	19	3760	16
HD10a	U (ppm)	Th (ppm)	Th/ U	²⁰⁷Pb (cps)	²⁰⁷Pb/ ²⁰⁶Pb	2s(%)	²⁰⁷Pb/ ²³⁵U	2s(%)	²⁰⁶Pb/ ²³⁸U	2s(%)	ρ	²⁰⁶Pb/ ²³⁸U	2s (abs)	²⁰⁷Pb/ ²³⁵U	2s(abs)	²⁰⁷Pb/ ²⁰⁶Pb	2s(abs)
HD10a-1	65	0	0.00	31619	0.1776	1.0084	9.6530	1.5127	0.3942	1.1277	0.75	2142	21	2402	16	2631	17
HD10a-2	40	0	0.00	22548	0.2011	1.0556	11.0654	1.5126	0.3992	1.0834	0.72	2165	20	2529	16	2835	17
HD10a-3	42	0	0.00	23052	0.1991	1.0066	10.9643	1.5494	0.3994	1.1778	0.76	2166	22	2520	17	2819	17
HD10a-4	29	0	0.00	17886	0.2186	1.0134	12.1799	1.4456	0.4040	1.0310	0.71	2188	19	2618	16	2971	16
HD10a-5	24	0	0.00	15397	0.2235	1.0224	12.4826	1.4875	0.4050	1.0805	0.73	2192	20	2641	16	3006	17
HD10a-6	52	0	0.00	26200	0.1853	1.0064	10.0087	1.4397	0.3917	1.0295	0.72	2131	19	2436	16	2701	17
HD10a-7	48	0	0.00	24379	0.1890	1.0072	10.1720	1.4260	0.3903	1.0095	0.71	2124	18	2451	15	2734	17
HD10a-8	46	0	0.00	24083	0.1916	1.0074	10.3464	1.4356	0.3917	1.0229	0.71	2131	19	2466	16	2756	17
HD10a-9	43	0	0.00	22481	0.1897	1.0289	10.4439	1.5092	0.3993	1.1041	0.73	2166	20	2475	16	2739	17
HD10a-10	47	0	0.00	24178	0.1868	1.0131	10.1695	1.6365	0.3949	1.2852	0.79	2146	23	2450	17	2714	17
HD10a-11	49	0	0.00	25395	0.1873	1.0063	10.2166	1.4673	0.3956	1.0679	0.73	2149	20	2455	16	2719	17
HD10a-12	53	0	0.00	25889	0.1779	1.0154	9.6105	1.4775	0.3917	1.0732	0.73	2131	20	2398	16	2634	17
HD10a-13	49	0	0.00	24431	0.1823	1.0071	9.9005	1.4630	0.3939	1.0612	0.73	2141	19	2426	16	2674	17
HD10a-14	45	0	0.00	22641	0.1846	1.0456	10.0534	2.0240	0.3949	1.7329	0.86	2145	32	2440	21	2695	17
HD10a-15	53	0	0.00	25853	0.1840	1.0051	9.8464	1.4146	0.3882	0.9953	0.70	2115	18	2421	15	2689	17
HD10a-16	46	0	0.01	22805	0.1824	1.0134	9.8784	1.4534	0.3929	1.0418	0.72	2136	19	2423	16	2675	17
HD10a-17	46	0	0.00	22297	0.1796	1.0101	9.6828	1.4226	0.3910	1.0018	0.70	2128	18	2405	15	2649	17
HD10a-18	48	0	0.00	22839	0.1806	1.0104	9.6499	1.4491	0.3875	1.0388	0.72	2111	19	2402	16	2659	17
HD10a-19	54	0	0.00	27230	0.1837	1.0115	10.0505	1.4980	0.3969	1.1049	0.74	2155	20	2439	16	2686	17
HD10a-20	45	0	0.00	22129	0.1825	1.0285	9.8391	1.4482	0.3909	1.0196	0.70	2127	19	2420	16	2676	17

HD10b	U (ppm)	Th (ppm)	Th/ U	²⁰⁷Pb (cps)	²⁰⁷Pb/ ²⁰⁶Pb	2s(%)	²⁰⁷Pb/ ²³⁵U	2s(%)	²⁰⁶Pb/ ²³⁸U	2s(%)	ρ	²⁰⁶Pb/ ²³⁸U	2s (abs)	²⁰⁷Pb/ ²³⁵U	2s(abs)	²⁰⁷Pb/ ²⁰⁶Pb	2s(abs)
HD10b-1	45	0	0.00	23575	0.1880	1.0085	10.2578	1.4358	0.3958	1.0221	0.71	2150	19	2458	16	2724	17
HD10b-2	44	0	0.00	22805	0.1865	1.0133	10.1349	1.4401	0.3941	1.0232	0.71	2142	19	2447	16	2712	17
HD10b-3	74	0	0.00	34976	0.1745	1.0099	9.3268	1.5571	0.3877	1.1851	0.76	2112	21	2371	17	2601	17
HD10b-4	74	0	0.00	38626	0.1900	1.4113	10.3417	1.8327	0.3947	1.1691	0.64	2145	21	2466	19	2742	23
HD10b-5	41	0	0.00	23006	0.2008	1.0155	10.9996	1.4341	0.3974	1.0126	0.71	2157	19	2523	16	2832	17
HD10b-6	36	0	0.00	20220	0.2004	1.0212	10.9306	1.4889	0.3956	1.0835	0.73	2149	20	2517	16	2830	17
HD10b-7	94	0	0.00	46097	0.1784	1.0134	9.7105	1.7981	0.3949	1.4854	0.83	2145	27	2408	19	2638	17
HD10b-8	21	0	0.00	16218	0.2559	1.1083	14.7121	1.7470	0.4169	1.3504	0.77	2246	26	2797	19	3222	18
HD10b-9	68	0	0.00	32463	0.1764	1.0123	9.3982	1.4128	0.3863	0.9854	0.70	2106	18	2378	15	2620	17
HD10b-10	57	0	0.00	28800	0.1847	1.0168	9.9393	1.5204	0.3903	1.1304	0.74	2124	20	2429	16	2696	17
HD10b-11	64	0	0.00	30856	0.1784	1.0195	9.5494	1.4343	0.3882	1.0088	0.70	2114	18	2392	15	2638	17
HD10b-12	78	0	0.00	37181	0.1750	1.0061	9.3720	1.5398	0.3884	1.1657	0.76	2115	21	2375	16	2606	17
HD10b-13	79	0	0.00	37712	0.1730	1.0071	9.3362	1.4166	0.3914	0.9963	0.70	2130	18	2372	15	2587	17
HD10b-14	81	0	0.00	38947	0.1759	1.2250	9.3988	2.1504	0.3875	1.7673	0.82	2111	32	2378	22	2615	21
HD10b-15	54	0	0.00	28068	0.1870	1.0065	10.1233	1.5561	0.3926	1.1868	0.76	2135	22	2446	17	2716	17
HD14	U (ppm)	Th (ppm)	Th/ U	²⁰⁷Pb (cps)	²⁰⁷Pb/ ²⁰⁶Pb	2s(%)	²⁰⁷Pb/ ²³⁵U	2s(%)	²⁰⁶Pb/ ²³⁸U	2s(%)	ρ	²⁰⁶Pb/ ²³⁸U	2s (abs)	²⁰⁷Pb/ ²³⁵U	2s(abs)	²⁰⁷Pb/ ²⁰⁶Pb	2s(abs)
HD14-1	29	0	0.01	27326	0.2880	1.0373	17.0373	1.5985	0.4291	1.2162	0.76	2302	24	2937	18	3407	16
HD14-2	25	0	0.01	25511	0.3091	1.0226	18.7426	1.8760	0.4398	1.5728	0.84	2350	31	3029	21	3516	16
HD14-3	19	0	0.01	20262	0.3156	1.0288	19.3080	1.7902	0.4437	1.4651	0.82	2367	29	3057	20	3549	16

