



Universidade de Brasília

Instituto de Geociências

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Petrologia de xenólitos mantélicos do kimberlito Canastra-1, SW do Cráton do São Francisco: química mineral e geoquímica isotópica (Sr-Nd e gases nobres)

Petrology of mantle xenoliths from the Canastra-1 kimberlite, SW of the São Francisco Craton: mineral chemistry and isotopic geochemistry (Sr-Nd and noble gases)

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Tese de doutorado N° 213

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LUIZA GOMES BRAGA

Tese apresentada ao Programa de Pós-Graduação em Geologia – Instituto de Geociências – IG da Universidade de Brasília – UnB como requisito parcial obrigatório para a obtenção do título de Doutor em Geologia.

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RESUMO

O kimberlito diamantífero Canastra-1 representa uma intrusão cretácea pertencente à Província Ígnea do Alto Paranaíba (APIP), Brasil. Esse kimberlito hospeda xenólitos portadores de granada, incluindo dunito, lherzolitos cisalhados, websteritos (anidros e hidratados), clinopiroxenitos e eclogitos. Análise petrográfica detalhada acompanhada por dados de química mineral e isotópicos (Sr-Nd) indicam que a litosfera cratônica na margem SW do Cráton São Francisco foi afinada. Os padrões de elementos de terras raras (ETR) para os clinopiroxênios exibem enriquecimento variável em ETR leves (ETRL) em relação aos ETR pesados (ETRP) ($Ce/Yb_N = 10,52-93,63$). Os eclogitos ($Ce/Yb_N = 60,90-93,63$) e websteritos hidratados ($Ce/Yb_N = 10,52-50,61$) são caracterizados pelas maiores concentrações de ETRL em relação aos ETRP. A pargasita exibe o mesmo padrão de ETR observado nos clinopiroxênios coexistentes ($Ce/Yb_N = 10,26-57,06$). Os grãos de granada mostram um padrão de ETR normal, caracterizado pelo enriquecimento de ETRP e fracionamento suave de ETRL ($Ce/Yb_N < 0,32$). Estimativas de temperatura (T) e pressão (P) demonstram que lherzolitos, clinopiroxenitos, websteritos anidros e dunito representam a coluna de manto mais profunda e quente da litosfera do Canastra-1 ($T = 1191-1290\text{ }^{\circ}\text{C}$; $5,3-5,6\text{ GPa}$), enquanto os websteritos hidratados ($T = 875-926\text{ }^{\circ}\text{C}$; $P = 2,0-3,0\text{ GPa}$) e os eclogitos ($T = 978-982\text{ }^{\circ}\text{C}$; $P \sim 4,0\text{ GPa}$) caracterizam-se como as amostras mais rasas e mais frias. Para os eclogitos, tanto o clinopiroxênio quanto a granada apresentam altas razões de $^{87}\text{Sr}/^{86}\text{Sr}$ ($0,70842-0,70912$) e valores ϵNd negativos ($-5,6$ a $-7,3$). Essas características sugerem um protólito máfico provavelmente metassomatizado por fluido/*melt* derivado de rochas sedimentares subjacentes. Websteritos hidratados, cumulados de andesito basáltico hidratado, representam as amostras mais enriquecidas, com clinopiroxênio exibindo as razões isotópicas $^{87}\text{Sr}/^{86}\text{Sr}$ mais altas ($0,70894-0,71094$), e expressivos valores negativos de ϵNd ($-7,2$ a $-13,3$). Lherzolitos cisalhados, clinopiroxenitos, websteritos anidros e dunito exibem bordas quelifíticas ao redor dos grãos de granada e indício de metassomatismo promovido pela percolação de um *melt* proto-kimberlítico de alta temperatura e enriquecido em Ti, Zr e Y. O metassomatismo proto-kimberlítico é apoiado pelo enriquecimento preferencial das razões $^{87}\text{Sr}/^{86}\text{Sr}$ ($0,70560-0,70869$) acompanhado por valores positivos de ϵNd ($+1,8$ a $+10,10$). As isócronas Sm-Nd forneceram uma idade média de $120 \pm 5\text{ Ma}$, que representa a idade de erupção/colocação do kimberlito hospedeiro. Na litosfera cratônica profunda,

o evento metassomático é coevo aos estágios iniciais do rompimento do Gondwana durante o Cretáceo, pouco antes da colocação do kimberlito em 120 Ma. O metassomatismo proto-kimberlítico ocorreu imediatamente antes da erupção do kimberlito, desencadeando um intenso afinamento litosférico e destruição parcial da margem SW do Cráton do São Francisco. Paralelamente, toda a coluna do manto exibe assinaturas extremamente radiogênicas de hélio ($^3\text{He}/^4\text{He}$ geralmente $<1 R_A$) e xenônio fissiogênico (alto- $^{136}\text{Xe}/^{130,132}\text{Xe}$), enquanto o neônio mostra predominantemente uma assinatura semelhante à MORB, além de razões nucleogênicas. As razões $^{40}\text{Ar}/^{36}\text{Ar}$ (304–8464) indicam mistura entre o ar e um componente mantélico, com forte contribuição atmosférica. As razões isotópicas de xenônio permitiram a construção de linhas de correlação para o manto litosférico cratônico. Estas linhas representam a primeira proposição bem definida para o manto cratônico do mundo, e indicam que o manto abaixo do Cráton do São Francisco encontra-se consideravelmente degaseificado em comparação ao manto litosférico fora de regiões cratônicas. Estas assinaturas indicam a efetiva reciclagem de crosta oceânica hidratada antiga e sedimentos subjacentes derivados de um sistema de subducção complexo e de longa duração desde o Arqueano-Paleoproterozoico.

Palavras-chave: xenólitos do manto; metassomatismo mantélico; afinamento litosférico; reciclagem de voláteis.

ABSTRACT

The diamond-bearing kimberlite Canastra-1 represents a Cretaceous intrusion from the Alto Paranaíba Igneous Province (APIP), Brazil. This kimberlite hosts garnet-bearing xenoliths, including dunite, sheared lherzolites, websterites (anhydrous and hydrated), clinopyroxenites, and eclogites. Detailed petrographic analyses accompanied by mineral chemistry and isotopic data (Sr-Nd) indicate that the cratonic lithosphere at the SW margin of the São Francisco Craton has been thinned. Rare earth element (REE) patterns for clinopyroxenes exhibit variable enrichment in light REE (LREE) relative to heavy REE (HREE) ($Ce/Yb_N = 10.52\text{--}93.63$). Eclogites ($Ce/Yb_N = 60.90\text{--}93.63$) and hydrated websterites ($Ce/Yb_N = 10.52\text{--}50.61$) are characterized by the highest concentrations of LREEs relative to HREEs. Pargasite exhibits the same upward REE pattern observed in the coexisting clinopyroxenes ($Ce/Yb_N = 10.26\text{--}57.06$). Garnet grains show a normal REE pattern, characterized by a predominance of HREEs and a smooth decrease of LREEs ($Ce/Yb_N < 0.32$). Temperature (T) and pressure (P) estimates demonstrate that lherzolites, clinopyroxenites, anhydrous websterites, and dunite represent the deepest and hottest mantle column of the Canastra-1 lithosphere ($T = 1191\text{--}1290\text{ }^{\circ}\text{C}$; $5.3\text{--}5.6\text{ GPa}$), whereas the hydrated websterites ($T = 875\text{--}926\text{ }^{\circ}\text{C}$; $P = 2.0\text{--}3.0\text{ GPa}$) and eclogites ($T = 978\text{--}982\text{ }^{\circ}\text{C}$; $P \sim 4.0\text{ GPa}$) are characterized as shallower and colder. For the eclogites, both clinopyroxene and garnet show high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ($0.70842\text{--}0.70912$) and negative ϵNd values (-5.6 to -7.3). These features suggest a mafic protolith probably metasomatized by fluid/melt derived from the overlying sediments. Hydrated websterites, cumulates from a hydrous basaltic andesite, represent the most enriched samples, with clinopyroxene exhibiting the highest $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios ($0.70894\text{--}0.71094$) and significant negative ϵNd values (-7.2 to -13.3). Sheared lherzolites, clinopyroxenites, anhydrous websterites, and dunite show kelyphitic rims around garnet grains and evidence of metasomatism promoted by the percolation of a high-temperature, Ti-, Zr-, and Y-enriched proto-kimberlite melt. The proto-kimberlite metasomatism is supported by the preferential enrichment of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ($0.70560\text{--}0.70869$) accompanied by positive ϵNd values ($+1.8$ to $+10.10$). Sm-Nd isochrons provided an average age of $120 \pm 5\text{ Ma}$, representing the eruption/emplacement age of the host kimberlite. In the deep cratonic lithosphere, the metasomatic event is coeval with the initial stages of the Gondwana breakup during the Cretaceous, shortly before the kimberlite emplacement at 120 Ma . The proto-kimberlitic metasomatism occurred immediately before the kimberlite

eruption, triggering intense lithospheric thinning and partial destruction of the SW margin of the São Francisco Craton. On the other hand, all xenoliths exhibit extremely radiogenic helium signatures ($^3\text{He}/^4\text{He}$ generally $<1 R_A$) and fissiogenic xenon (high- $^{136}\text{Xe}/^{130,132}\text{Xe}$), while neon shows mostly a MORB-like signature with subordinated contribution of a nucleogenic component. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (304–8464) indicate mixing between air and a mantle component, with a strong atmospheric contribution. The xenon isotopic ratios allowed the construction of correlation lines for the cratonic lithospheric mantle. These lines represent the first well-defined proposition for the cratonic mantle in the world and suggest that the mantle beneath the São Francisco Craton is considerably degassed compared to the off-craton lithospheric mantle. These signatures indicate the effective recycling of ancient hydrated oceanic crust and overlying sediments derived from a complex and long-lived subduction system since the Archean-Paleoproterozoic.

Keywords: mantle xenoliths; mantle metasomatism; lithospheric thinning; volatile recycling

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CAPÍTULO 1

INTRODUÇÃO

1 INTRODUÇÃO

1.1 Apresentação e Escopo da Tese

Este documento é pré-requisito para obtenção do título de doutora pelo Programa de Pós-graduação em Geologia (PPGGeo) da Universidade de Brasília (UnB). O presente trabalho teve a orientação do Prof. Dr. Tiago Jalowitzki e contou com período sanduíche na Universidade de Tóquio, sob supervisão do Prof. Dr. Hirochika Sumino. O documento está estruturado em 7 capítulos e contempla a metodologia, os dados obtidos e as interpretações e conclusões. As heterogeneidades mantélicas no manto litosférico subcontinental sob o sudoeste do Cráton do São Francisco foram abordadas através do estudo petrográfico, de química mineral e isotópico (Sr-Nd e gases nobres) de uma diversa suíte de xenólitos mantélicos hospedados pelo Kimberlito Canastra-1, Minas Gerais.

O **Capítulo 1** mostra a contextualização e as justificativas que motivaram o desenvolvimento do trabalho, além dos objetivos e da localização da área de estudo. O **Capítulo 2** apresenta uma contextualização acerca do contexto geotectônico e geológico da área de estudo através da revisão de artigos científicos e capítulos de livros, além de dissertações, teses e resumos de eventos. O **Capítulo 3** expõe uma revisão simplificada de literatura existente sobre assuntos relevantes para o desenvolvimento da tese de doutorado. O **Capítulo 4** mostra as etapas de trabalho e as principais metodologias empregadas para a realização das análises químicas e isotópicas. Detalhes analíticos são apresentados nos artigos.

Os **capítulos 5 e 6** constituem o corpo principal da tese, visto que abordam os resultados obtidos e estão organizados em dois artigos científicos. O **Capítulo 5** apresenta o primeiro artigo aceito e publicado na revista *Journal of Petrology* (<https://doi.org/10.1093/petrology/egae087>), cujo título é “*Destruction of the lithosphere beneath the SW margin of the São Francisco Craton evidenced by refertilized and deformed mantle xenoliths*”. Neste trabalho, as composições minerais e texturas petrográficas, dados de química mineral e isotópicos (Sr-Nd) de um diverso conjunto de xenólitos mantélicos do Kimberlito Canastra-1 são usados para discutir a petrogênese dessas rochas. Nesse cenário, é proposta a destruição parcial da margem SW do Cráton do São Francisco, registrada pela primeira vez por amostras da litosfera cratônica

profunda. Esses resultados também evidenciam intenso metassomatismo. Os xenólitos estáveis no limite litosfera-astenosfera interagiram com *melt* proto-kimberlítico, enquanto os mais rasos (litosféricos) foram intensamente afetados por fluidos/*melts* derivados da subducção da placa oceânica.

O **Capítulo 6** apresenta os resultados que integram o segundo manuscrito e aborda as primeiras razões isotópicas para todos os gases nobres (He, Ne, Ar, Kr e Xe) de xenólitos da margem SW do Cráton de São Francisco. Os resultados evidenciam assinaturas fortemente radiogênica e fissiogênica para He e Xe, respectivamente. Para o Ne, a maioria dos dados apresenta similaridade àqueles descritos para basaltos de dorsais meso-oceânicas (MORB), enquanto o pargasita websterito é caracterizado por composição nucleogênica (crustal). O Ar e Kr registram forte contribuição atmosférica. Estes resultados evidenciam a intensa influência de um complexo e extensivo sistema de subducção. Ainda, esse estudo apresenta os primeiros resultados de Xe para a litosférica cratônica. Finalmente, o **Capítulo 7** integra e sumariza as conclusões obtidas a partir da realização do presente trabalho.

1.2 Contextualização e Justificativa

O manto terrestre tem sido composicionalmente modificado ao longo de sua história evolutiva por uma série de processos geológicos, que envolvem o empobrecimento e o enriquecimento em elementos maiores, traço e terras-raras. Essas heterogeneidades são decorrentes da fusão parcial e do metassomatismo, e se manifestam em escala temporal e espacial. A tectônica de placas introduz mudanças laterais no manto, enquanto as diferenças nas densidades dos materiais tendem a estratificá-lo (Wilson, 1989; Anderson, 2006).

O entendimento dos processos mantélicos é de extrema relevância para se compreender a evolução da Terra, a dinâmica do tectonismo, a gênese de rochas direta ou indiretamente derivadas do manto, bem como a geração de mineralizações associadas a essas rochas, como os diamantes. Os xenólitos mantélicos ultramáficos são os principais materiais que fornecem evidências diretas da composição petrográfica e geoquímica do manto litosférico subcontinental (SCLM, da sigla em inglês), e representam os reservatórios mais importantes dos quais são derivados os magmas que constituem a crosta terrestre. Essas amostras possibilitam a realização de estudos sobre os processos

atuantes no SCLM, além do entendimento dos mecanismos de formação e evolução da litosfera ao longo do tempo geológico.

O SCLM, sob várias regiões cratônicas do planeta, vem sendo amplamente estudado. O interesse pelo estudo de xenólitos mantélicos de kimberlitos foi incentivado na década de 70, devido a descoberta de expressivos campos kimberlíticos mineralizados, sendo, as principais linhas de pesquisa, àquelas relacionadas à dinâmica e evolução do manto e sua relação com a preservação de diamantes. Apesar do manto litosférico sob o Cráton do São Francisco ser um dos principais ambientes de formação de diamantes do Brasil (Pereira & Fuck, 2005), o estudo da raiz mantélica dessa unidade geológica ainda é pouco desenvolvido quando comparado aos outros crátons do mundo.

A porção sul do Orógeno Brasília, circundante à borda sudoeste do Cráton do São Francisco, foi cenário, no Cretáceo, de um importante evento magmático ultramáfico-ultrapotássico, ao qual se associam numerosas intrusões kimberlíticas pertencentes à Província Ígnea do Alto Paranaíba (do inglês APIP – *Alto Paranaíba Igneous Province*, Gibson *et al.*, 1995). Essa província se resalta no contexto da exploração diamantífera no Brasil por abranger a primeira reserva comprovadamente dimensionada em uma rocha-fonte primária, no Kimberlito Canastra-1 (Chaves *et al.*, 2008).

Informações sobre a natureza do SCLM na APIP são relativamente escassas. Dissertações de mestrado e teses de doutorado caracterizam os xenólitos mantélicos hospedados por kimberlitos, principalmente quanto a sua petrografia e química mineral, embora a maioria dos resultados não tenha sido publicada em periódicos científicos indexados (Costa, 2008; Thomaz, 2009; Nannini, 2011, 2016; Costa, 2012). A assinatura isotópica do manto na APIP tem sido inferida com base em rochas vulcânicas e plutônicas, sendo raros os dados obtidos diretamente de xenólitos mantélicos (Carlson *et al.*, 2007; Costa, 2012). A escassez de dados também é decorrente da dificuldade de identificação e amostragem dessas rochas, devido ao pequeno volume e intensa alteração intempérica a que normalmente estão submetidas.