3.4 Table S7 – Sm-Nd data for monazite samples

PRIMARY REFERENCE MATERIAL

Steenkampskraal monazite	Ndtot (V)	¹⁴⁷Sm/¹⁴⁴Nd	±2s	¹⁴⁵Nd/¹⁴⁴Nd	¹⁴³Nd/¹⁴⁴Nd	±2s	¹⁴³Nd/¹⁴⁴Ndi	±2s	eNdi	±2s
Steen-1	52.6	0.0977	0.0004	0.34843	0.51189	0.00006	0.51122	0.00006	-1.6	0.8
Steen-2	53.3	0.0981	0.0006	0.34844	0.51190	0.00009	0.51123	0.00009	-1.4	1.1
Steen-3	54.5	0.0982	0.0005	0.34843	0.51189	0.00006	0.51123	0.00006	-1.5	0.8
Steen-4	52.9	0.0981	0.0004	0.34843	0.51190	0.00007	0.51123	0.00007	-1.5	0.9
Steen-5	53.7	0.0980	0.0005	0.34844	0.51191	0.00008	0.51124	0.00008	-1.3	1.0
Steen-6	50.7	0.0982	0.0006	0.34843	0.51190	0.00009	0.51123	0.00009	-1.4	1.2
Steen-7	49.8	0.0982	0.0006	0.34842	0.51191	0.00009	0.51124	0.00009	-1.2	1.2
Steen-8	52.0	0.0983	0.0006	0.34843	0.51191	0.00010	0.51125	0.00010	-1.1	1.3
Steen-9	52.3	0.0982	0.0006	0.34843	0.51187	0.00009	0.51121	0.00009	-1.9	1.1
Steen-10	52.1	0.0985	0.0006	0.34844	0.51193	0.00010	0.51127	0.00010	-0.8	1.3
Steen-11	69.1	0.1195	0.0008	0.34844	0.51223	0.00007	0.51189	0.00007	-3.9	0.9
Steen-12	71.0	0.1212	0.0006	0.34844	0.51227	0.00007	0.51194	0.00007	-3.0	0.9
Steen-13	65.7	0.1247	0.0006	0.34844	0.51217	0.00010	0.51183	0.00010	-5.1	1.2
Steen-14	65.2	0.1239	0.0005	0.34845	0.51222	0.00005	0.51188	0.00005	-4.2	0.7

SECONDARY REFERENCE MATERIAL

USGS 44069 monazite	Ndtot (V)	¹⁴⁷Sm/¹⁴⁴Nd	±2s	¹⁴⁵Nd/¹⁴⁴Nd	¹⁴³Nd/¹⁴⁴Nd	±2s	¹⁴³Nd/¹⁴⁴Ndi	±2s	eNdi	±2s
USGS 44069-1	65.5	0.1199	0.0012	0.34844	0.51221	0.00005	0.51187	0.00005	-4.2	0.7
USGS 44069-2	59.9	0.1225	0.0006	0.34855	0.51255	0.00015	0.51221	0.00015	2.2	1.8
USGS 44069-3	70.9	0.1214	0.0006	0.34844	0.51222	0.00006	0.51188	0.00006	-4.0	0.8
USGS 44069-4	70.7	0.1186	0.0004	0.34843	0.51219	0.00006	0.51186	0.00006	-4.4	0.8
USGS 44069-5	71.8	0.1180	0.0006	0.34844	0.51223	0.00007	0.51190	0.00007	-3.7	0.8
USGS 44069-6	71.3	0.1258	0.0006	0.34843	0.51226	0.00007	0.51191	0.00007	-3.5	0.9
Thompson Mine monazite	Ndtot (V)	¹⁴⁷Sm/¹⁴⁴Nd	±2s	¹⁴⁵Nd/¹⁴⁴Nd	¹⁴³Nd/¹⁴⁴Nd	±2s	¹⁴³Nd/¹⁴⁴Ndi	±2s	eNdi	±2s
TM-1	57.1	0.0949	0.0005	0.34844	0.51080	0.00006	0.50969	0.00006	-12.8	0.7

TM-2	53.9	0.0848	0.0006	0.34843	0.51072	0.00007	0.50973	0.00007	-12.0	0.8
TM-3	56.5	0.0933	0.0004	0.34844	0.51085	0.00007	0.50976	0.00007	-11.4	0.8
TM-4	55.6	0.0991	0.0006	0.34843	0.51089	0.00006	0.50973	0.00006	-11.9	0.8
TM-5	55.6	0.0925	0.0004	0.34843	0.51082	0.00006	0.50974	0.00006	-11.7	0.7
TM-6	55.4	0.1089	0.0008	0.34845	0.51092	0.00010	0.50965	0.00010	-13.5	1.3
TM-7	55.0	0.1101	0.0008	0.34843	0.51099	0.00011	0.50970	0.00011	-12.5	1.3
TM-8	60.3	0.0838	0.0005	0.34841	0.51064	0.00008	0.50966	0.00008	-13.4	1.0
TM-9	58.0	0.0972	0.0017	0.34842	0.51076	0.00008	0.50963	0.00008	-14.0	1.0
TM-10	59.1	0.0849	0.0005	0.34842	0.51069	0.00008	0.50970	0.00008	-12.6	1.0
Vermilion monazite	Ndtot (V)	$^{147}\text{Sm}/^{144}\text{Nd}$	$\pm 2s$	$^{145}\text{Nd}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2s$	$^{143}\text{Nd}/^{144}\text{Ndi}$	$\pm 2s$	eNdi	$\pm 2s$
Verm-1	60.1	0.0874	0.0005	0.34843	0.51070	0.00007	0.50916	0.00007	-0.4	0.9
Verm-2	59.2	0.0871	0.0004	0.34843	0.51067	0.00006	0.50914	0.00006	-0.8	0.7
Verm-3	59.1	0.0876	0.0005	0.34843	0.51067	0.00008	0.50912	0.00008	-1.1	0.9
Verm-4	60.5	0.0871	0.0004	0.34842	0.51071	0.00008	0.50918	0.00008	0.0	0.9
Verm-5	59.8	0.0865	0.0004	0.34843	0.51063	0.00006	0.50910	0.00006	-1.5	0.8
Verm-6	60.0	0.0867	0.0004	0.34842	0.51067	0.00008	0.50915	0.00008	-0.6	0.9
Verm-7	58.3	0.0889	0.0004	0.34844	0.51072	0.00007	0.50916	0.00007	-0.4	0.8
Verm-8	58.5	0.0872	0.0005	0.34844	0.51069	0.00008	0.50916	0.00008	-0.4	0.9
Verm-9	59.2	0.0886	0.0004	0.34844	0.51075	0.00007	0.50919	0.00007	0.2	0.8
Verm-10	58.5	0.0848	0.0004	0.34844	0.51068	0.00007	0.50919	0.00007	0.1	0.8
Bananeiro monazite	Ndtot (V)	$^{147}\text{Sm}/^{144}\text{Nd}$	$\pm 2s$	$^{145}\text{Nd}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2s$	$^{143}\text{Nd}/^{144}\text{Ndi}$	$\pm 2s$	eNdi	$\pm 2s$
Ban-1	56.9	0.2900	0.0017	0.34844	0.51280	0.00021	0.51185	0.00021	-2.8	2.5
Ban-2	57.2	0.2904	0.0022	0.34845	0.51285	0.00019	0.51190	0.00019	-1.8	2.3
Ban-3	58.3	0.2824	0.0048	0.34838	0.51279	0.00031	0.51187	0.00031	-2.4	3.6
Ban-4	57.6	0.2863	0.0027	0.34841	0.51276	0.00022	0.51183	0.00022	-3.3	2.7
Ban-5	58.2	0.2842	0.0035	0.34838	0.51285	0.00027	0.51192	0.00027	-1.5	3.5
Ban-6	56.6	0.2884	0.0015	0.34845	0.51283	0.00018	0.51189	0.00018	-2.1	2.2
Ban-7	56.0	0.2905	0.0016	0.34846	0.51291	0.00016	0.51196	0.00016	-0.8	2.1

Ban-8	55.7	0.2889	0.0027	0.34846	0.51296	0.00016	0.51202	0.00016	0.4	2.0
Ban-9	56.3	0.2875	0.0027	0.34843	0.51287	0.00025	0.51193	0.00025	-1.2	3.2
Ban-10	54.2	0.2880	0.0027	0.34847	0.51294	0.00022	0.51199	0.00022	0.0	2.8
Diamantina monazite	Ndtot (V)	$^{147}\text{Sm}/^{144}\text{Nd}$	$\pm 2s$	$^{145}\text{Nd}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2s$	$^{143}\text{Nd}/^{144}\text{Ndi}$	$\pm 2s$	eNdi	$\pm 2s$
Dia-1	59.2	0.1180	0.0006	0.34845	0.51145	0.00010	0.51107	0.00010	-18.2	1.2
Dia-2	58.4	0.1186	0.0006	0.34843	0.51141	0.00009	0.51103	0.00009	-19.0	1.1
Dia-3	58.9	0.1183	0.0007	0.34843	0.51140	0.00010	0.51102	0.00010	-19.2	1.2
Dia-4	57.2	0.1186	0.0007	0.34843	0.51148	0.00009	0.51110	0.00009	-17.7	1.2
Dia-5	58.0	0.1188	0.0006	0.34843	0.51141	0.00009	0.51102	0.00009	-19.1	1.1
Dia-6	58.7	0.1188	0.0005	0.34843	0.51144	0.00007	0.51105	0.00007	-18.5	0.8
Dia-7	58.7	0.1184	0.0006	0.34843	0.51141	0.00007	0.51103	0.00007	-19.0	0.9
Dia-8	58.6	0.1188	0.0006	0.34844	0.51144	0.00009	0.51106	0.00009	-18.4	1.1
Dia-9	59.3	0.1186	0.0005	0.34843	0.51144	0.00009	0.51105	0.00009	-18.5	1.1
Dia-10	58.0	0.1186	0.0005	0.34844	0.51144	0.00007	0.51106	0.00007	-18.4	0.9
SAMPLES										
HD02b	Ndtot (V)	$^{147}\text{Sm}/^{144}\text{Nd}$	$\pm 2s$	$^{145}\text{Nd}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2s$	$^{143}\text{Nd}/^{144}\text{Ndi}$	$\pm 2s$	eNdi	$\pm 2s$
HD02b - 1	67.5	0.1175	0.0007	0.34843	0.51094	0.00010	0.50883	0.00010	-5.7	1.2
HD02b - 2	65.1	0.1172	0.0007	0.34843	0.51095	0.00010	0.50886	0.00010	-5.2	1.2
HD02b - 3	44.3	0.1210	0.0028	0.34871	0.51128	0.00038	0.50911	0.00038	-0.2	4.4
HD02b - 4	66.2	0.1137	0.0006	0.34843	0.51097	0.00009	0.50893	0.00009	-3.7	1.1
HD02b - 5	67.0	0.1156	0.0008	0.34842	0.51096	0.00009	0.50889	0.00009	-4.6	1.1
HD02b - 6	68.2	0.1192	0.0007	0.34845	0.51113	0.00009	0.50899	0.00009	-2.5	1.2
HD02b - 7	62.2	0.0999	0.0006	0.34844	0.51072	0.00009	0.50893	0.00009	-3.8	1.2
HD02b - 8	65.3	0.1170	0.0006	0.34845	0.51101	0.00010	0.50892	0.00010	-4.0	1.2
HD10a	Ndtot (V)	$^{147}\text{Sm}/^{144}\text{Nd}$	$\pm 2s$	$^{145}\text{Nd}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2s$	$^{143}\text{Nd}/^{144}\text{Ndi}$	$\pm 2s$	eNdi	$\pm 2s$
HD10a-1	66.5	0.1151	0.0006	0.34845	0.51102	0.00008	0.50896	0.00008	-3.2	1.0
HD10a-2	66.0	0.1119	0.0007	0.34843	0.51092	0.00011	0.50892	0.00011	-4.1	1.3