Dados sismológicos e gravimétricos indicam que o SCLM próximo a borda sudoeste do Cráton do São Francisco possui espessura variável, podendo se estender a oeste além dos limites observados em superfície, até o Orógeno Brasília (ex. Ussami, 1993; Rocha *et al.*, 2019). As ocorrências de intrusões alcalinas na APIP normalmente coincidem com zonas de baixas velocidades de ondas sísmicas e SCLM mais raso (Assumpção *et al.*, 2017; Rocha *et al.*, 2019). Desta forma, o estudo de xenólitos

mantélicos auxiliará a identificação de raízes cratônicas. A investigação do manto sob o Cráton do São Francisco também pode contribuir para melhor compreensão do ambiente de formação dos diamantes.

Esse contexto justifica a relevância do tema proposto e fundamenta a imprescindibilidade de estudos detalhados integrando dados de química mineral de elementos maiores e traço e isotópicos para os xenólitos mantélicos hospedados em kimberlitos na APIP, uma vez que essas rochas constituem importantes ferramentas para estudos petrogenéticos do SCLM e dos processos que resultam nas heterogeneidades desse manto na região.

As razões isotópicas dos gases nobres obtidas neste trabalho representam os primeiros resultados para amostras cratônicas do Continente Sul-Americano. Esses dados fundamentam as discussões acerca do fluxo de voláteis no interior do planeta, além de tecer considerações acerca de processos tectônicos que os geraram.

Esse estudo conta com amostras de dunito, lherzolitos cisalhados, clinopiroxenitos, websteritos (anidro e hidratado) e eclogitos, que confirmam a existência de um manto heterogêneo e intensamente metassomatizado abaixo do Kimberlito Canastra-1. Todas as amostras contêm granada como fase aluminosa.

1.3 Objetivos

Fundamentado no cenário apresentado, o objetivo principal esperado com este trabalho consiste na caracterização petrogenética de xenólitos mantélicos do Kimberlito Canastra-1, que ocorrem no sudoeste do Cráton do São Francisco. Para tanto, foram investigados os principais agentes metassomáticos responsáveis pelo enriquecimento do SCLM nessa região. Os objetivos específicos podem ser sumarizados em:

- Estabelecer a composição modal e a caracterização textural das amostras através do estudo petrográfico detalhado dos litotipos constituintes da suíte de xenólitos do Canastra-1;
- Determinar a composição química das fases minerais e as condições de temperatura e pressão de equilíbrio dos xenólitos, por meio de dados de química mineral (geotermobarometria);
- Determinar as composições isotópicas de Sr e Sm-Nd para essas amostras.

- Caracterizar a natureza, heterogeneidade e evolução tectônica do SCLM na APIP, comparando as amostras estudadas com xenólitos de outras localidades;
- Identificar e compreender processos de metassomatismo, a ocorrência de anomalias térmicas e discutir a possibilidade da influência de zonas de subducção na heterogeneidade litogeoquímica do manto;
- Determinar as composições isotópicas de gases nobres (He, Ne, Ar, Kr e Xe) em amostras de rocha total e concentrados de minerais (clinopiroxênio, ortopiroxênio, anfibólio e granada);
- Contribuir para o avanço do conhecimento científico na APIP e do manto litosférico cratônico.

1.4 Localização da área

O Kimberlito Canastra-1 está localizado no município de São Roque de Minas, sudoeste do estado de Minas Gerais (Fig. 1.1). A intrusão está inserida na região do Alto Rio São Francisco, próximo ao escarpamento da Serra da Canastra. O acesso ao local, desde Belo Horizonte, é feito pela rodovia MG-050 até Piumhi, por onde são percorridos 260 km. Posteriormente, segue-se por 57 km até Vargem Bonita. A partir desta cidade percorre-se, por estrada de terra, 17,5 km até o vilarejo de São José do Barreiro. O kimberlito situa-se cerca de 7 km a oeste do vilarejo (Chaves *et al.*, 2008).

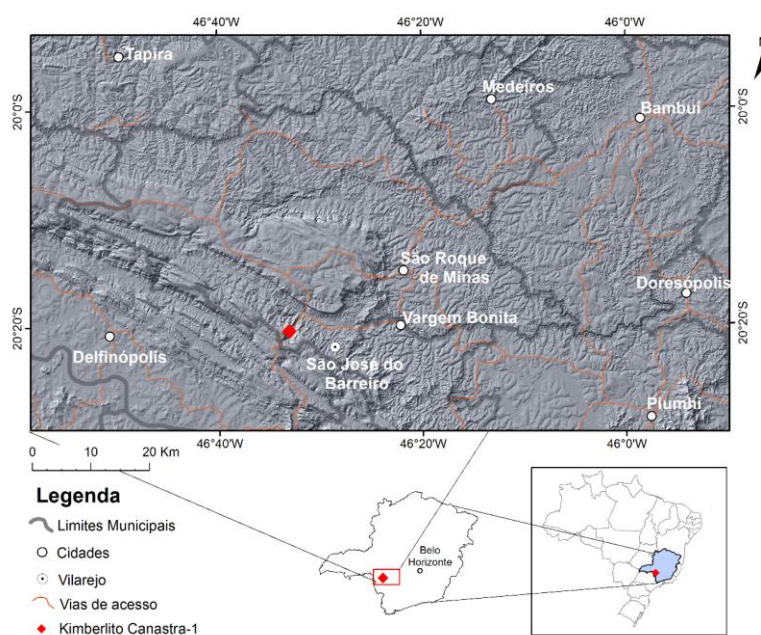


Fig. 1.1. Mapa de localização do Kimberlito Canastra-1.

CAPÍTULO 2

CONTEXTO GEOLÓGICO E GEOTECTÔNICO

2 CONTEXTO GEOLÓGICO E GEOTECTÔNICO

2.1 Cráton do São Francisco

O Cráton do São Francisco, juntamente com os demais crátons identificados na Plataforma Sul-Americana, representam porções internas da placa que participaram da assembleia do Gondwana Ocidental (Heilbron *et al.*, 2017) (Fig. 2.1). Os sistemas orogênicos brasileiros e seus equivalentes no Continente Africano (Orogenia Pan-Africana) englobam margens de placas, micro continentes e arcos magmáticos intraoceânicos, que também estavam envolvidos no amalgamento do supercontinente entre 640 e 500 Ma (Campos Neto, 2000; Almeida *et al.*, 2000; Heilbron *et al.*, 2017) (Fig. 2.1).

O Cráton do São Francisco é composto por um núcleo arqueano e dois segmentos de orógenos paleoproterozoicos. Embora quase inteiramente cobertas por sucessões sedimentares proterozoicas a fanerozoicas, rochas do embasamento arqueano, constituídas por terrenos metamórficos de médio e alto grau, bem como associações granito-*greenstone*, são expostas principalmente nas regiões sul e norte do cráton (Teixeira *et al.*, 2000; Barbosa & Sabaté, 2004).

O Cinturão Mineiro e o Quadrilátero Ferrífero representam os segmentos do orógeno paleoproterozoico preservados no extremo sul do cráton. O Cinturão Mineiro é constituído por grande volume de rochas graníticas relacionadas à subducção (2,47 – 2,10 Ga) e associações metavulcânicas-sedimentares depositadas em configurações de arco de ilha. O Quadrilátero Ferrífero inclui uma seção completa do embasamento sobreposto discordantemente por sucessões metassedimentares que registram evolução de margem passiva para bacia pós-orogênica (Alkmim & Teixeira, 2017 e referências nele contidas).

Em conjunto com o domínio orogênico do Leste da Bahia, porção norte do cráton, esses segmentos caracterizam-se como componentes de um orógeno colisional desenvolvido durante a transição entre os Períodos Riachiano e Orosiriano (Barbosa & Barbosa, 2017). Essa orogenia registra a colisão entre os paleocontinentes do São Francisco e Congo (Alkmim & Teixeira, 2017) (Fig. 2.1; 2.4).

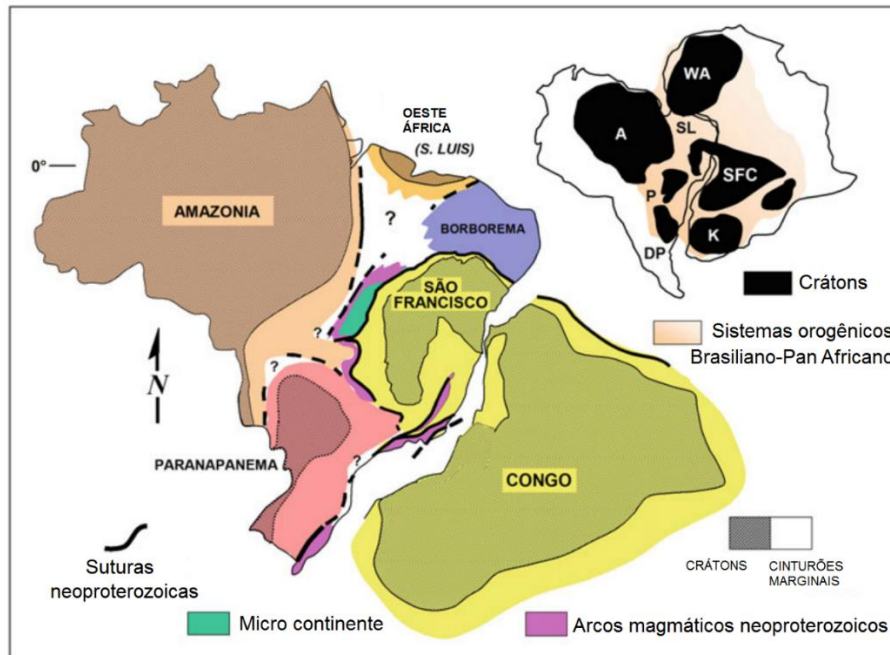


Fig. 2.1. Massas continentais (crátons e sistemas orogênicos Brasileiro/Pan-africano) que compunham o Gondwana Ocidental (América do Sul e África). SFC: Cráton do São Francisco-Congo; K: Kalahari; WA: Oeste Africano; A: Amazônico; P: Bloco Paranapanema; DP: Rio de la Plata; SL: São Luís. (Modificado de Heilbron *et al.*, 2017).

2.2 Orógeno Brasília

A individualização do contorno atual do Cráton do São Francisco ocorreu durante a acreção do Gondwana Ocidental (Cordani *et al.*, 2013). O Orógeno Brasília, com extensão de cerca de 1100 km na direção N-S, delimita o oeste e sudoeste do cráton (Pimentel, 2016; Fuck *et al.*, 2017; Valeriano, 2017). Esse cinturão orogênico desenvolveu-se através de uma longa sucessão de eventos colisionais. A convergência e colisão final ocorreram no final do Neoproterozoico, durante a Orogenia Brasileira (Fuck *et al.*, 2017). O Orógeno Brasília é resultado de eventos de subducção de uma ampla litosfera oceânica relacionada ao Oceano Goiás-Farusiano, seguido pelo desenvolvimento de um arco continental (670 Ma) e a colisão continental dos paleocontinentes Amazonas, São Francisco e Paranapanema (640-610 Ma) (Valeriano *et al.*, 2008; Fuck *et al.*, 2017; Frugis *et al.*, 2018).

O Orógeno Brasília compõe a porção leste da Província Tocantins e encontra-se compartimentada em dois segmentos com orientação e estilos metamórfico-deformacionais distintos (Fig. 2.2). O segmento norte possui orientação NNE-SSW, enquanto O Orógeno Brasília Sul exibe tendência estrutural NNW-SSE (Araújo Filho, 2000). Em ambos os segmentos, a deformação tectônica é progressivamente mais intensa

para oeste. O grau metamórfico aumenta progressivamente da fácies xisto verde a anfibolito, e a até granulito na parte mais ocidental do orógeno (Dardenne, 2000). O Orógeno Brasília Sul na área de estudo é representado por associações metassedimentares dos grupos Canastra e parte do Araxá, típicos de ambiente de margem passiva, de idades meso e neoproterozoicas (Seer & Moraes, 2013) (Fig. 2.2).

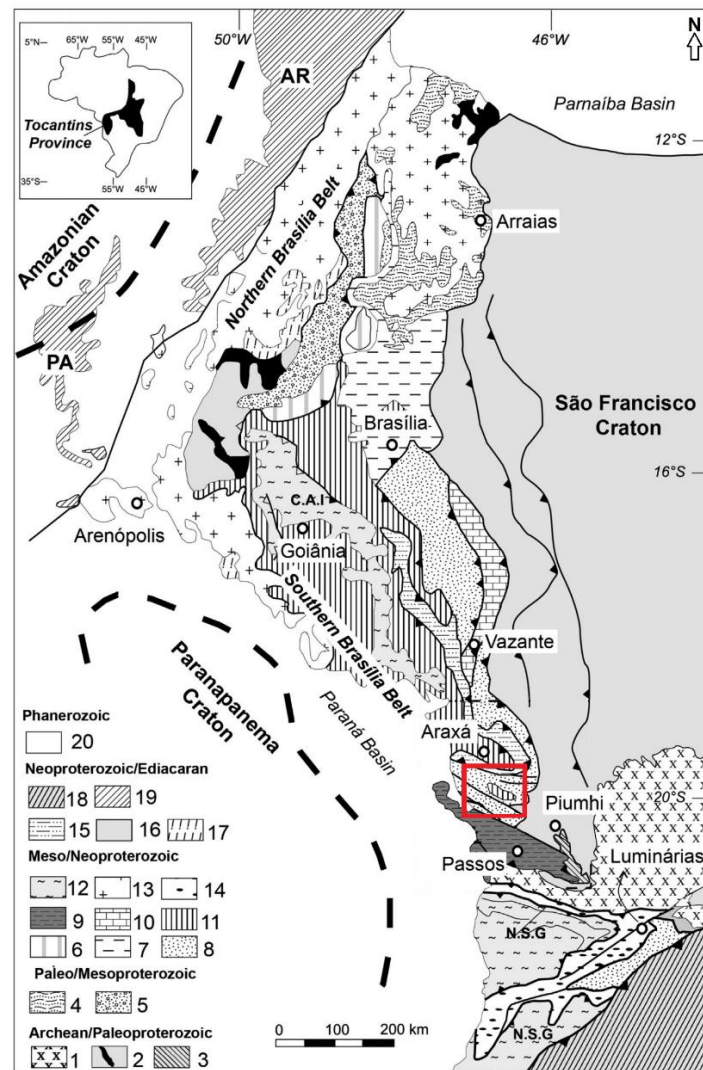


Fig. 2.2. Unidades tectônicas do Orógeno Brasília, com indicação da área de estudo em vermelho. 1: Embasamento arqueano e paleoproterozoico; 2: Maciço Arqueano de Goiás; 3: Sistema de empuxo Ilicínea-Piumhi; 4: Sucessões de riftes paleo-mesoproterozoicos (Grupo Araí); 5: Grupo Serra da Mesa paleo/mesoproterozoico; 6: Complexos básicos-ultrabásicos estratificados do Meso-Neoproterozoico; 7: Grupo Paranoá; 8: Grupo Canastra; 9: Nappe de Passos; 10: Grupo Vazante; 11: Grupo Araxá; 12: Nappes granulíticas (C.A.I.); 13: Arco Magmático Goiás; 14: Megasequência Andrelândia; 15: Grupo Ibiá; 16: Cobertura cratônica (Grupo Bambuí); 17: Rochas supracrustais (metavulcânicas/sedimentares) neoproterozoicas; 18: Faixa Ribeira; 19: Faixas Paraguai (PA) e Araguaia (AR); 20: Cobertura fanerozoica. (Modificado de Valeriano *et al.*, 2008).

Dados gravimétricos de anomalia *Bouguer* (Pereira & Fuck, 2005) sugerem que os limites sul-sudoeste do Cráton do São Francisco com o Orógeno Brasília se estendem a oeste além dos limites observados em superfície (Fig. 2.3a). Nesse sentido, durante a Orogenia Brasileira as rochas crustais que compõe o Orógeno Brasília teriam sido empurradas sobre o paleocontinente São Francisco. No mesmo contexto, a tomografia sísmica de ondas P- exibem velocidades mais altas para as porções cratônicas que extrapolam os limites superficiais do cráton. Os contatos com outros blocos são marcados por anomalias de baixas velocidades em profundidades litosféricas (Rocha *et al.*, 2019), corroborando que a extensão em subsuperfície do cráton é mais extensa do que a aflorante (Fig. 2.3b).