HD10a-3	60.3	0.1096	0.0006	0.34844	0.51087	0.00010	0.50890	0.00010	-4.0	1.2
HD10a-4	61.8	0.1117	0.0006	0.34844	0.51093	0.00008	0.50891	0.00008	-3.6	1.0
HD10a-5	63.7	0.1107	0.0006	0.34843	0.51088	0.00007	0.50889	0.00007	-4.1	0.8
HD10a-6	64.2	0.1112	0.0007	0.34843	0.51089	0.00009	0.50888	0.00009	-4.2	1.1
HD10a-7	61.4	0.1204	0.0007	0.34846	0.51119	0.00011	0.50902	0.00011	-1.5	1.3
HD10a-8	65.4	0.1090	0.0006	0.34842	0.51085	0.00009	0.50890	0.00009	-4.4	1.2
HD10a-9	61.8	0.1087	0.0006	0.34843	0.51089	0.00010	0.50894	0.00010	-3.5	1.2
HD10a-10	61.7	0.1109	0.0006	0.34843	0.51088	0.00006	0.50890	0.00006	-4.4	0.8
HD14	Ndtot (V)	$^{147}\text{Sm}/^{144}\text{Nd}$	$\pm 2s$	$^{145}\text{Nd}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2s$	$^{143}\text{Nd}/^{144}\text{Ndi}$	$\pm 2s$	eNdi	$\pm 2s$
HD14-1	61.4	0.1088	0.0005	0.34842	0.51083	0.00008	0.50888	0.00008	-4.8	1.0
HD14-2	63.2	0.1099	0.0006	0.34844	0.51087	0.00009	0.50890	0.00009	-4.4	1.2
HD14-3	67.8	0.1094	0.0006	0.34843	0.51088	0.00007	0.50891	0.00007	-3.5	0.9
HD14-4	66.9	0.1167	0.0007	0.34843	0.51094	0.00009	0.50883	0.00009	-5.0	1.1
HD14-5	64.1	0.1271	0.0008	0.34842	0.51117	0.00008	0.50887	0.00008	-4.1	1.0
HD14-6	60.8	0.1173	0.0013	0.34844	0.51100	0.00009	0.50888	0.00009	-3.9	1.1
HD14-7	67.5	0.1144	0.0006	0.34843	0.51097	0.00009	0.50890	0.00009	-3.7	1.1
HD14-8	66.1	0.1051	0.0009	0.34843	0.51074	0.00007	0.50886	0.00007	-5.1	0.9
HD14-9	68.5	0.1076	0.0006	0.34843	0.51088	0.00007	0.50895	0.00007	-3.3	0.9
HD14-10	67.4	0.1291	0.0007	0.34845	0.51121	0.00010	0.50890	0.00010	-4.4	1.2
HD14-11	67.5	0.1243	0.0008	0.34844	0.51118	0.00012	0.50896	0.00012	-3.2	1.4
HD14-12	62.7	0.1211	0.0007	0.34843	0.51113	0.00010	0.50896	0.00010	-3.1	1.3

3.5 Table S8 – Sm-Nd data for apatite samples

PRIMARY REFERENCE MATERIAL										
Madagascar blue apatite	Ndtot (V)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	±2s	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	±2s	¹⁴³ Nd/ ¹⁴⁴ Ndi	±2s	eNdi	±2s
MAD blue-1	0.9	0.0785	0.0002	0.34840	0.51123	0.00012	0.51098	0.00012	-20.1	1.9
MAD blue-2	0.9	0.0785	0.0002	0.34836	0.51131	0.00010	0.51106	0.00010	-18.7	1.7
MAD blue-3	0.9	0.0784	0.0002	0.34839	0.51136	0.00009	0.51111	0.00009	-17.7	1.4
MAD blue-4	0.9	0.0782	0.0002	0.34848	0.51106	0.00012	0.51081	0.00012	-23.4	2.0
MAD blue-5	0.9	0.0781	0.0002	0.34836	0.51133	0.00007	0.51109	0.00007	-18.3	1.1
MAD blue-6	1.0	0.0780	0.0002	0.34839	0.51135	0.00006	0.51111	0.00006	-17.9	1.0
MAD blue-7	1.0	0.0783	0.0002	0.34844	0.51128	0.00007	0.51104	0.00007	-19.3	1.1
MAD blue-8	1.0	0.0783	0.0002	0.34856	0.51138	0.00008	0.51113	0.00008	-17.4	1.2
MAD blue-9	1.0	0.0784	0.0002	0.34831	0.51140	0.00008	0.51116	0.00008	-17.0	1.3
MAD blue-10	0.9	0.0783	0.0002	0.34840	0.51131	0.00012	0.51106	0.00012	-18.6	1.9
MAD blue-11	0.9	0.0783	0.0002	0.34836	0.51138	0.00010	0.51113	0.00010	-17.2	1.7
MAD blue-12	0.9	0.0781	0.0002	0.34839	0.51144	0.00009	0.51119	0.00009	-16.1	1.4
MAD blue-13	0.9	0.0779	0.0002	0.34848	0.51114	0.00012	0.51089	0.00012	-21.9	2.0
MAD blue-14	0.9	0.0785	0.0002	0.34840	0.51131	0.00007	0.51107	0.00007	-18.8	1.1
MAD blue-15	0.9	0.0785	0.0002	0.34836	0.51138	0.00006	0.51114	0.00006	-17.3	1.0
MAD blue-16	0.9	0.0784	0.0002	0.34839	0.51144	0.00005	0.51119	0.00005	-16.3	0.8
MAD blue-17	0.9	0.0782	0.0002	0.34848	0.51114	0.00007	0.51090	0.00007	-22.1	1.2
MAD blue-18	0.9	0.0781	0.0002	0.34841	0.51142	0.00007	0.51117	0.00007	-16.7	1.2
SECONDARY REFERENCE MATERIAL										
401 apatite	Ndtot (V)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	±2s	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	±2s	¹⁴³ Nd/ ¹⁴⁴ Ndi	±2s	eNdi	±2s
401-1	2.5	0.0840	0.0001	0.34841	0.51226	0.00004	0.51198	0.00004	0.0	0.6
401-2	2.4	0.0841	0.0001	0.34843	0.51219	0.00004	0.51191	0.00004	-1.4	0.6
401-3	2.4	0.0843	0.0001	0.34844	0.51216	0.00004	0.51188	0.00004	-2.0	0.6
401-4	4.2	0.0813	0.0006	0.34838	0.51225	0.00005	0.51198	0.00005	-0.2	0.7
401-5	2.4	0.0843	0.0001	0.34842	0.51230	0.00005	0.51202	0.00005	0.8	0.8

401-6	2.2	0.0847	0.0002	0.34840	0.51217	0.00004	0.51189	0.00004	-1.8	0.6
401-7	2.3	0.0846	0.0001	0.34842	0.51214	0.00003	0.51186	0.00003	-2.4	0.6
401-8	2.1	0.0851	0.0002	0.34838	0.51228	0.00004	0.51200	0.00004	0.3	0.7
401-9	2.3	0.0844	0.0001	0.34835	0.51232	0.00004	0.51204	0.00004	1.0	0.7
401-10	2.1	0.0853	0.0001	0.34839	0.51229	0.00003	0.51201	0.00003	0.5	0.6
401-11	2.0	0.0851	0.0002	0.34839	0.51228	0.00006	0.51200	0.00006	0.3	0.9
401-12	2.1	0.0846	0.0002	0.34835	0.51220	0.00003	0.51192	0.00003	-1.3	0.5
401-13	2.1	0.0846	0.0002	0.34843	0.51216	0.00004	0.51188	0.00004	-2.1	0.7
401-14	2.1	0.0844	0.0001	0.34841	0.51219	0.00004	0.51191	0.00004	-1.5	0.6
401-15	2.1	0.0850	0.0001	0.34840	0.51226	0.00005	0.51198	0.00005	-0.1	0.8
Bear Lake titanite	Ndtot (V)	¹⁴⁷Sm/¹⁴⁴Nd	±2s	¹⁴⁵Nd/¹⁴⁴Nd	¹⁴³Nd/¹⁴⁴Nd	±2s	¹⁴³Nd/¹⁴⁴Ndi	±2s	eNdi	±2s
BL-1	1.0	0.1282	0.0003	0.34841	0.51235	0.00008	0.51145	0.00008	3.7	1.3
BL-2	0.9	0.1277	0.0003	0.34831	0.51232	0.00009	0.51143	0.00009	3.3	1.4
BL-3	0.9	0.1277	0.0003	0.34835	0.51242	0.00008	0.51153	0.00008	5.2	1.2
BL-4	0.9	0.1279	0.0003	0.34838	0.51224	0.00007	0.51134	0.00007	1.6	1.2
BL-5	0.9	0.1276	0.0002	0.34840	0.51241	0.00008	0.51152	0.00008	5.0	1.3
BL-6	0.9	0.1281	0.0003	0.34841	0.51220	0.00009	0.51131	0.00009	0.8	1.4
BL-7	0.8	0.1281	0.0003	0.34846	0.51225	0.00009	0.51135	0.00009	1.7	1.5
BL-8	0.9	0.1281	0.0002	0.34838	0.51228	0.00006	0.51139	0.00006	2.4	1.0
BL-9	0.8	0.1283	0.0003	0.34842	0.51233	0.00009	0.51143	0.00009	3.3	1.4
BL-10	0.8	0.1281	0.0003	0.34836	0.51242	0.00007	0.51153	0.00007	5.1	1.1
BL-11	0.8	0.1284	0.0002	0.34849	0.51233	0.00007	0.51143	0.00007	3.3	1.1
BL-12	0.9	0.1284	0.0002	0.34843	0.51237	0.00008	0.51147	0.00008	4.0	1.3
BL-13	0.9	0.1281	0.0002	0.34836	0.51231	0.00008	0.51141	0.00008	3.0	1.3
BL-14	0.9	0.1284	0.0002	0.34842	0.51232	0.00007	0.51142	0.00007	3.2	1.1
Khan River titanite	Ndtot (V)	¹⁴⁷Sm/¹⁴⁴Nd	±2s	¹⁴⁵Nd/¹⁴⁴Nd	¹⁴³Nd/¹⁴⁴Nd	±2s	¹⁴³Nd/¹⁴⁴Ndi	±2s	eNdi	±2s
KR-1	1.3	0.1247	0.0003	0.34840	0.51154	0.00006	0.51111	0.00006	-16.8	1.0
KR-2	1.2	0.1246	0.0003	0.34845	0.51150	0.00007	0.51108	0.00007	-17.4	1.2