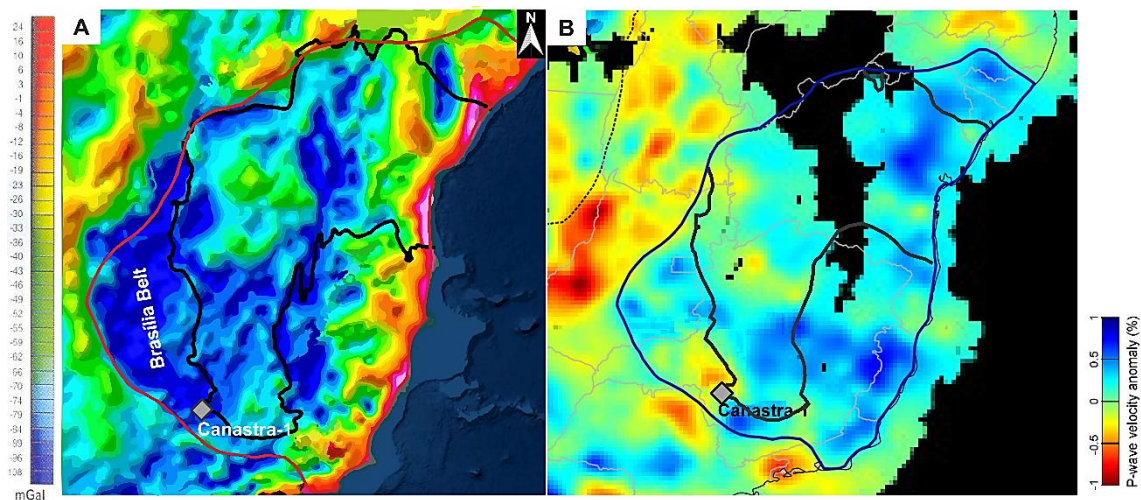


Fig. 2.3. Dados geofísicos para o Cráton do São Francisco e localização do Kimberlito Canastra-1. A) Mapa da anomalia *Bouguer* com os limites do cráton definidos (em vermelho) a partir dos dados gravimétricos (adaptado de Pereira & Fuck, 2005). B) Modelo de tomografia sísmica de onda P- a 200 km de profundidade, com a extensão do cráton deduzida por Rocha *et al.* (2019) em azul. As linhas pretas indicam a borda do Cráton do São Francisco proposta por Alkimin *et al.* (1993) a partir das rochas aflorantes.

As características sismológicas e os modelos tomográficos do manto sob o Cráton do São Francisco mostram caráter típico de crátons arqueanos (Rocha *et al.*, 2019). No entanto, abaixo da porção oriental do Orógeno Brasília e próximo ao Kimberlito Canastra-1 (Fig. 2.3), propriedades diferentes daquelas observadas no restante do cráton, como anomalias *Bouguer* negativas e anomalias de ondas P- de mais baixas velocidades sugerem que o manto litosférico nessa região foi modificado pelo extenso magmatismo relacionado à APIP, que se estende desde a região de Catalão (sul de Goiás) até a Nappe de Passos (sudoeste de Minas Gerais) (Fernandes *et al.*, 2021).

2.3 Província Ígnea do Alto Paranaíba (APIP)

A APIP, orientada NW-SE, se estende ao longo do Orógeno Brasília, entre a borda sudoeste do Cráton do São Francisco e a margem nordeste da Bacia do Paraná (Fig. 2.4). Ela representa uma das mais volumosas províncias máficas-ultramáficas de afinidades potássica a ultrapotássica do mundo (ca. 20000 km³; Gibson *et al.*, 1995).

De idade cretácea, esta província consiste principalmente de lavas e sucessões piroclásticas, que são intrudidas por numerosos corpos de afinidades kimberlíticas e kamafugíticas, além de intrusões hipoabissais e complexos plutônicos alcalinos-carbonatíticos (Gibson *et al.*, 1995; Guarino *et al.*, 2013; Azzone *et al.*, 2022).

A fonte do magmatismo da APIP é tema de debates na literatura ao longo dos anos. Apesar das divergências, estudos sugerem que a gênese desse exótico magmatismo está relacionada a uma fonte mantélica heterogênea e enriquecida metassomaticamente (Gibson *et al.*, 1995; Araujo *et al.*, 2001; Carlson *et al.*, 1996, 2007; Guarino *et al.*, 2013; Woodhead *et al.*, 2019; Carvalho *et al.*, 2022).

Um primeiro modelo relaciona a influência de plumas mantélicas para explicar a fonte de calor responsável pela migração de *metls* astenosféricos (Bizzi, 1995; Gibson *et al.*, 1995; Araujo *et al.*, 2001; Sgarbi *et al.*, 2004). A segunda linha de pensamento propõe que o magmatismo da APIP pode estar relacionado a presença de heterogeneidades químicas e mineralógicas em uma fonte mantélica, que possibilitaria fusão em diferentes pressões, não sendo necessária a presença de pluma mantélica (Carlson *et al.*, 1996, 2007; Guarino *et al.*, 2013).

Apesar de estar localizada no Orógeno Brasília, estudos de xenólitos indicam que a gênese das rochas da APIP está relacionada com manto litosférico subcontinental (Leonardos *et al.*, 1993; Fernandes *et al.*, 2021). Trabalhos anteriores sobre xenólitos do manto também registram evidências de fusão parcial seguida de processos metassomáticos (Leonardos *et al.*, 1993; Almeida *et al.*, 2014; Nannini, 2016; Fernandes *et al.*, 2021; Rodrigues *et al.*, 2023).

Os kamafugitos representam as expressões mais jovens da APIP, suas idades variam de 90 a 75 Ma (U-Pb em perovskita e Rb-Sr em flogopita; Sgarbi *et al.*, 2004; Guarino *et al.*, 2013; Felgate, 2014). Estudos geocronológicos para kimberlitos fornecem idades entre 91 e 80 Ma (U-Pb em perovskita, Guarino *et al.*, 2013; U-Pb em zircão, Carvalho *et al.*, 2022). Felgate (2014) usando técnicas variadas (Kr-Ar em flogopita, Rb-

Sr em flogopita e U-Pb em perovskita) obteve idades de 99 a 74 Ma para um conjunto de kimberlitos. Alternativamente, Azzone *et al.* (2024) obteve idade U-Pb em perovskita de 120.6 ± 6.7 Ma para o Kimberlito Catalão-1b. Neste trabalho, foram geradas isócronas Sm–Nd de dois pontos (clinopiroxênio e granada). A idade média obtida para lherzolitos do Kimberlito Canastra-1 foi de 120 ± 5 Ma (Braga *et al.*, 2024).

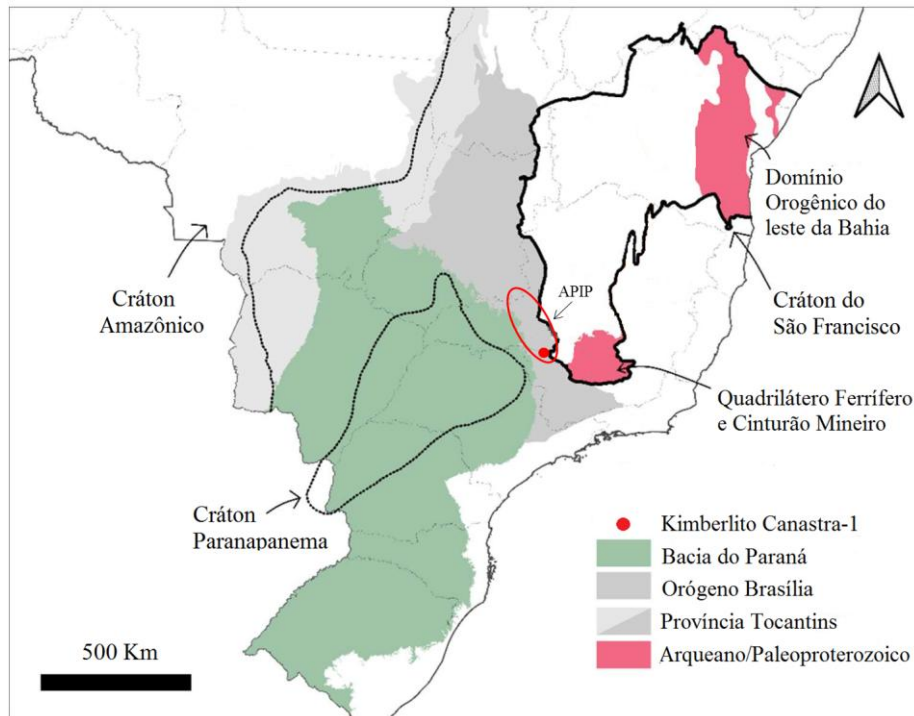


Fig. 2.4. Delimitação da APIP e localização do Kimberlito Canastra-1 com relação ao Cráton do São Francisco, à bacia do Paraná e ao Orógeno Brasília/Província Tocantins. No Domínio Orogênico Leste da Bahia e no Quadrilátero Ferrífero e Cinturão Mineiro estão expostas as rochas Arqueanas/Paleoproterozoicas que compõem o embasamento do Cráton São Francisco. Dados geológicos de Cordani *et al.* (2016).

2.3.1 *Kimberlito Canastra-1*

O Kimberlito Canastra-1 foi o primeiro corpo kimberlítico mineralizado economicamente viável descoberto no Brasil (Chaves *et al.*, 2008). Ele ocorre como um *pipe* intrusivo nos metassedimentos neoproterozoicos do Orógeno Brasília (Fig. 2.4 e 5.1) e faz parte de um *cluster* com aproximadamente 47 intrusões que compõem o campo kimberlítico Serra da Canastra (Cabral Neto *et al.*, 2007). Durante a sua ascensão, esse kimberlito amostrou uma variada suíte de xenólitos do manto, que é o foco do presente trabalho.

CAPÍTULO 3

REFERENCIAL TEÓRICO

3 REFERENCIAL TEÓRICO

3.1 Xenólitos e heterogeneidades mantélicas

Os xenólitos do manto caracterizam-se pela sua importância científica, visto que fornecem informações diretas sobre alterações químicas e mineralógicas decorrentes de processos de fusão parcial e metassomatismo. Tais processos podem, por exemplo, ser causados pela interação com fluidos derivados de placas subductadas ou ressurgências astenosféricas, mesmo antes da geração do magma hospedeiro (Downes, 2001; Pearson *et al.*, 2003).

Maciços peridotíticos exumados tectonicamente também fornecem informações acerca do manto terrestre. Essas amostras exibem relações de campo bem definidas, além de amostrarem uma maior porção do manto. Os xenólitos mantélicos, em contrapartida, são transportados rapidamente para superfície. Desta forma, eles preservam as características geoquímicas e isotópicas da fonte, não sendo reequilibrados durante a ascensão. Além disso, um único evento vulcânico pode amostrar variadas profundidades da coluna estratigráfica do manto. Assim, as paragêneses minerais em equilíbrio são úteis para compreensão da geodinâmica do manto, uma vez que permitem o cálculo de equações geotermobarométricas e a definição de geotermas (Downes, 2001).

Os xenólitos mantélicos são frequentemente transportados por magmas básicos e ultrabásicos, principalmente de natureza alcalina, como basaltos alcalinos (basaltos alcalinos *sensu stricto*, basanitos, tefritos), lamproítos e magmas relacionados, nefelinitos e melilititos, além de kimberlitos (Grupos I, II e transicionais) (Pearson *et al.*, 2003). Os xenólitos apresentam composição ultramáfica e máfica. Lherzolitos, compostos principalmente de olivina e quantidades menores variáveis de ortopiroxênio e clinopiroxênio, são a litologia mais abundante do manto superior. Esses peridotitos, bem como os demais litotipos mantélicos, podem apresentar fases aluminosas, como plagioclásio, espinélio e granada. Diferentes condições de pressão definem campos de estabilidade para cada uma dessas fácies (Pearson *et al.*, 2003; Fig. 3.1).

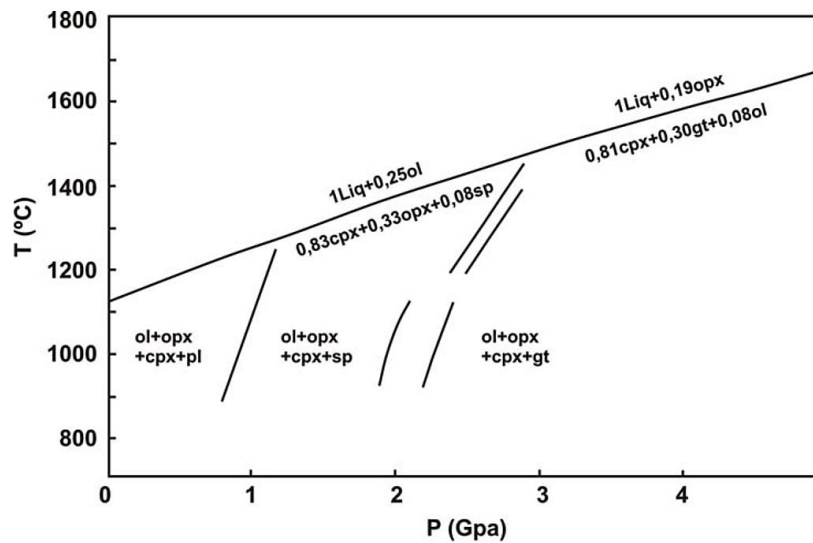


Fig. 3.1. Diagrama de pressão e temperatura mostrando os campos de estabilidade das fases que definem as fácies plagioclásio (pl), espinélio (sp) e granada (gt) no manto (retirado de Pearson *et al.*, 2003).

As configurações tectônicas e a natureza da rocha vulcânica hospedeira comumente estão relacionadas a variabilidade litológica dos xenólitos mantélicos. Os xenólitos encontrados em regiões não cratônicas ocorrem em basaltos alcalinos e estão localizados em porções afetadas por adelgaçamento da litosfera. Por outro lado, os xenólitos sob ou próximos a crátons são transportados para a superfície por kimberlitos ou rochas vulcânicas alcalinas associadas. Essas rochas podem amostrar regiões profundas (mais de 150 km) do manto litosférico subcontinental, em que predominam xenólitos em fácies granada (Mitchell, 1986; Pearson *et al.*, 2003).

Em kimberlitos, frequentemente encontram-se xenólitos ricos em mica e anfibólio (Dawson & Smith, 1977) e eclogitos (Aulbach *et al.*, 2007; Pearson *et al.*, 2013). Esses xenólitos representam uma parte estratificada e heterogênea do manto superior, com intensas porções metassomatizadas. Além do mais, em regiões cratônicas, extensos episódios de fusão podem gerar resíduos com composições empobrecidas, com alto Mg/Fe e baixos conteúdos de Al_2O_3 em relação ao manto astenosférico subjacente (Herzberg, 2004; Aulbach *et al.*, 2013; Ionov *et al.*, 2018).

3.1.1 Metassomatismo mantélico

Heterogeneidades químicas e mineralógicas no manto superior relacionam-se aos processos metassomáticos. No metassomatismo, através dos contatos dos grãos ou por fraturas, fluidos percolam nas rochas do manto. A infiltração entre os contatos dos

minerais é controlada pela energia interfacial, o que torna esse mecanismo um processo lento quando comparado com a propagação por fraturas (O'Reilly & Griffin, 2013).

A ascensão, e consequente resfriamento, de magmas através das fraturas na litosfera é responsável pela liberação de voláteis e metassomatismo mantélico. *Melts* ou fluidos retrabalham e reenriquecem o manto litosférico, modificando as raízes cratônicas (Menzies *et al.*, 1987; Foley, 1992, 2008). Da mesma forma, a base da litosfera cratônica pode ser intensamente afetada por zonas de subducção e plumas mantélicas.

Em zonas de subducção da crosta oceânica, a desidratação da placa ocasiona em expressiva introdução de H₂O no manto superior. Esse processo pode ser responsável pela ocorrência de xenólitos eclogíticos (Aulbach & Stachel, 2022). As plumas mantélicas são responsáveis pelo afinamento litosférico e, posterior recratonização (Liu *et al.*, 2021). Esses processos podem ocasionar no enriquecimento da rocha sem adição de novas fases minerais, denominado de metassomatismo críptico. Nesse metassomatismo, é possível que a adição de elementos ocorra nos interstícios dos grãos, podendo ser evidenciado pelo conteúdo de elementos traços (Menzies *et al.*, 1987).

O metassomatismo também pode ser caracterizado pela cristalização de novas fases minerais nas rochas do manto (metassomatismo modal). As rochas resultantes são compostas por minerais hidratados, como micas e anfibólios (Foley, 1992, 2008). Os xenólitos metassomatizados do manto são fundamentais para identificação dos processos causados por fluidos e/ou *melts* alcalinos hidratados no manto litosférico (Fitzpayne *et al.*, 2018).

3.1.2 Texturas em xenólitos

Segundo Dawson (1980), as texturas de xenólitos mantélicos podem ser divididas em dois grupos. O primeiro envolve as texturas resultantes de deformação e recristalização de rochas com textura originalmente equigranular grossa (*coarse*). O segundo representa aquelas com indicativos de interação sub-sólidas entre fases.

Os minerais que compõe os xenólitos do primeiro grupo reagem de maneiras diferentes ao aumento de pressão sobre a rocha. Os cristais de olivina são os mais sensíveis à pressão e, juntamente ortopiroxênio e clinopiroxênio, sofrem recristalização (neoblastos). Granada e espinélio sofrem fragmentação somente em resposta a uma deformação considerável (Dawson, 1980). As estruturas e texturas observadas podem ser

geradas em decorrência da ascensão dos xenólitos junto ao kimberlito, ou em resposta a movimentos laterais no manto. As principais texturas resultantes da deformação são definidas por Harte (1997). Os autores mencionam que embora as classificações tenham sido adotadas em xenólitos ricos em olivina, a terminologia também é aplicável a piroxenitos.