KR-3	1.2	0.1246	0.0002	0.34839	0.51153	0.00006	0.51111	0.00006	-17.0	0.9
KR-4	1.3	0.1248	0.0002	0.34846	0.51155	0.00007	0.51113	0.00007	-16.5	1.2
KR-5	1.3	0.1246	0.0003	0.34843	0.51168	0.00006	0.51126	0.00006	-13.9	1.0
KR-6	1.1	0.1253	0.0002	0.34847	0.51148	0.00005	0.51106	0.00005	-17.9	0.8
KR-7	1.2	0.1254	0.0002	0.34843	0.51164	0.00007	0.51122	0.00007	-14.7	1.1
KR-8	1.2	0.1255	0.0002	0.34842	0.51170	0.00006	0.51128	0.00006	-13.6	0.9
KR-9	1.2	0.1251	0.0002	0.34844	0.51154	0.00005	0.51112	0.00005	-16.8	0.8
KR-10	1.2	0.1248	0.0002	0.34842	0.51153	0.00006	0.51111	0.00006	-16.9	0.9
KR-11	1.2	0.1256	0.0003	0.34841	0.51159	0.00007	0.51116	0.00007	-15.8	1.1
KR-12	1.2	0.1254	0.0002	0.34845	0.51166	0.00007	0.51123	0.00007	-14.5	1.1
KR-13	1.1	0.1256	0.0002	0.34842	0.51164	0.00005	0.51122	0.00005	-14.8	0.8
KR-14	1.1	0.1254	0.0003	0.34842	0.51157	0.00004	0.51115	0.00004	-16.1	0.6
KR-15	1.1	0.1252	0.0002	0.34843	0.51163	0.00006	0.51121	0.00006	-15.0	0.9
Madagascar green apatite	Ndtot (V)	¹⁴⁷Sm/¹⁴⁴Nd	±2s	¹⁴⁵Nd/¹⁴⁴Nd	¹⁴³Nd/¹⁴⁴Nd	±2s	¹⁴³Nd/¹⁴⁴Ndi	±2s	eNdi	±2s
MAD G-1	1.1	0.0813	0.0002	0.34834	0.51134	0.00007	0.51108	0.00007	-18.4	1.1
MAD G-2	1.1	0.0812	0.0002	0.34842	0.51127	0.00006	0.51102	0.00006	-19.6	1.0
MAD G-3	1.1	0.0812	0.0002	0.34845	0.51119	0.00008	0.51094	0.00008	-21.2	1.3
MAD G-4	1.1	0.0815	0.0002	0.34842	0.51123	0.00006	0.51098	0.00006	-20.4	0.9
MAD G-5	1.1	0.0814	0.0002	0.34841	0.51124	0.00005	0.51099	0.00005	-20.2	0.8
MAD G-6	1.1	0.0814	0.0002	0.34847	0.51139	0.00006	0.51114	0.00006	-17.4	1.0
MAD G-7	1.0	0.0814	0.0002	0.34844	0.51137	0.00006	0.51112	0.00006	-17.8	1.0
MAD G-8	1.0	0.0811	0.0002	0.34836	0.51136	0.00007	0.51110	0.00007	-18.0	1.1
MAD G-9	1.0	0.0812	0.0002	0.34845	0.51125	0.00007	0.51100	0.00007	-20.0	1.1
MAD G-10	1.0	0.0809	0.0003	0.34837	0.51133	0.00008	0.51108	0.00008	-18.5	1.3
Durango apatite	Ndtot (V)	¹⁴⁷Sm/¹⁴⁴Nd	±2s	¹⁴⁵Nd/¹⁴⁴Nd	¹⁴³Nd/¹⁴⁴Nd	±2s	¹⁴³Nd/¹⁴⁴Ndi	±2s	eNdi	±2s
Dur-1	1.4	0.0873	0.0002	0.34840	0.51248	0.00004	0.51246	0.00004	-2.6	0.7
Dur-2	1.4	0.0875	0.0002	0.34836	0.51246	0.00005	0.51244	0.00005	-3.0	0.9
Dur-3	1.4	0.0871	0.0002	0.34836	0.51237	0.00005	0.51235	0.00005	-4.8	0.9

Dur-4	1.3	0.0867	0.0002	0.34838	0.51240	0.00006	0.51238	0.00006	-4.1	0.9
Dur-5	1.3	0.0865	0.0002	0.34844	0.51233	0.00006	0.51232	0.00006	-5.5	0.9
Dur-6	1.3	0.0864	0.0002	0.34839	0.51243	0.00006	0.51241	0.00006	-3.6	0.9
Dur-7	1.3	0.0861	0.0002	0.34841	0.51243	0.00007	0.51241	0.00007	-3.6	1.1
Dur-8	1.3	0.0857	0.0002	0.34835	0.51243	0.00004	0.51241	0.00004	-3.6	0.7
Dur-9	1.3	0.0852	0.0002	0.34835	0.51245	0.00005	0.51243	0.00005	-3.3	0.8
Dur-10	1.3	0.0851	0.0002	0.34850	0.51243	0.00006	0.51241	0.00006	-3.6	1.0
Dur-11	1.3	0.0850	0.0002	0.34840	0.51237	0.00006	0.51235	0.00006	-4.7	0.9

SAMPLES

HD02b	Ndtot (V)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	±2s	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	±2s	¹⁴³ Nd/ ¹⁴⁴ Ndi	±2s	eNdi	±2s	
HD02b-1	0.4	0.2982	0.0011	0.34850	0.51404	0.00017	0.50871	0.00017	-8.1	2.8	
HD02b-2	0.6	0.2123	0.0007	0.34824	0.51271	0.00010	0.50892	0.00010	-4.0	1.6	
HD02b-3	0.5	0.2927	0.0047	0.34834	0.51404	0.00030	0.50880	0.00030	-6.3	4.8	
HD02b-4	0.4	0.3535	0.0023	0.34820	0.51509	0.00075	0.50877	0.00075	-6.9	12.1	
HD02b-5	0.4	0.3004	0.0005	0.34835	0.51420	0.00011	0.50882	0.00011	-5.9	1.7	
HD02b-6	0.7	0.1750	0.0028	0.34849	0.51422	0.00008	0.51109	0.00008	38.6	1.2	outlier
HD02b-7	0.5	0.2426	0.0004	0.34819	0.51361	0.00009	0.50927	0.00009	2.9	1.4	
HD02b-8	0.3	0.3553	0.0013	0.34850	0.51459	0.00016	0.50824	0.00016	-17.3	2.6	*
HD02b-9	0.3	0.3557	0.0008	0.34840	0.51537	0.00023	0.50901	0.00023	-2.2	3.8	
HD10a	Ndtot (V)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	±2s	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	±2s	¹⁴³ Nd/ ¹⁴⁴ Ndi	±2s	eNdi	±2s	
HD10a-1	0.2	0.3015	0.0006	0.34848	0.51404	0.00021	0.50859	0.00021	-9.7	3.4	
HD10a-2	0.2	0.3836	0.0019	0.34834	0.51574	0.00020	0.50880	0.00020	-5.5	3.2	
HD10a-3	0.3	0.3807	0.0009	0.34872	0.51561	0.00020	0.50873	0.00020	-6.9	3.3	
HD10a-4	0.2	0.4013	0.0010	0.34827	0.51565	0.00019	0.50839	0.00019	-13.6	3.1	*
HD10a-5	0.4	0.3689	0.0025	0.34838	0.51547	0.00019	0.50880	0.00019	-5.6	3.0	
HD10a-6	0.2	0.3179	0.0019	0.34805	0.51546	0.00025	0.50971	0.00025	12.4	4.1	outlier
HD10a-7	0.2	0.3681	0.0016	0.34831	0.51596	0.00028	0.50930	0.00028	4.3	4.6	outlier
HD10a-8	0.3	0.3773	0.0014	0.34834	0.51564	0.00018	0.50882	0.00018	-5.1	2.8	