A textura equigranular grossa (*coarse*) é marcada por uma rocha sem porfiroclastos, normalmente constituída por minerais com granulação superior a 2,0 mm (equidimensionais), em que os limites entre os grãos são retos ou suavemente encurvados. É conhecida também como “protogranular” por Mercier & Nicolas (1975).

As texturas porfiroclástica e mosaico porfiroclástica são resultantes da recristalização da rocha equigranular pretérita. A porfiroclástica caracteriza-se por rocha em que a olivina ocorre em maior proporção nos porfiroclastos em relação à matriz. Já a textura porfiroclástica em mosaico, a olivina deve ocorrer principalmente na matriz (> 90%). A matriz é constituída por pequenos grãos com textura em mosaico (grãos aproximadamente equidimensionais e com limites poligonais), são consideradas produto de recristalização e podem apresentar evidências de deformação. Os subtipos de texturas mais comuns são as microfraturas (em espinélio e granada), laminada, e fluidal (Harte, 1997). A textura granuloblástica é interpretada como uma textura resultante de intensa recristalização sobre todos os minerais, em que os cristais apresentam pequena dimensão e poucos (< 5%) ou nenhum porfiroclasto são identificados.

O segundo grupo está relacionado a reação sub-sólida entre os constituintes minerais. Dawson (1980) destaca principalmente a feição quelifítica, que ocorre no entorno dos cristais de granada. As bordas quelifíticas consistem em um agregado microcristalino de cor escura, no qual o espinélio e mica são as fases principais identificadas ao microscópio. Microcristais de piroxênio, anfibólio, plagioclásio e clorita também podem ser identificados.

3.2 Isótopos de gases nobres

Os gases nobres ocorrem em baixas concentrações em rochas terrestres, exceto pelo Ar, visto que eles foram excluídos dos materiais sólidos durante a formação planetária no interior do sistema solar. Nesse contexto, representam uma poderosa

ferramenta para compreensão da geodinâmica e das heterogeneidades químicas do manto terrestre, assim como da origem e evolução da atmosfera (Porcelli & Ballentine, 2002).

Por serem quimicamente inertes, as mudanças em suas abundâncias elementares e isotópicas estão relacionadas a processos físicos. Alterações mensuráveis nas composições de isótopos de gases nobres estão estreitamente relacionadas com os processos geoquímicos que controlam a distribuição de K, U e Th. A composição isotópica de cada gás nobre é modificada através do decaimento radioativo de um ou mais desses elementos (Porcelli & Ballentine, 2002).

A distribuição geoquímica de ^4He está diretamente relacionada à produção de partículas α pelo decaimento do U e Th. A composição isotópica do Ne em sistemas terrestres é modificada por processos em que o ^{21}Ne é predominantemente produzido quando nêutrons ou partículas α colidem com átomos de Mg e O.

O decaimento radioativo de ^{40}K geralmente controla a composição isotópica de Ar. Pequenas quantidades de ^{84}Kr e ^{86}Kr são produzidos ao longo do tempo geológico pela fissão espontânea do ^{238}U . A produção de $^{131,132,134,136}\text{Xe}$ ocorreu pela fissão espontânea do ^{238}U e do extinto ^{244}Pu (meia-vida $t_{1/2} = 82 \text{ Ma}$), enquanto a produção de ^{129}Xe ocorreu através do decaimento radioativo do ^{129}I extinto ($t_{1/2} = 17 \text{ Ma}$).

Nas rochas terrestres, os sistemas isotópicos de gases nobres são compostos por componentes de diferentes origens. As assinaturas primordiais estão associadas a razões enriquecidas em ^3He , ^{20}Ne , ^{22}Ne , ^{36}Ar , ^{38}Ar e ^{130}Xe . As razões enriquecidas em ^4He , ^{40}Ar e ^{129}Xe são classificadas como radiogênicas, enquanto as nucleogênicas exibem razões enriquecidas em ^{21}Ne e as cosmogênicas/nucleogênicas estão enriquecidas em razões ^3He e ^{21}Ne , respectivamente. A figura 3.2 mostra o modelo mantélico de duas camadas contendo os valores das razões $^3\text{He}/^4\text{He}$ e $^{40}\text{Ar}/^{36}\text{Ar}$ de diferentes fontes e ambientes tectônicos.

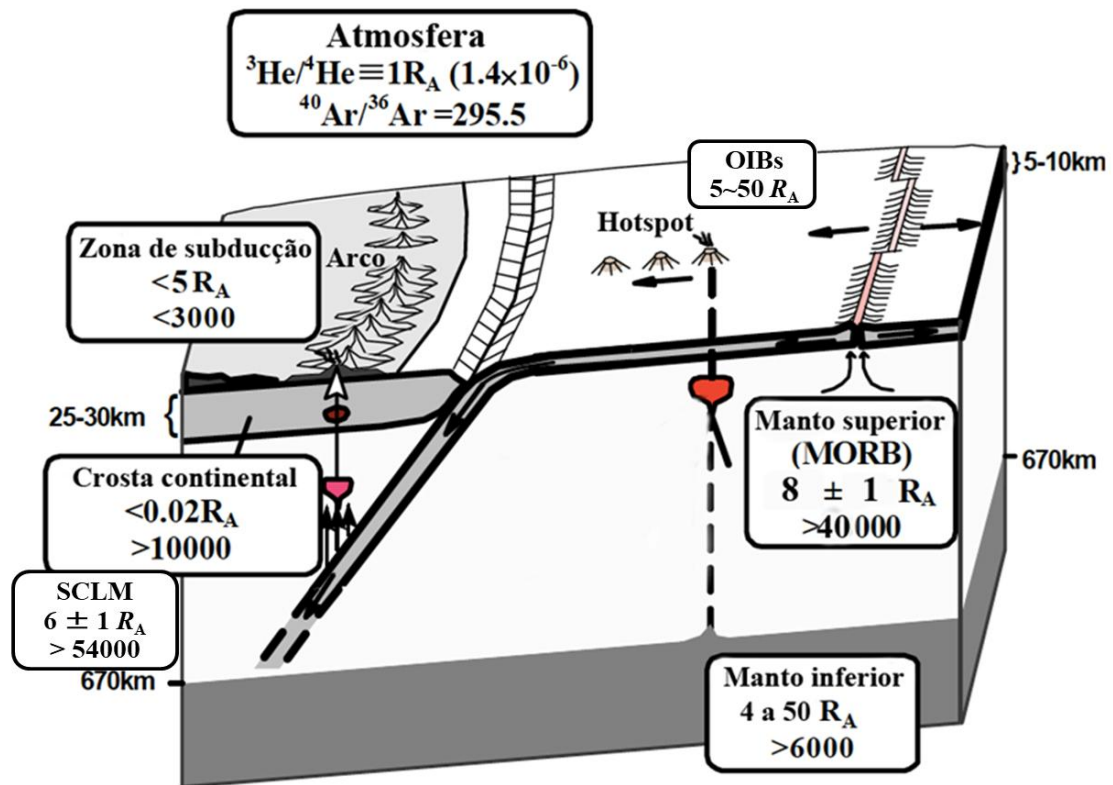


Fig. 3.2. Diagrama esquemático mostrando o modelo mantélico de duas camadas contendo as razões $^3\text{He}/^4\text{He}$ e $^{40}\text{Ar}/^{36}\text{Ar}$ de cada uma das fontes de ambientes tectônicos (modificado de Sumino, 2000).

CAPÍTULO 4

METODOLOGIA

4 METODOLOGIA

A execução deste projeto envolveu etapas de escritório e de laboratório. Os procedimentos metodológicos são individualizados e detalhados a seguir:

4.1 Levantamento bibliográfico

Esta etapa consistiu na revisão e compilação de dados bibliográficos referentes à área de estudo, assuntos pertinentes ao tema e estudo detalhado de técnicas analíticas que foram adotadas no projeto.

4.2 Amostragem

Os testemunhos de sondagem contendo amostras da suíte de xenólitos mantélicos intrusivos no kimberlito Canastra-1 foram disponibilizadas pela empresa De Beers através de professores da UnB.

4.3 Petrografia

A confecção de 22 lâminas delgadas polidas foi realizada no Laboratório de Laminação da LapidarGeo, em Belo Horizonte. A descrição petrográfica teve como objetivo identificar a paragênese mineral e as principais texturas dos peridotitos com o auxílio de um microscópio óptico petrográfico. O detalhamento da determinação das fases minerais, assim como das feições texturais foram realizadas no Laboratório de Microscopia, localizado nas dependências do IG-UnB. A quantificação das fases foi determinada através do escaneamento das lâminas delgadas, seguido da contagem de pontos em meio digital, com uso do *software* JMicroVision (Roduit, 2007). Para cada seção petrográfica foram contados 3000 pontos. As descrições petrográficas fundamentaram a seleção de amostras para análises de química mineral e isotópicas.

4.4 Microsonda Eletrônica (EPMA)

A composição química das fases minerais foi determinada por meio da microsonda eletrônica JEOL® JXA-8230 *Superprobe*, operando em modo WDS

(*Wavelength Dispersive X-Ray Spectrometry*), no Laboratório de Microsonda Eletrônica da Universidade de Brasília. As condições analíticas e os padrões de calibração empregados estão sumarizadas no primeiro artigo científico que integra esse documento (Capítulo 5).

4.5 Química mineral de elementos traço por LA-ICP-MS

Para cristais selecionados de granada, clinopiroxênio e anfibólio, analisados na etapa anterior, foram realizadas análises *in situ* por ablação a laser (LA) por ICP-MS no laboratório do CSC (*Centro Interdipartimentale Grandi Strumenti*) da Universidade de Módena e Reggio Emilia, Itália. Medições adicionais foram realizadas no Instituto de Geociências da Universidade de São Paulo (USP). Detalhes analíticos são apresentados no tópico *Analytical methods* no Capítulo 5.

4.6 Análises isotópicas de rocha total e minerais nos sistemas ^{87}Sr - ^{86}Sr e ^{147}Sm - ^{143}Nd

As razões isotópicas $^{147}\text{Sm}/^{143}\text{Nd}$, $^{143}\text{Nd}/^{144}\text{Nd}$ (incluindo a notação ϵNd) ($n = 32$) e $^{87}\text{Sr}/^{86}\text{Sr}$ ($n = 25$) foram determinadas para minerais separados (clinopiroxênio e granada) e amostras de rocha total (sem dados de Sr). Os xenólitos do manto foram desagregados mecanicamente usando um almofariz e pilão de ágata e, em seguida, o clinopiroxênio e a granada foram cuidadosamente selecionados manualmente sob um microscópio binocular. Os pós minerais e de rocha total foram produzidos manualmente usando um almofariz e pilão de ágata. as medidas foram realizadas por Espectrometria de Massa por Ionização Térmica (TIMS) por meio de um espectrômetro de massa *Thermo-Finnigan Triton* no Laboratório de Estudos Geodinâmicos, Geocronológicos e Ambientais (LEGGA), UnB, Brasil.

4.7 Análises isotópicas de gases nobres

4.7.1 Preparação das amostras

Para as análises de gases nobres, 24 amostras de xenólitos mantélicos foram selecionados. Destes xenólitos, cristais de clinopiroxênio, ortopiroxênio, anfibólio e granada foram separados. Para avaliar possíveis variações isotópicas e checar a

acuracidade dos dados também foi separada uma alíquota que representa a composição da rocha total do lherzolito cisalhado.

As amostras foram desagregadas manualmente com o uso de um gral de ágata e foram peneiradas e separadas em três frações (0,5-1; 1-2 e >2 mm), sendo que apenas as frações entre 1-2 e >2 mm foram utilizadas para esse estudo. Com auxílio de uma lupa binocular, foram selecionados os minerais sem alterações e fraturas (Fig. 4.1a,b). Os minerais selecionados foram dispostos em beckers com ácido nítrico (HNO_3 60%) e concentração de 2 mol/L. As amostras foram levadas a um ultrassom durante 5 minutos e, posteriormente, foram colocadas, por 30 minutos, em uma chapa aquecedora a 70 °C em capela de exaustão de gases.

Na etapa seguinte, as amostras foram lavadas duas vezes com água deionizada em banho ultrassônico por 5 minutos, seguido de etanol (EtOH 99,5%) em ultrassom também por 5 minutos e por duas vezes. Em seguida, as amostras foram deixadas para secar a temperatura ambiente por 24 horas.

Após a secagem e com auxílio de uma balança de precisão, foram pesadas cerca de 1,1 g de material para as análises, sendo as amostras acondicionadas no papel para pesagem (Fig. 4.1c). Após o procedimento de análises envolvendo a quebra de minerais (ver detalhes a seguir), as amostras foram novamente pesadas e foram selecionadas ~0,5 g para análises por fusão, sendo eliminados possíveis fragmentos remanescentes da quebra e selecionados apenas a porção mais fina (pó). Nesta etapa, as amostras foram embrulhadas em papel alumínio de 10 μm de espessura e dispostas no porta amostras.

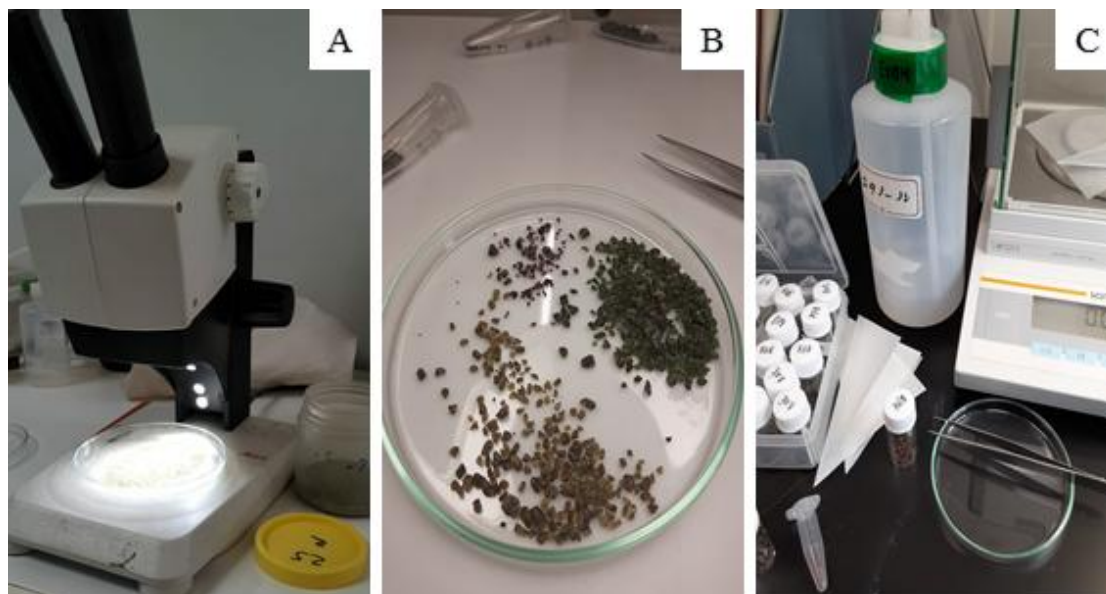


Fig. 4.1. Preparação de amostras para análises de gases nobres. (A) Lupa binocular utilizada para a separação de minerais. (B) Concentrados minerais selecionados para as análises. (C) Etapa de pesagem das amostras em balança de precisão.

4.7.2 Determinação de isótopos de gases nobres

As análises isotópicas de He, Ne, Ar, Kr e Xe foram realizadas primeiramente por quebra (*crushing*). Este método é o mais indicado para obtenção de razões isotópicas da fonte mantélica, pois ele libera apenas os gases aprisionados nas inclusões fluidas dos minerais, com contribuição mínima de gases nobres secundários derivados do decaimento radioativo e da irradiação de raios cósmicos contidos na superfície dos minerais. O procedimento de análise envolve a realização de 5 medições (branco, 100, 500, 1000 e 2000 golpes para liberar os gases aprisionados) para cada amostra. A duração de cada uma dessas análises é de pouco mais de 4 horas, além do tempo para preparação do equipamento no início e fim do dia de trabalho. No total foram realizadas 120 análises isotópicas através desse método.

Após a realização das análises por quebra, as mesmas amostras foram submetidas às análises isotópicas de He, Ne e Ar através do método de fusão total (*single step heating*). Esta etapa foi realizada com a finalidade de se identificar possíveis contribuições de componentes cosmogênicos, radiogênicos e nucleogênicos presentes na estrutura cristalina dos minerais, além de atestar a veracidade dos resultados obtidos na etapa anterior. Para análises de fusão total, apenas uma medição de branco foi realizada por rodada analítica, sendo que para cada rodada 10 amostras foram comportadas no porta

amostras. Nesse caos, cada análise tem duração de aproximadamente 3 horas. No total foram realizadas 26 análises isotópicas através desse método.

Os gases nobres foram extraídos sob condição de alto vácuo pelo método descrito por Nagao *et al.* (1996) e Sumino *et al.* (2001). A extração dos gases é realizada de duas maneiras em cada uma das etapas. A primeira ocorre por meio da quebra de minerais (*crushing*), em que a amostra (~1,1 g) depositada na base do tubo de aço inoxidável (*crusher*) é triturada com o uso de um pistão de níquel movido a partir de campo magnético externo gerado por bobinas magnéticas solenoides (Fig. 4.2). No segundo método de extração (fusão total ou *single step heating*), a amostra (~0,5 g) é completamente fundida a 1800 °C em um forno de tântalo, em que ocorre a completa extração dos gases, incluindo aqueles presentes na estrutura cristalina e na superfície das amostras (Fig. 4.3).

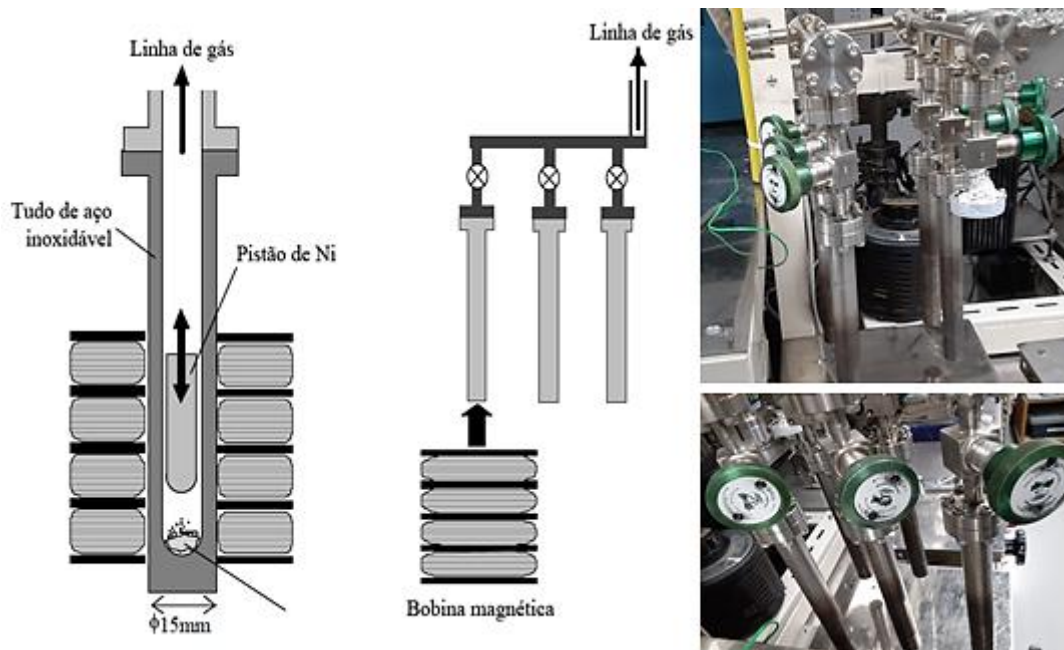


Fig. 4.2. Diagrama esquemático adaptado de Sumino *et al.* (2001) mostrando a sistemática empregada na análise por quebra de amostras e fotografias da disposição dos *crushers*. Os tubos de aço inoxidável (*crushers*) são conectados com a linha de gás através de algumas válvulas. Atualmente é possível conectar 7 *crushers* à linhas de gás. A amostra é depositada na base do *crusher* e é submetida a diferentes números de batidas (*strokes*) para que os gases sejam liberados das inclusões fluidas dos minerais. O movimento do pistão de Ni se dá através de uma bobina magnética que é acoplada na parte externa do *crusher*.

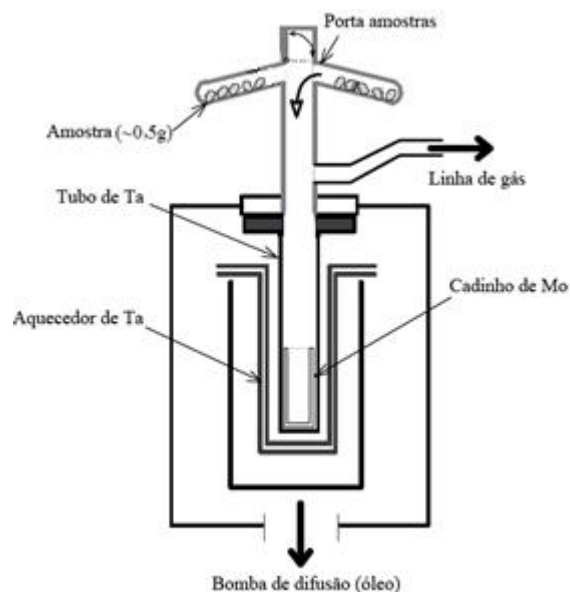


Fig. 4.3. Diagrama esquemático adaptado de Sumino *et al.* (2001) e fotografia mostrando o porta amostras e o forno de tântalo (Ta) que são utilizados nas análises por fusão. Os porta amostras têm 2 “braços” e cada um deles acomoda até 5 amostras de ~0,5 g. A amostra a ser analisada é movida com o auxílio de ímãs, que são utilizados para mover o porta amostras até a cavidade que dá acesso ao cadinho de molibdênio (Mo). Como as amostras são “lançadas” no cadinho, as análises devem ser realizadas de forma sequencial, partindo da primeira localizada mais próxima à cavidade até a última mais distante da mesma.

As composições elementares e isotópicas dos gases nobres foram obtidas por meio de uma linha de gás acoplada a um espectrômetro de massa (Fig. 4.4). É na linha de gás em que ocorrem as etapas de separação dos diferentes isótopos e a purificação, que consiste na eliminação dos gases residuais durante a análise. O espectrômetro de massa utilizado para realizar as leituras isotópicas é do tipo *sector*, versão modificada de um VG5400. A sensibilidade e os fatores de correção de discriminação de massa para o sistema de espectrometria de massa são determinados através da medição de constantes atmosféricas conhecidas por meio do mesmo procedimento aplicado para análise de amostras. Incertezas experimentais nas concentrações de cada um dos gases nobres foram estimadas em 5 % para He e Ar; e em 10 % para Ne, Kr e Xe, com base na reprodutibilidade das medições dos padrões de gás (*e.g.* HESJ = He *standard of Japan*). Os erros admitidos para as razões isotópicas estão em um desvio-padrão (1σ), incluindo erros de correção do branco e discriminação em massa.

Após a colocação das amostras nos compartimentos (*crushers* e porta amostras), e antes do início de cada rodada de análise, toda a linha de gás e os compartimentos são aquecidos a 200 °C por mais de 24 horas sob vácuo, com objetivo de reduzir os gases nobres atmosféricos adsorvidos na linha de extração. Brancos foram determinados antes

do início das análises isotópicas, sendo que para cada uma das amostras são determinados brancos individuais nas análises por quebra e a cada nova troca de amostras nas análises por fusão (a cada 10 amostras). Cabe ressaltar que em alguns casos de análises por fusão, os valores obtidos para o branco foram muito elevados. Para reduzir gases nobres atmosféricos adsorvidos foi necessário realizar novamente a desgaseificação do forno por 60 minutos. Em seguida, foi preciso aguardar cerca de 60 minutos para seu completo resfriamento.

Após a conclusão da etapa de preparação e análises dos brancos, os gases nobres aprisionados nas amostras são liberados de acordo com cada um dos métodos de extração (fusão ou quebra) e em seguida são inseridos na linha de gás. Cada um dos processos descritos a seguir envolve a abertura e fechamento de válvulas que isolam ou conectam as diferentes partes da linha de gás (Fig. 4.4).

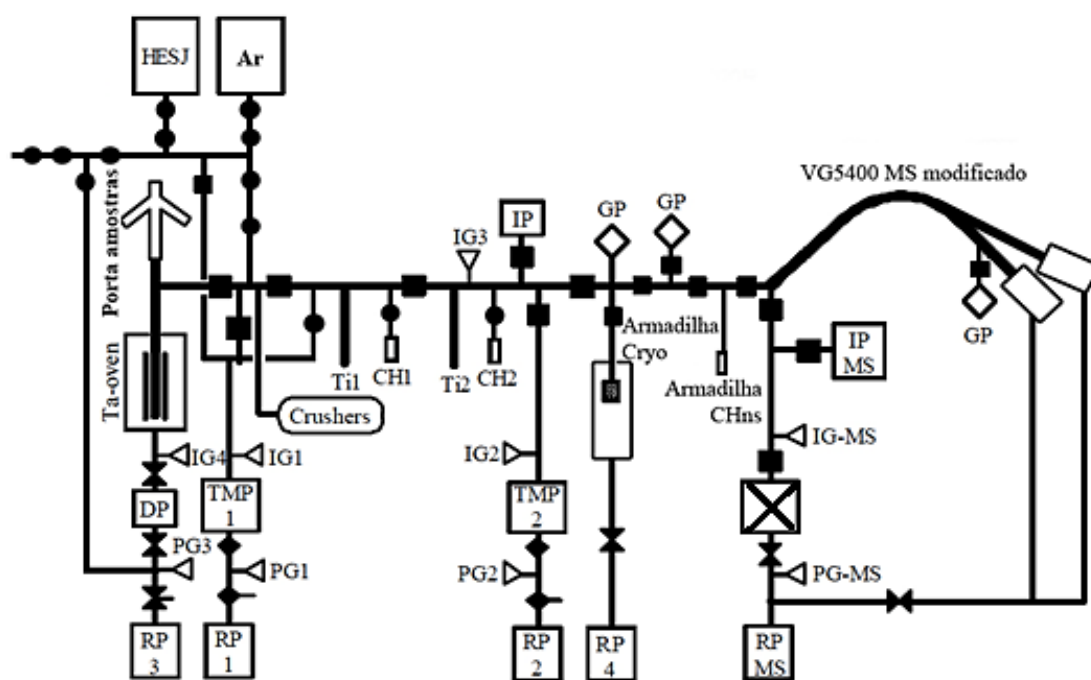


Fig. 4.4. Diagrama esquemático adaptado de Sumino *et al.* (2001) do sistema de análise de gases nobres (MS-IV). Ta-oven = extração de gases nobres através de um forno de Ta. Crushers = tubos de aço inoxidável em que ocorre a quebra das amostras na condição de vácuo. Armadilha Cryo = local onde ocorre o aprisionamento do Ne, Kr e Xe através de baixas temperaturas. Ti1 = armadilha de Ti-Zr usada para aprisionar os gases que interferem e prejudicam as análises; CH1 e CH2 = armadilhas de carvão (o Ar, Kr e Xe são aprisionados/separados no início da análise com o uso de nitrogênio líquido na CH1). IG1-3 e IG-MS = ion gauge. PG1-PG3 e PG-PMS = pirani gauge. TMP1, 2 = bomba turbo molecular. IP e IP-MS = ion pump. RP1-RP4 e RP-MS = rotary pump. DP = bomba de difusão (óleo). GP = getter pump.

Primeiramente, os gases nobres liberados são purificados com o uso de uma armadilha aquecida a ~800 °C composta por Ti e Zr (Ti1; Ti-Zr getter), que aprisiona os

demaís gases (ex. H, CO^{2++} , CO^{2+}). Posteriormente, Ar, Kr e Xe são aprisionados em uma armadilha de carvão (*charcoal trap*, CH1), que é resfriada com nitrogênio líquido. O He e o Ne, não são aprisionados durante esses processos iniciais de purificação e separação isotópica. Em seguida, um segundo processo de purificação é realizado através de uma segunda *charcoal trap* (CH2), também resfriada com nitrogênio líquido. Finalmente, o Ne é separado do He com o uso de uma terceira armadilha resfriada a 15 K (-260 °C; *Cryo trap*).

Cada um dos gases nobres separados é sequencialmente introduzido e analisado no espectrômetro de massas. Os isótopos de He são os primeiros a serem medidos e a análise é realizada com o uso de dois coletores: Axial para o ^3He e *High Faraday* no caso do ^4He . Os isótopos de Ne são liberados da *Cryo* ao se elevar a temperatura a 45 K (-230 °C), sendo analisados através do Axial. Com o objetivo de reduzir a interferência do $^{40}\text{Ar}^{++}$ e CO_2^{++} ($M = 44$) sobre os isótopos de ^{20}Ne e ^{22}Ne , respectivamente, outra armadilha composta pelo mesmo material da *Cryo* está localizada na entrada do espectrômetro de massas (armadilha CHns). A CHns é resfriada com nitrogênio líquido pouco antes do Ne ser introduzido no espectrômetro de massas e volta a ser aquecida após sua análise isotópica. As alturas dos picos definidos para ^{40}Ar e CO_2 são medidos no início e no final de cada análise de Ne para que os valores obtidos sejam corrigidos. Cabe ressaltar que os campos magnéticos para todos os elementos (He, Ne, Ar, Kr e Xe) são definidos manualmente antes do início de cada medição.

Em seguida, Ar, Kr e Xe, que ficaram aprisionados na CH1, são liberados através da remoção do nitrogênio líquido. Para que o aquecimento ocorra com maior eficácia, a CH1 é aquecida como uso de recipiente contendo água quente e de pipeta. Em seguida, o forno é recolocado na CH1 e os gases presentes na linha de gás são novamente purificados pela armadilha aquecida de Ti-Zr (Ti1). Neste momento, Kr e Xe são aprisionados na *Cryo* a uma temperatura de 95 K (-180 °C) e o Ar é introduzido no espectrômetro de massas para ser analisado por meio do multi-coletor *Daly* (*Daly multiplier collector*). A 135 K (-140 °C) e a 200 K (-73 °C) Kr e Xe são, respectivamente, liberados da *Cryo* e introduzidos no espectrômetro de massas. Ambos são analisados pelo Axial.

CAPÍTULO 5

ARTIGO I

5 ARTIGO I

O primeiro artigo científico foi publicado em agosto de 2024 no periódico *Journal of Petrology*. A publicação, bem como os materiais suplementares, pode ser acessada em: <https://doi.org/10.1093/petrology/egae087>.

Destruction of the lithosphere beneath the SW margin of the São Francisco Craton evidenced by refertilized and deformed mantle xenoliths

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Abstract

The destruction of the cratonic root has been documented for multiple cratons worldwide and is characterized by severe lithospheric thinning, extensive extensional deformation, and intense thermal activity. Here, we present detailed petrography accompanied by comprehensive geochemical and isotopic data for peridotites, pyroxenites, and eclogites from the SW margin of the São Francisco Craton that has also been severely thinned. The diamond-bearing Canastra-1 kimberlite represents a Cretaceous intrusion from the Alto Paranaíba Igneous Province and hosts garnet-bearing mantle xenoliths from different mantle sources, revealing a complex history of metasomatism/refertilization related to superimposed tectonic events since the cratonic consolidation.

Eclogites ($T = 978\text{--}982\text{ }^{\circ}\text{C}$; $P \sim 4.0\text{ GPa}$) and pargasite-bearing websterites ($T = 875\text{--}926\text{ }^{\circ}\text{C}$; $P = 2.0\text{--}3.0\text{ GPa}$) represent the shallower and colder cratonic lithosphere. Mantle-derived high-MgO eclogitic clinopyroxenes show a light rare earth element (LREE)-enriched pattern ($\text{Ce/Yb}_N = 60.90\text{--}93.63$) while both clinopyroxene and garnet present high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ($0.70842\text{--}0.70912$) and negative ϵNd values (-5.6 to -7.3). These features, supported by the reconstructed whole-rock composition, suggest a mafic protolith probably metasomatized by fluid/melt derived from the overlying sedimentary rocks. The pargasite websterites are cumulates from an evolved (SiO_2 -rich) and hydrated basaltic andesitic magma. These xenoliths are characterized by high concentration of LREE relative to heavy-REE (HREE) in clinopyroxenes ($\text{Ce/Yb}_N = 10.52\text{--}50.61$) and pargasite ($\text{Ce/Yb}_N = 10.26\text{--}57.06$), and by the presence of Al-rich orthopyroxene. As observed in eclogites, clinopyroxene and garnet from pargasite websterites display high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ($0.70894\text{--}0.71094$) and strong negative ϵNd values (-7.2 to -13.3). Trace elements (i.e., Zr, Ti, and Y) in garnets of both rock types indicate the role of a depleted component affected by a metasomatic agent. Although we were unable to date the formation of these rocks or the metasomatic events, we suggest a possible relationship with the consolidation of Gondwana during the Neoproterozoic.

Sheared lherzolites, clinopyroxenites, anhydrous websterites, and dunite are deeper fragments from the lithosphere-asthenosphere boundary (LAB: $1191\text{--}1290\text{ }^{\circ}\text{C}$; $5.3\text{--}5.6\text{ GPa}$). They have abundant kelyphitic rims around garnet grains, which indicate metasomatism promoted by the percolation of a high-temperature proto-kimberlite melt enriched in Ti, Zr, and Y. The presence of kelyphitic phlogopite with high-Ti-Cr contents reinforces this assumption. LREE-enriched clinopyroxenes ($\text{Ce/Yb}_N = 12.06\text{--}48.02$)

confirm the enriched character of the silicate melt responsible for the refertilization process within the cratonic root. The proto-kimberlite metasomatism is further supported by the preferential enrichment of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70560–0.70869) accompanied by positive ϵNd values (+1.8 to +10.10). The two-point clinopyroxene-garnet Sm-Nd isochrons yielded an average age of 120 ± 5 Ma, representing the kimberlite eruption/emplacement age of the host kimberlite. These deeper LAB xenoliths reveal intense lithospheric thinning triggered by percolation of a high-temperature proto-kimberlite melt since the early stages of Gondwana break-up during the Cretaceous, shortly before the kimberlite emplacement at 120 Ma. Therefore, they provide remarkable evidence of the destruction of the São Francisco Craton through thermal-mechanical erosion that triggered its rejuvenation.