HD10a-9	0.2	0.3870	0.0011	0.34840	0.51569	0.00028	0.50869	0.00028	-7.7	4.5	
HD10b	Ndtot (V)	¹⁴⁷Sm/¹⁴⁴Nd	±2s	¹⁴⁵Nd/¹⁴⁴Nd	¹⁴³Nd/¹⁴⁴Nd	±2s	¹⁴³Nd/¹⁴⁴Ndi	±2s	eNdi	±2s	
HD10b-1	0.7	0.3960	0.0080	0.34843	0.51556	0.00027	0.50840	0.00027	-13.4	4.3	*
HD10b-2	0.3	0.3777	0.0009	0.34858	0.51524	0.00018	0.50841	0.00018	-13.2	3.0	*
HD10b-3	0.3	0.2578	0.0094	0.34852	0.51277	0.00029	0.50811	0.00029	-19.1	4.6	*
HD10b-4	0.3	0.4020	0.0013	0.34851	0.51554	0.00020	0.50827	0.00020	-16.0	3.2	*
HD10b-5	0.3	0.4041	0.0013	0.34851	0.51552	0.00020	0.50822	0.00020	-17.0	3.2	*
~~HD10b-6~~	~~0.2~~	~~0.4315~~	~~0.0007~~	~~0.34868~~	~~0.51526~~	~~0.00021~~	~~0.50746~~	~~0.00021~~	~~-31.9~~	~~3.4~~	outlier
~~HD10b-7~~	~~0.2~~	~~0.4311~~	~~0.0010~~	~~0.34821~~	~~0.51563~~	~~0.00026~~	~~0.50783~~	~~0.00026~~	~~-24.6~~	~~4.2~~	outlier
HD10b-8	0.3	0.3871	0.0008	0.34841	0.51536	0.00018	0.50836	0.00018	-14.2	2.9	*
HD10b-9	0.3	0.3834	0.0009	0.34854	0.51542	0.00019	0.50849	0.00019	-11.7	3.1	*
HD10b-10	0.9	0.3736	0.0246	0.34844	0.51496	0.00034	0.50820	0.00034	-17.3	5.6	*
HD10b-11	0.2	0.4052	0.0013	0.34832	0.51576	0.00041	0.50843	0.00041	-12.7	6.6	*

Note: the spots with * represents the population that plots below the main isochron

3.6 Table S9 – Sr-Sr data for apatite samples

PRIMARY REFERENCE MATERIAL

NIST 610 glass	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{s}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{s}$	$^{84}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{s}$	$^{84}\text{Sr}/^{88}\text{Sr}$	$\pm 2\text{s}$
NIST610-1	0.7091	0.0011	0.7091	0.0011	0.0570	0.0007	0.0068	0.0001
NIST610-2	0.7089	0.0010	0.7089	0.0010	0.0564	0.0009	0.0067	0.0001
NIST610-3	0.7088	0.0007	0.7088	0.0007	0.0562	0.0005	0.0067	0.0001
NIST610-4	0.7092	0.0009	0.7092	0.0009	0.0562	0.0005	0.0067	0.0001
NIST610-5	0.7091	0.0003	0.7091	0.0003	0.0566	0.0004	0.0068	0.0001
NIST610-6	0.7092	0.0005	0.7092	0.0005	0.0564	0.0004	0.0067	0.0000
NIST610-7	0.7091	0.0006	0.7091	0.0006	0.0563	0.0006	0.0067	0.0001
NIST610-8	0.7092	0.0004	0.7092	0.0004	0.0565	0.0004	0.0067	0.0001
NIST610-9	0.7092	0.0022	0.7092	0.0022	0.0557	0.0057	0.0066	0.0007
NIST610-10	0.7095	0.0038	0.7095	0.0038	0.0560	0.0049	0.0067	0.0006
NIST610-11	0.7091	0.0006	0.7091	0.0006	0.0562	0.0012	0.0067	0.0001
NIST610-12	0.7091	0.0006	0.7091	0.0006	0.0566	0.0008	0.0068	0.0001
NIST610-13	0.7092	0.0007	0.7092	0.0007	0.0561	0.0006	0.0067	0.0001
NIST610-14	0.7090	0.0005	0.7090	0.0005	0.0561	0.0005	0.0067	0.0001
NIST610-15	0.7091	0.0005	0.7091	0.0005	0.0567	0.0004	0.0068	0.0000
NIST610-16	0.7092	0.0003	0.7092	0.0003	0.0562	0.0005	0.0067	0.0001
NIST610-17	0.7095	0.0011	0.7095	0.0011	0.0547	0.0019	0.0065	0.0002
NIST610-18	0.7089	0.0006	0.7089	0.0006	0.0557	0.0010	0.0067	0.0001
NIST610-19	0.7090	0.0021	0.7090	0.0021	0.0560	0.0012	0.0067	0.0001
NIST610-20	0.7091	0.0011	0.7091	0.0011	0.0560	0.0010	0.0067	0.0001

SECONDARY REFERENCE MATERIAL

Beleminite	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{s}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{s}$	$^{84}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{s}$	$^{84}\text{Sr}/^{88}\text{Sr}$	$\pm 2\text{s}$
Bele-1	0.7070	0.0010	0.7070	0.0010	0.0565	0.0003	0.0067	0.0000
Bele-2	0.7071	0.0010	0.7071	0.0010	0.0567	0.0004	0.0068	0.0001
Bele-3	0.7070	0.0011	0.7070	0.0011	0.0576	0.0014	0.0069	0.0002
Bele-4	0.7073	0.0006	0.7073	0.0006	0.0564	0.0010	0.0067	0.0001

Bele-5	0.7070	0.0004	0.7070	0.0004	0.0574	0.0005	0.0068	0.0001
Bele-6	0.7070	0.0012	0.7070	0.0012	0.0560	0.0010	0.0067	0.0001
Madagascar green	$^{87}\text{Sr}/^{86}\text{Sr}_i$	$\pm 2s$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2s$	$^{84}\text{Sr}/^{86}\text{Sr}$	$\pm 2s$	$^{84}\text{Sr}/^{88}\text{Sr}$	$\pm 2s$
Mad green-1	0.7118	0.0031	0.7118	0.0031	0.0565	0.0005	0.0067	0.0001
Mad green-2	0.7119	0.0008	0.7119	0.0008	0.0566	0.0005	0.0068	0.0001
Mad green-3	0.7118	0.0006	0.7118	0.0006	0.0560	0.0008	0.0067	0.0001
Mad green-4	0.7118	0.0014	0.7118	0.0014	0.0565	0.0010	0.0067	0.0001
Mad green-5	0.7119	0.0008	0.7119	0.0008	0.0569	0.0011	0.0068	0.0001
Mad green-6	0.7119	0.0013	0.7119	0.0013	0.0561	0.0007	0.0067	0.0001
MIR	$^{87}\text{Sr}/^{86}\text{Sr}_i$	$\pm 2s$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2s$	$^{84}\text{Sr}/^{86}\text{Sr}$	$\pm 2s$	$^{84}\text{Sr}/^{88}\text{Sr}$	$\pm 2s$
MIR-1	0.7030	0.0020	0.7030	0.0020	0.0548	0.0018	0.0065	0.0002
MIR-2	0.7031	0.0013	0.7031	0.0013	0.0546	0.0010	0.0065	0.0001
MIR-3	0.7032	0.0024	0.7032	0.0024	0.0551	0.0013	0.0066	0.0002
MIR-4	0.7030	0.0010	0.7030	0.0010	0.0561	0.0004	0.0067	0.0001
MIR-5	0.7030	0.0009	0.7030	0.0009	0.0552	0.0011	0.0066	0.0001
MIR-6	0.7032	0.0012	0.7032	0.0012	0.0571	0.0018	0.0068	0.0002
MIR-7	0.7030	0.0007	0.7030	0.0007	0.0564	0.0008	0.0067	0.0001
MIR-8	0.7030	0.0006	0.7030	0.0006	0.0558	0.0004	0.0067	0.0000
MIR-9	0.7029	0.0011	0.7029	0.0011	0.0559	0.0008	0.0067	0.0001
MIR-10	0.7030	0.0005	0.7030	0.0005	0.0556	0.0004	0.0066	0.0001
TUB	$^{87}\text{Sr}/^{86}\text{Sr}_i$	$\pm 2s$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2s$	$^{84}\text{Sr}/^{86}\text{Sr}$	$\pm 2s$	$^{84}\text{Sr}/^{88}\text{Sr}$	$\pm 2s$
TUB-1	0.7088	0.0004	0.7088	0.0004	0.0563	0.0003	0.0067	0.0000
TUB-2	0.7088	0.0008	0.7088	0.0008	0.0563	0.0001	0.0067	0.0000
TUB-3	0.7088	0.0006	0.7088	0.0006	0.0562	0.0005	0.0067	0.0001
TUB-4	0.7089	0.0005	0.7089	0.0005	0.0555	0.0011	0.0066	0.0001
TUB-5	0.7087	0.0010	0.7087	0.0010	0.0562	0.0010	0.0067	0.0001

SAMPLES

HD02b	⁸⁷ Sr/ ⁸⁶ Sr	±2s	⁸⁷ Sr/ ⁸⁶ Sr	±2s	⁸⁴ Sr/ ⁸⁶ Sr	±2s	⁸⁴ Sr/ ⁸⁸ Sr	±2s	
HD02b-1	0.7129	0.0017	0.7129	0.0017	0.0547	0.0015	0.0065	0.0002	
HD02b-2	0.7067	0.0024	0.7067	0.0024	0.0547	0.0021	0.0065	0.0003	
HD02b-3	0.7119	0.0017	0.7119	0.0017	0.0549	0.0016	0.0066	0.0002	
HD02b-4	0.7139	0.0009	0.7139	0.0009	0.0557	0.0011	0.0067	0.0001	
HD02b-5	0.7146	0.0016	0.7146	0.0016	0.0544	0.0015	0.0065	0.0002	
HD02b-6	0.7091	0.0013	0.7091	0.0013	0.0557	0.0014	0.0067	0.0002	
HD02b-7	0.7142	0.0013	0.7142	0.0013	0.0555	0.0015	0.0066	0.0002	
HD02b-8	0.7147	0.0015	0.7147	0.0015	0.0547	0.0011	0.0065	0.0001	
HD010a	⁸⁷ Sr/ ⁸⁶ Sr	±2s	⁸⁷ Sr/ ⁸⁶ Sr	±2s	⁸⁴ Sr/ ⁸⁶ Sr	±2s	⁸⁴ Sr/ ⁸⁸ Sr	±2s	
HD10a-1	0.5293	0.0507	0.5293	0.0507	2.2563	4.8424	-0.2694	0.5781	outlier
HD10a-2	0.6186	0.1613	0.6186	0.1613	-0.5654	0.4160	-0.0675	0.0497	outlier
HD10a-3	0.7178	0.0020	0.7178	0.0020	0.0558	0.0023	0.0067	0.0003	
HD10a-4	0.7129	0.0017	0.7129	0.0017	0.0537	0.0020	0.0064	0.0002	
HD10a-5	0.7152	0.0023	0.7152	0.0023	0.0547	0.0023	0.0065	0.0003	spot excluded only in the figure comparing the Sr-Nd data
HD10a-6	0.7137	0.0025	0.7137	0.0025	0.0529	0.0025	0.0063	0.0003	
HD10a-7	0.7391	0.0059	0.7391	0.0059	0.0547	0.0029	0.0065	0.0003	outlier
HD10a-8	0.7175	0.0018	0.7175	0.0018	0.0582	0.0015	0.0070	0.0002	
HD10a-9	0.7261	0.0027	0.7261	0.0027	0.0550	0.0016	0.0066	0.0002	outlier
HD10a-10	0.7028	0.0035	0.7028	0.0035	0.0489	0.0040	0.0058	0.0005	outlier
HD10a-11	0.7209	0.0037	0.7209	0.0037	0.0541	0.0025	0.0065	0.0003	outlier
HD010b	⁸⁷ Sr/ ⁸⁶ Sr	±2s	⁸⁷ Sr/ ⁸⁶ Sr	±2s	⁸⁴ Sr/ ⁸⁶ Sr	±2s	⁸⁴ Sr/ ⁸⁸ Sr	±2s	
HD10b-1	0.7180	0.0064	0.7180	0.0064	0.0544	0.0050	0.0065	0.0006	outlier
HD10b-2	0.7123	0.0020	0.7123	0.0020	0.0523	0.0018	0.0062	0.0002	
HD10b-3	0.7033	0.0027	0.7033	0.0027	0.0501	0.0034	0.0060	0.0004	
HD10b-4	0.7081	0.0022	0.7081	0.0022	0.0561	0.0012	0.0067	0.0001	
HD10b-5	0.7176	0.0020	0.7176	0.0020	0.0517	0.0020	0.0062	0.0002	
HD10b-6	0.7089	0.0025	0.7089	0.0025	0.0512	0.0031	0.0061	0.0004	
HD10b-7	0.7097	0.0025	0.7097	0.0025	0.0527	0.0030	0.0063	0.0004	
HD10b-8	0.7240	0.0020	0.7240	0.0020	0.0543	0.0018	0.0065	0.0002	outlier
HD10b-9	0.7076	0.0019	0.7076	0.0019	0.0530	0.0018	0.0063	0.0002	