Highlights

- Canastra-1 xenoliths show strong lithological, chemical, and isotopic heterogeneity
- Rejuvenation and decratonization supported by sheared and refertilized lherzolites
- Extensive lithospheric thinning corroborates the destruction of the São Francisco Craton
- Lithospheric xenoliths (875–982 °C; ~100–130 km) are subduction-related
- Proto-kimberlite metasomatism affected the deeper LAB xenoliths (1191–1290 °C; 174–186 km)

Keywords: Mantle metasomatism; Mantle xenoliths; Mineral chemistry; Sr-Nd isotopes

5.1 Introduction

Although most Archean to Paleoproterozoic cratonic nuclei are believed to be tectonically stable, the base of the lithosphere in these terrains may have been reworked by episodic rejuvenation events associated to thermal anomalies promoted by mantle plumes, or even by small-scale convection (edge-driving convection) that generates lateral thermal erosion as a response to the upwelling of the hot asthenosphere (Menzies *et al.*, 1987; King & Anderson, 1998; King & Ritsema, 2000; Foley, 1992, 2008; Aulbach, 2018; Liu *et al.*, 2019; 2021). In addition, recycling of oceanic slabs may also contribute to mantle metasomatism (cryptic and/or modal), re-enriching the lithosphere through the

percolation of melts and/or fluids derived from the slab melt or dehydration (Foley, 1992; Konzett *et al.*, 2000; Aulbach *et al.*, 2007). These mechanisms favor a succession of events such as rejuvenation, weakness, and erosion of the deep lithosphere at cratonic margins (Carlson *et al.*, 2004; Downes *et al.*, 2004; Tappe *et al.*, 2007; Foley, 2008; Tang *et al.*, 2013; Giuliani *et al.*, 2016; Liao *et al.*, 2017; Liu & Li, 2018; Fitzpayne *et al.*, 2018, 2019, 2020; Liu *et al.*, 2019; Dessai *et al.*, 2021; Carvalho *et al.*, 2022a).

Several mineralogical, chemical, and isotopic investigations on mantle xenoliths hosted by kimberlites from cratonic regions worldwide have demonstrated lithological and compositional heterogeneity in the upper mantle (Griffin *et al.*, 1999; Konzett *et al.*, 2000, 2013; Grégoire *et al.*, 2002; Carlson *et al.*, 2007; Ionov *et al.*, 2010; Agashev *et al.*, 2013; Aulbach *et al.*, 2013, 2020; Guo *et al.*, 2020; Fernandes *et al.*, 2021; Gervasoni *et al.*, 2022, Rodrigues *et al.*, 2023). Complementary temporal and spatial information provided by geochronological and geophysical studies also supports geochemical heterogeneity studies about the structure and evolution of the cratonic lithosphere (Aulbach, 2018). However, xenoliths from the São Francisco and Amazonian cratons, bearing some the most important Archean nuclei in Brazil, lack detailed geochemical and geophysical investigations. Besides the studies based on mineral xenocrysts (Read *et al.*, 2004; Hunt *et al.*, 2009; Donatti-Filho *et al.*, 2013; Guarino *et al.*, 2013; Coldebella *et al.*, 2020; Carvalho *et al.*, 2022a, b), a few scientific contributions concerning mantle xenoliths have addressed the long-lived tectonic evolution of the lithospheric mantle beneath Brazilian cratons (Carvalho, 1997; Carlson *et al.*, 2007; Costa, 2008; Thomaz, 2009; Costa, 2012; Almeida *et al.*, 2014, 2022; Nannini, 2011, 2016; Fernandes *et al.*, 2021; Gervasoni *et al.*, 2022; Rodrigues *et al.*, 2023).

In this context, we present a comprehensive and detailed study based on petrography, mineral chemistry, and isotope geochemistry of fresh mantle xenoliths hosted by the Canastra-1 kimberlite. These xenoliths, which represent heterogeneous fragments from the cratonic mantle within the garnet stability field, include sheared lherzolites (n = 12), clinopyroxenites (n = 6), websterites (olivine-free anhydrous and hydrated xenoliths, n = 5), eclogites (n = 2), and dunite (n=1). Here we propose the partial destruction of the SW margin of the São Francisco Craton registered for the first time by samples of the deep cratonic lithosphere. The discussion about this tectonic setting is based on the mineral chemistry mainly of clinopyroxene, garnet, phlogopite,

orthopyroxene, and amphibole. Sr-Nd isotopic ratios and Sm-Nd isochrons of whole-rock, clinopyroxene, and garnet support these data.

5.2 Geological setting

The São Francisco Craton is one of the major cratonic areas of the South American platform, composed of Archean blocks accreted and reworked during Paleoproterozoic and Neoproterozoic orogenies (e.g., Almeida *et al.*, 1981; Ganade *et al.*, 2021; Neves, 2021). This craton, together with the Amazonian Craton and the Paranapanema Block, limit the Tocantins Province, the latter being entirely covered by the sedimentary successions of the Paraná Basin (Fig. 5.1) (Almeida *et al.*, 1981; Valeriano *et al.*, 2008).

In the context of the southern São Francisco Craton, segments of a Paleoproterozoic orogen are represented by the Mineiro Belt and the Quadrilátero Ferrífero mining district (Alkmim & Teixeira, 2017). Besides the Eastern Bahia orogenic domain (northern São Francisco Craton), these orogens record the collision between the Archean core of the São Francisco and Congo cratons during the transition between the Rhyacian and Orosirian periods (~2.0–1.9 Ga), which led to the consolidation of the São Francisco paleocontinent (Alkmim & Teixeira, 2017; Barbosa & Barbosa, 2017 and references therein).

The current outline of the São Francisco Craton was defined during the amalgamation of West Gondwana (Cordani *et al.*, 2013). In its southwestern and western margins, the Brasília Mobile Belt developed through a long succession of collisional events in which the final convergence and collision took place in the late Neoproterozoic, during the Brasiliano Orogeny (Fuck *et al.*, 2017). The Brasília Mobile Belt resulted from subduction of a wide oceanic lithosphere named Goiás-Pharusian Ocean, forming an oceanic island arc (~900–800 Ma), followed by the development of a continental arc (770–630 Ma) and the continental collision of the Amazonian, São Francisco, and Paranapanema paleocontinents (640–610 Ma) (Valeriano *et al.*, 2008; Fuck *et al.*, 2017; Frugis *et al.*, 2018).

In the Cretaceous, heterogeneous NW-SE oriented mafic potassic to ultrapotassic magmatism occurred in the Alto Paranaíba Igneous Province (APIP), extending from southwest Minas Gerais to the south of Goiás. The APIP mainly

comprises kimberlites, lamproites, lamprophyres, kamafigites, and minor carbonatite intrusions (e.g., Gibson *et al.*, 1995; Guarino *et al.*, 2013; Azzone *et al.*, 2022; Carvalho *et al.*, 2022a, b). The magmatism related to the APIP is widespread along the Brasília Mobile Belt that overthrusts the São Francisco Craton, between the SW margin of the craton and the NE margin of the Paraná Basin. Although placed within the Brasília Mobile Belt, previous studies of mantle xenoliths and xenocrysts associated with the APIP magmatism indicate that these rocks were likely sourced from the cratonic subcontinental lithospheric mantle (e.g., Carlson *et al.*, 2007; Fernandes *et al.*, 2021; Carvalho *et al.*, 2022a, b). Additionally, gravimetric (Pereira & Fuck, 2005) and seismic tomographic (Rocha *et al.*, 2019a, b) data suggest that the APIP belongs to the cratonic area. Therefore, the Canastra-1 kimberlite and its mantle xenoliths are inserted in the “on-craton” context, representing the SW edge of the São Francisco Craton. Studies of the exotic magmatism of APIP have suggested that a heterogeneous and metasomatically enriched mantle source is needed to explain the genesis of these rocks in a single province (Gibson *et al.*, 1995; Araujo *et al.*, 2001; Guarino *et al.*, 2013; Woodhead *et al.*, 2019; Carvalho *et al.*, 2022a, b).

In general, kimberlites and kamafigites from APIP are coeval with chronological ages mainly from ~90 to 80 Ma (e.g., Sgarbi *et al.*, 2004; Guarino *et al.*, 2013; Felgate, 2014; Carvalho *et al.*, 2022b). In contrast, the diamond-bearing Canastra-1 kimberlite, located in the SW of Minas Gerais, presents an older emplacement age of 120 Ma (Read *et al.*, 2004 after personal communication of Martin Doyle, De Beers). This kimberlite was emplaced at the SW margin of the São Francisco Craton and hosts the mantle xenoliths investigated here (Fig. 5.1). It is intrusive into Neoproterozoic metasedimentary rocks of the Brasília Mobile Belt (Canastra Group) and is part of a cluster with approximately 47 kimberlite intrusions that comprise the Serra da Canastra field (Cabral Neto *et al.*, 2017).

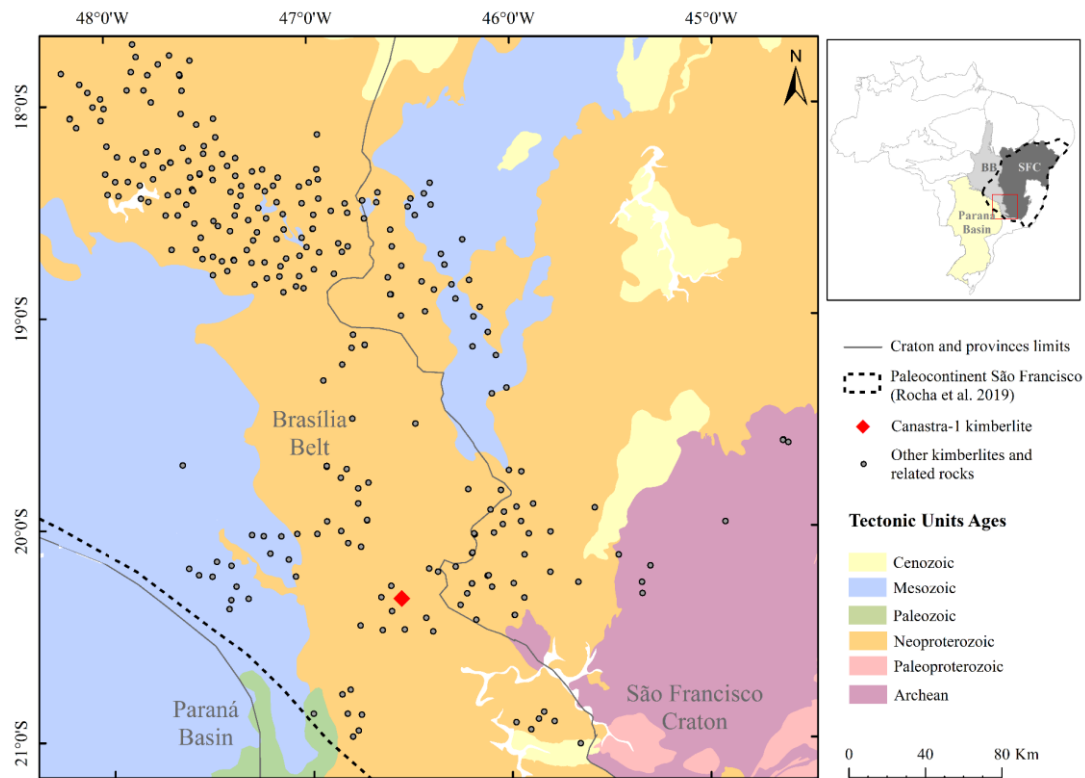


Fig. 5.1. Simplified geological map of the SW portion of the São Francisco Craton and surroundings with the location of Canastra-1 kimberlite. SFC: São Francisco Craton, BB: Brasília Belt. Delimitation of the São Francisco Palecontinent after Rocha *et al.* (2019a) (dashed line).

5.3 Analytical methods

The twenty-six mantle xenoliths analyzed to elaborate this paper were provided by De Beers Brazil Ltda. They represent a set of fresh (free of secondary alteration) xenoliths sampled as large drill-holes with no contact with the host kimberlite. Among these samples, twelve had their Electron Probe Microanalysis (EPMA) data obtained during the Master dissertation of Costa (2008) (Supplementary Tables S1–S2).

5.3.1 Electron Probe Microanalysis

Major element and compositional averages of mineral phases from Canastra-1 mantle xenoliths (olivine, orthopyroxene, clinopyroxene, garnet, amphibole, phlogopite, spinel, rutile, and ilmenite) were determined by wavelength-dispersive spectrometry (WDS) using a JEOL JXA-8230 Electron Probe Micro Analyzer (EPMA) at the Laboratório de Microsonda Eletrônica, Instituto de Geociências (IG), Universidade de Brasília (UnB), Brazil (Supplementary Tables S1–S3). The analyses were performed

using an accelerating voltage of 15 kV, a beam current of 10 nA, and a beam diameter of 1 μm in the spot mode. For amphibole and phlogopite we employed the circle mode with 5 μm . Counting time on peak were 10 s per analyte peak and 5 s for the background. All results were reduced using an in-house ZAF correction program. The measurements were calibrated with the following mineral standards: andradite (CaO and FeO), albite (Na₂O), forsterite (MgO), microcline (K₂O, Al₂O₃ and SiO₂), pyrophanite (TiO₂ and MnO), chromium oxide (Cr₂O₃), nickel oxide (NiO), topaz (F), and vanadinite (Cl). To verify the data quality, we compared our new results for samples CAN1-88, CAN1-94, and CAN1-95 with those previously analyzed by Costa (2008). The detection limits are provided in the Supplementary Table S2.

5.3.2 *Laser ablation inductively coupled plasma mass spectrometry*

Most of the trace and rare earth elements (REE) were determined at the Laboratory of the Centro Interdipartimentale Grandi Strumenti (CIGS), the Università di Modena e Reggio Emilia, by Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) (Supplementary Tables S1 and S2). Additional measurements were conducted at the NAP Geoanalítica Laboratory of Geoscience Institute, University of São Paulo (USP) (Supplementary Tables S1 and S2).

At CIGS, analyses were performed using a Thermo Fisher Scientific XSERIES 2 mass spectrometer coupled to a New Wave UP 213 laser ablation. Data reduction was performed with the Thermo Fisher Scientific PlasmaLab® software using NIST610, NIST612 and NIST614 as reference materials (Jochum *et al.*, 2005) (Supplementary Table S4). First, standard NIST612 was used to check the calibration with only NIST610 and NIST614, resulting in accuracy <10%. Then it was added to the sample calibration. The analysis conditions were laser spot 55 μm , an output 70 % (on-sample fluency of 9 J/cm²), a 10 Hz repetition rate, and a dwell time 30 s. Prior to analyses, each spot surface was pre-ablated on a 65 μm laser spot size with an output of 45 % and a 10 Hz repetition rate. ⁴⁴Ca was used as internal standard for clinopyroxene, garnet and amphibole.

At NAP, the trace elements were obtained using a New Wave 216 nm laser ablation system coupled to a Quadrupole ICP-MS PerkinElmer ELAN-6100 DRC (Dynamic Reaction Cell). ⁴⁴Ca was used as internal standard for clinopyroxene and garnet. The laser spot size varied between 20 and 40 μm and laser beam fluency was set

at 20 J/cm². Prior to sample analyses, the system was tuned with the BCR-2G, BHVO-2G, and BIR-1G reference glasses (Supplementary Table S4) for maximum sensitivity, stability, and low oxide production rates ($^{232}\text{Th}^{16}\text{O}/^{232}\text{Th} < 0.1\%$). The detection limits are provided in the Supplementary Table S2.

5.3.3 $^{147}\text{Sm}/^{143}\text{Nd}$ systematics and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios

The $^{147}\text{Sm}/^{143}\text{Nd}$, $^{143}\text{Nd}/^{144}\text{Nd}$ ($n = 32$), and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios ($n = 25$) were determined for mineral separates (clinopyroxene and garnet) and whole-rock (with no Sr data) samples (Supplementary Table S5). Mantle xenoliths were wrapped in clean paper and plastic bags and then mechanically disaggregated into smaller pieces using a hammer. Afterwards clinopyroxene and garnet grains were carefully handpicked under a binocular microscope. The mineral and whole-rock powders were produced manually using an agate mortar and pestle. Individual aliquots of samples were used for Sm-Nd (0.1 g for Sm and 0.5 g for Nd with addition of mixed ^{149}Sm - ^{150}Nd spike) and Sr (0.1 g; without addition of spike) isotope analysis. Sample digestion for both analyses followed the procedure described by Gioia & Pimentel (2000). Sm and Nd were separated in Teflon columns in two steps: cationic resin AG-50W-X8 (200–400 mesh) to separate REE, anionic Eichrom LN Resin (100–150 μm) to separate Sm and Nd. Sr was separated using Eichrom SR-B100-S (100–150 μm) resin. Sm-Nd and Sr aliquots were loaded onto double Re filament assembly and the measurements were carried out by Thermal Ionization Mass Spectrometry (TIMS) using a Thermo-Finnigan Triton mass spectrometer at the Laboratório de Estudos Geodinâmicos, Geocronológicos e Ambientais (LEGGA), UnB, Brazil. The data were corrected for mass fractionation by normalizing to $^{146}\text{Nd}/^{144}\text{Nd}$ of 0.7219 and $^{88}\text{Sr}/^{86}\text{Sr}$ value of 8.3752. The analyses of BHVO-2 and NIST-SRM NBS-987 standards gave $^{143}\text{Nd}/^{144}\text{Nd} = 0.512962 \pm 0.000005$ ($n = 4$, 2σ) and $^{87}\text{Sr}/^{86}\text{Sr} = 0.71026 \pm 0.00001$ ($n = 2$, 4σ), respectively. These values are identical within uncertainty to the reference values of 0.512957 ± 0.000006 (Raczek *et al.*, 2003) and 0.71025 ± 0.00011 (Thirlwall, 1991). Blank values are lower than 50 pg.

5.4 Results

5.4.1 Petrograph

The collection of garnet-bearing xenoliths from drill cores of the Canastra-1 kimberlite includes twelve sheared lherzolites (from which nine samples were selected for petrography analyses), six clinopyroxenites, two websterites, three pargasite websterites, two eclogites, and one dunite (Supplementary Table S6 and Supplementary Fig. S1). Modal percentages of mineral phases were determined by digital point counting using the JMicroVision software (Roduit, 2007). For each thin section (each one with 37–43 x 21–25 mm) at least 3000 points were counted (Supplementary Table S6 and Supplementary Information).

Macroscopically, the xenoliths are ovoid in shape, they do not display interaction with the host kimberlite, and usually are <15 cm in diameter. Sheared lherzolites exhibit mosaic-porphyroclastic texture showing porphyroclasts of orthopyroxene, clinopyroxene, and garnet surrounded by fine-grained recrystallized neoblasts of olivine. Pyroxenites (websterites and clinopyroxenites) and eclogites show coarse texture, whereas the dunite displays granuloblastic texture (Harte, 1977). Clinopyroxenites and eclogites are petrographically similar, being differentiated only by mineral chemistry data.

Sheared garnet lherzolites are composed of olivine (52–72 %), orthopyroxene (9–23 %), clinopyroxene (8–23 %), and garnet (5–18 %). *Olivine* dominantly occurs as neoblasts (up to 0.5 mm in diameter, ~94% of total olivine) with subordinate porphyroclasts (1.0–2.8 mm in diameter). The former olivine exhibits polygonal habit, with straight grain boundaries and common 120° triple point junctions (Fig. 5.2a). The relict grains show signs of deformation such as undulose extinction and kink bands. Serpentine is developed along fractures in porphyroclasts and in the boundary of neoblasts. *Orthopyroxene* porphyroclasts (1.5–4.0 mm in diameter) tend to be rounded to elongated. They also display undulose extinction and recrystallization features along grain boundaries, such as tiny neoblast “tails” stretching out from larger pyroxene porphyroclasts (Fig. 5.2b, c, f). Rarely, kink bands were observed in some grains. *Clinopyroxene* porphyroclasts (1.5–5.1 mm in diameter) show irregular to rounded shape, with smoothly curved grain boundaries. These porphyroclasts normally show thin

exsolution of orthopyroxene (Fig. 5.2d). They display reaction features as spongy and cloudy margins (Fig. 5.2e). Subhedral rounded *garnet* (0.9–2.8 mm in diameter) occurs as porphyroclasts or as subrounded inclusions (~0.8 mm) within clino- and orthopyroxenes (Fig. 5.2b). Pyroxenes within garnet crystals is less frequent. In most instances, garnet crystals are systematically surrounded by kelyphitic coronae (reaction rims) of variable thickness (Fig. 5.2f). Lherzolithic samples represent a transition sequence from low to moderate deformation evidenced by non-fluidal to fluidal textures (Fig. 5.2g, h). None of the studied samples have high degree of deformation expressed by the presence of garnet neoblasts in disrupted textures (Harte, 1977).

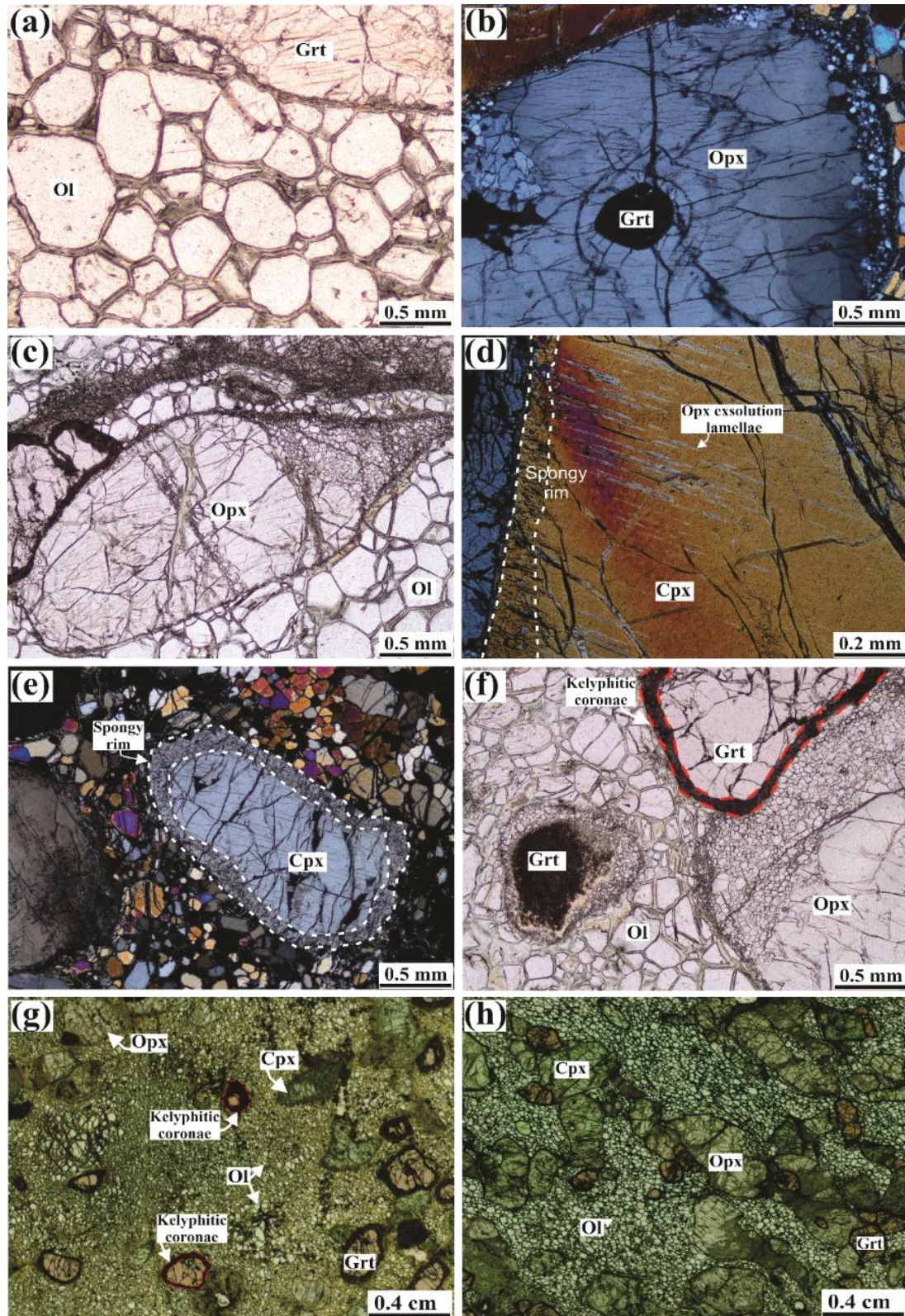


Fig. 5.2. Photomicrographs and scanned thin sections of garnet lherzolites from Canastra-1 kimberlite showing the main mineral assemblages and main textures. (a) Neoblasts of olivine (CAN1-101). (b) Recrystallization along orthopyroxene grain boundaries and (c) into tiny orthopyroxene neoblasts “tails” stretching out from larger pyroxene porphyroclasts (CAN1-88). (d) Clinopyroxene with orthopyroxene exsolution lamellae (CAN1-107). (e) Well-developed clinopyroxene spongy rim (CAN1-86). (f) Garnets surrounded by kelyphitic coronae of variable thickness (CAN1-88). (g-h) Scanned images of thin sections showing the main aspects of lherzolitic xenoliths highlighting the progressive deformation illustrated by

the mineral orientation (CAN1-97 and CAN1-88). Plane- (a, c, f) and crossed- (b, d, e) polarized lights. Abbreviations: Cpx = clinopyroxene; Opx = orthopyroxene; Grt = garnet; Ol = olivine.

Garnet clinopyroxenites are the coarsest-grained lithotype, exhibiting crystals with similar dimensions (Fig. 5.3a). Clinopyroxene (46–56 %) and garnet (44–55 %) have subrounded to subhedral habits. *Clinopyroxene* crystals vary from 1.7 to 5.0 mm in diameter, and rarely show exsolution lamellae of orthopyroxene. They commonly exhibit thick spongy rims (Fig. 5.3b). *Garnet* (2.2–5.5 mm in diameter) occurs as highly fractured grains, in which a thick kelyphite rim (corona) is ubiquitous in all samples (Fig. 5.3c). The poikilitic texture may be seen in some garnet with subrounded inclusions of clinopyroxene (Fig. 5.3d).

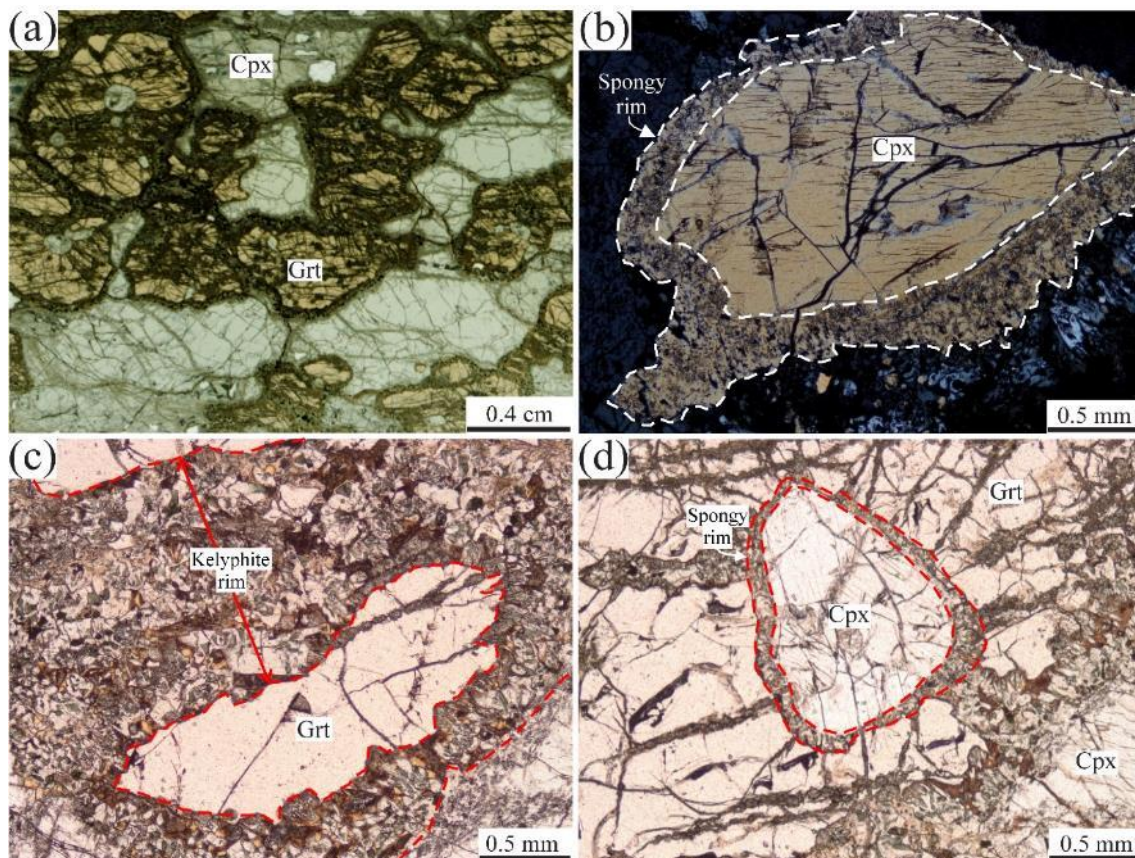


Fig. 5.3. Photomicrographs and scanned thin section of garnet-clinopyroxenites xenoliths from Canastra-1 kimberlite showing the main mineral assemblages and texture. (a) Scanned image of the thin section CAN1-94. (b) Well-developed spongy rim in clinopyroxene (CAN1-126). (c) Fractured garnet with thick kelyphite rim (CAN1-142). (d) Poikilitic texture in garnet (CAN1-213). Plane- (c, d) and crossed- (b) polarized lights. Abbreviations: Cpx = clinopyroxene; Grt = garnet.

Garnet websterites may be anhydrous (2 samples) or hydrated (3 samples). The anhydrous websterites are medium- to coarse-grained and present variable modal

abundance expressed by clinopyroxene (13–56 %), orthopyroxene (25–78 %), and garnet (9–19 %). Crystals are intensely fractured and show triple point junctions and lobate contacts, typical of equilibrated mantle assemblages (Fig. 5.4a). *Clinopyroxene* occurs with bimodal distribution sizes (1.4–3.0 and 4.5–7.0 mm in diameter), usually exhibiting a turbid appearance, and shows fine exsolution lamellae of orthopyroxene (Fig. 5.4b). *Orthopyroxene* mainly appears as large (5.0–6.2 mm in diameter) and elongated crystals, but small and anhedral grains were also observed (1.2–2.8 mm in diameter) (Fig. 5.4c). *Garnet* (1.4–3.7 mm in diameter) occurs interstitially in aggregates as deformed crystals, with highly irregular shapes. Occasionally, crystals are completely resorbed by phlogopite and pyroxenes, forming kelyphitic rims. The hydrated (amphibole-bearing) garnet websterites are coarse-grained samples with clinopyroxene (33–42 %), orthopyroxene (24–35 %), garnet (12–29 %), and amphibole (5–18 %) (Fig. 5.4d). *Clinopyroxene* sizes vary from 0.8 to 3.8 mm in diameter; it has subhedral shapes, often displays undulose extinction, and exsolution lamellae of orthopyroxene. *Orthopyroxene* (0.7–3.0 mm in diameter) forms equant habits with curvilinear grain boundaries. *Garnet* (0.8–3.0 mm in diameter) has irregular shapes, but sometimes is slightly elongated. It is generally fresh, with only minor reaction rims when in contact with amphibole (Fig. 5.4e). Garnet generally exhibits poikilitic texture, in which a single crystal may include both pyroxenes as inclusions. *Amphibole* occurs as brown to greenish-brown grains (Fig. 5.4d, e, f), which are typically interstitial (~1.3 mm in diameter), mainly in contact with garnet and orthopyroxene grains. Nevertheless, subhedral and larger grains are also identified (up to 2.2 mm in diameter).

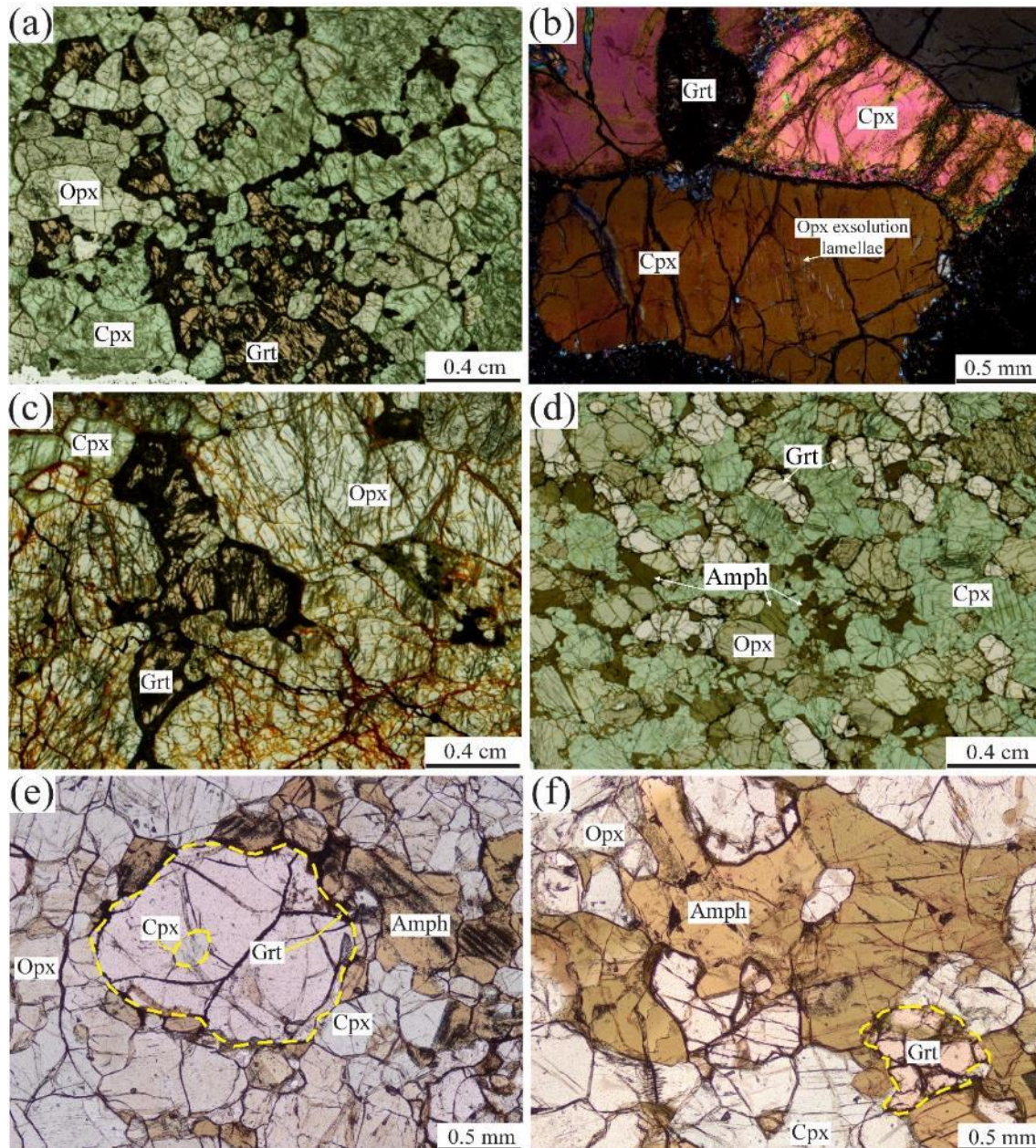


Fig. 5.4. Photomicrographs and scanned thin sections of anhydrous (a-c) and hydrated (d-f) olivine-free websterites from Canastra-1 kimberlite. (a) Triple point junctions and lobate contacts (CAN1-182). (b) Clinopyroxene shows turbid appearance and discrete exsolution lamellae of orthopyroxene (CAN1-182). (c) Large and extremely fractured orthopyroxene crystals with serpentine filling the spaces (CAN1-209). (d) Representative mineral assemblage and texture of hydrated websterites (CAN1-95). (e) Fresh garnet grains with minor reaction rims when in contact with amphibole (CAN1-143). (f) Greenish-brown amphibole crystals (CAN1-95). Plane- (e, f) and crossed- (b) polarized lights, and scanned thin sections (a, b, d). Abbreviations: Cpx = clinopyroxene; Opx = orthopyroxene; Grt = garnet; Amph = amphibole.

Eclogites are essentially biminerallitic samples composed of clinopyroxene (40–48 %) and garnet (52–60 %) (Fig. 5.5a), which is a common characteristic of this rock type (Jacob, 2004). *Clinopyroxene* (3.0–5.5 mm in diameter) appears to have been pervasively generated, as exemplified by its spongy (reacted) nature (Fig. 5.5b).

Conversely, subhedral *garnet* (4.0–6.0 mm in diameter) has fresh cores, although commonly fractured. Comparatively, this mineral shows lighter colors than those observed in clinopyroxenites. Crystal rims exhibit kelyphitic texture with an assemblage of secondary minerals (orthopyroxene and clinopyroxene) that surrounds every grain (Fig. 5.5a).

The **dunite** sample displays complete recrystallization of *olivine* to a granuloblastic texture of small equant mosaic crystals (<0.6 mm in diameter; Fig. 5.5c) (Harte, 1977). *Garnet* (1.0–2.3 mm in diameter) occurs as porphyroclasts with 2 % of modal abundance. These rounded fractured grains are rimmed and sometimes nearly completely replaced by kelyphitic intergrowths (Fig. 5.5d).

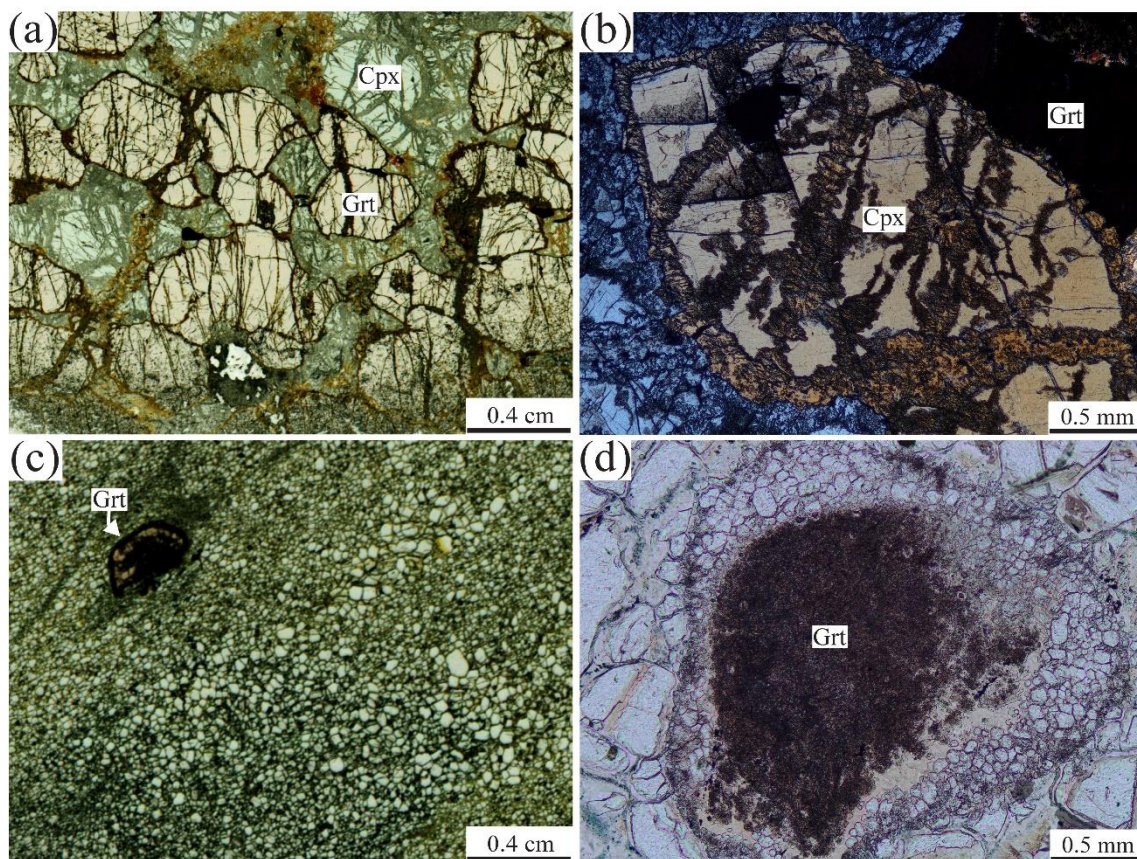


Fig. 5.5. Scanned thin sections and photomicrograph of eclogite (a,b) and dunite (c,d) xenoliths from Canastra-1 kimberlite. (a) Scanned thin section and photomicrograph in crossed-polarized light showing the representative mineral assemblage and texture (b) of eclogite xenolith (CAN1-206). Scanned images of the thin section from dunite xenolith (CAN1-180) showing the texture with equant olivine neoblasts (d) and garnet porphyroclasts surrounded by kelyphitic coronae (e). Abbreviations: Cpx = clinopyroxene omphacite; Grt = garnet.

Late textures observed in Canastra-1 mantle xenoliths encompass secondary minerals and textures developed by reactions with metasomatic agents. In the studied

samples, these textures are frequently associated with clinopyroxene and garnet (Fig. 5.6). Spongy clinopyroxene occurs in all rock types except in amphibole-bearing websterites. It typically occurs as variable thick coronae ($<300\text{ }\mu\text{m}$), and as cross-cutting veinlets or irregular patches and domains (Figs. 5.2e; 5.3b; 5.4d-f; 5.5a, b). The boundaries between spongy-textured clinopyroxenes and surrounding minerals are sharp and seem not to be controlled by cracks across the crystals. The spongy texture of clinopyroxenes is more pervasive in eclogites than in other rock types. In these samples, each grain is surrounded and crosscut by zones of spongy clinopyroxene, which dominate in up to 50 % of the mineral volume (Fig. 5.5b). This process affects practically all the clinopyroxene grains observed in the studied rock types.

Other important reaction processes common to all xenoliths, except for amphibole-bearing websterites, are the kelyphitic rims around garnet crystals (Fig. 5.2f-h; 4.3a, c; 4.4a, c; 4.5a, d). In lherzolites and eclogites, this texture occurs as a brownish rim (50–500 μm) surrounding garnet, in which minerals are barely recognizable under cross-polarized light (Fig. 5.6a). However, the cores of these grains remain fresh. Garnet may be partially or entirely replaced by extremely fine-grained minerals in amphibole-free websterites and in the dunite (Fig. 5.6b). Clinopyroxenites exhibit the most notable fine-grained, fibrous intergrowth of multiple phases, with clear fibrous and radial structures (Fig. 5.6c).

The main secondary phases involved in these reactions consist of orthopyroxene, clinopyroxene, spinel, rutile, and ilmenite. Subhedral phlogopite occurs at the edges of the kelyphitic rims. Distinct structures and domains can only be confirmed through the backscattered electron images (BSE) (Fig. 5.6d).

The first domain adjacent to garnet is composed of large crystals of orthopyroxene that contain several small, irregularly shaped patches of clinopyroxene (Fig. 5.6e). These minerals enclose thin vermicular lamellae of spinel, forming a fine-scale pyroxene-spinel kelyphite (Fig. 5.6f). Therefore, the spinel habit gives rise to the fibrous appearance of kelyphites recognized under an optical-microscope transmitted light (Obata & Ozawa, 2011). Very fine-grained opaque minerals are distributed in this zone. Nodular green spinels occur at or around the boundaries of the first domain (Fig. 5.6g). In lherzolites, the kelyphite is surrounded by a thin rim of coarser orthopyroxene and clinopyroxene, separating the kelyphitic coronae from the surrounding neoblasts of olivine. Phlogopite (90–300 μm) surrounds the garnet grains. In clinopyroxenites, rutile

occurs associated with phlogopite (Fig. 5.6a, h). These grains have rounded to subangular interstitial habit and exhibit exsolution of ~15 % ilmenite as lamellae and rims (Fig. 5.6h).

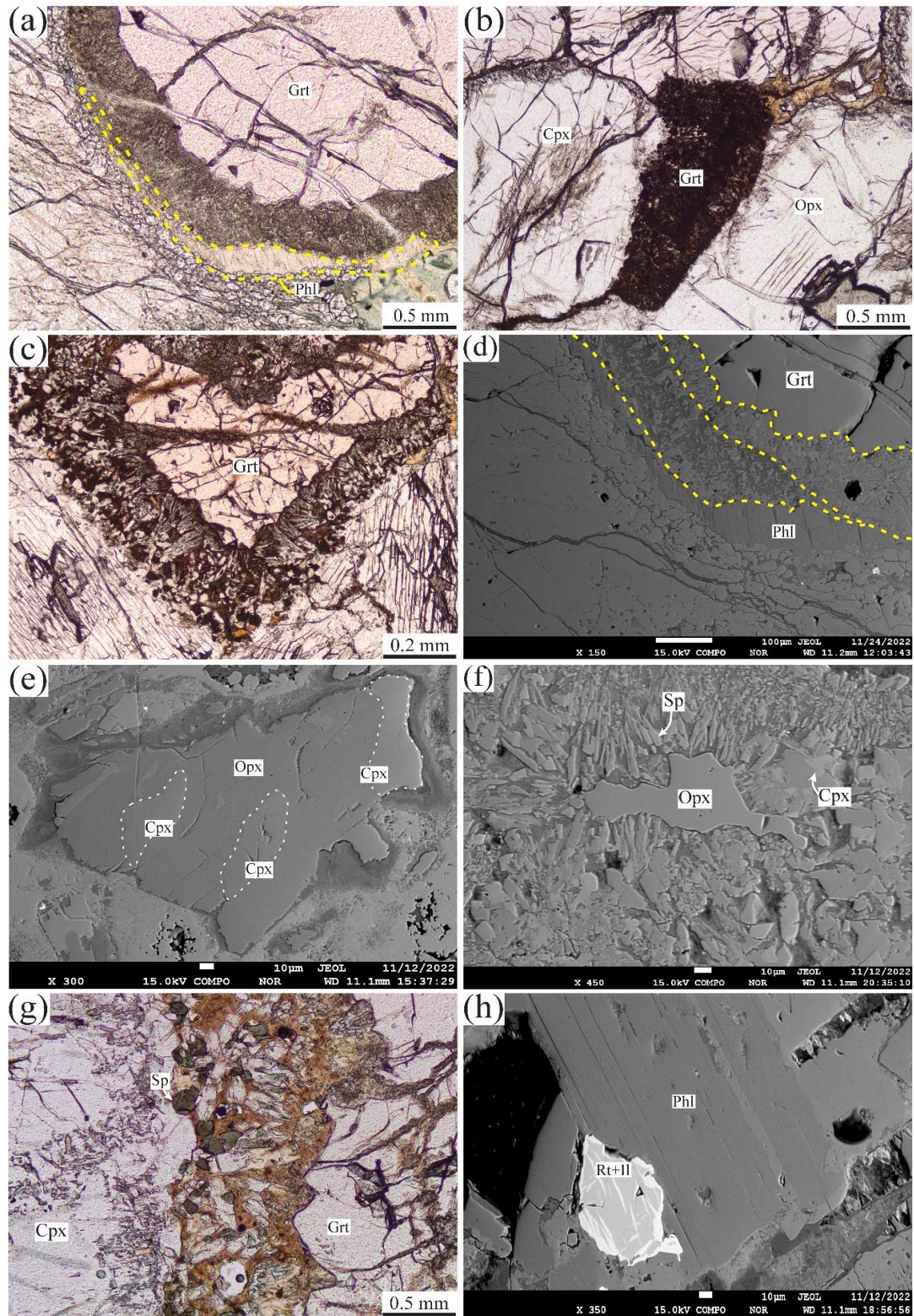


Fig. 5.6. Thin sections and backscatter electron (BSE) images of late textures observed in Canastra-1 kimberlite mantle xenoliths. (a) Garnet crystal containing kelyphitic brownish rim with phlogopite

occurring along its boundaries (CAN1-86: lherzolite). (b) Garnet completely replaced by extremely fine-grained minerals (CAN1-182: anhydrous websterite). (c) Garnet exhibiting the most expressive kelyphitic rim among studied xenoliths (CAN1-213: clinopyroxenite). (d) Distinct domains with phlogopite occurring along kelyphitic boundaries (CAN1-86: lherzolite). (e) Large crystal of orthopyroxene that contains several small, irregularly shaped patches of clinopyroxene (CAN1-94: clinopyroxenite). (f) Vermicular lamellae of spinel, forming a fine-scale pyroxene-spinel symplectite (CAN1-209: anhydrous websterite). (g) Nodular green spinels (CAN1-142: clinopyroxenite). (h) rutile with exsolution of ilmenite as lamellae and rims associated with phlogopite (CAN1-174: clinopyroxenite). BSE images (d, e, f, h) and plane-polarized light (a, b, c, g). Abbreviations: Phl = phlogopite; Cpx = clinopyroxene; Opx = orthopyroxene; Grt = garnet; Sp = spinel; Rt = rutile; Il = ilmenite.

5.4.2 Major and trace elements

Supplementary Tables S1 and S2 present individual measurements of primary mineral phases (olivine, type 1 orthopyroxene, type 1 clinopyroxene, garnet, and amphibole), as well as their representative (average) compositions. Since no core-rim differences of main oxides (<0.5 %) were observed in primary mineral phases, the average compositions were plotted in the major element diagrams. In addition, secondary phases related to kelyphitic rims (phlogopite, type 2 orthopyroxene, type 2 clinopyroxene, spinel, rutile, and ilmenite) had their major element compositions determined (Supplementary Table S3).

The occurrence of **olivine** is restricted to lherzolites and dunite. It has homogeneous and typical mantle forsterite composition ($\text{Fo}_{0.88-0.91}$), $\text{Mg\#}$ (0.89–0.91; $\text{Mg\#} = \text{Mg}/(\text{Fe}+\text{Mg})$ molar), NiO (0.33–0.40 wt.%), and CaO (<0.10 wt.%) in both porphyroclasts and neoblasts. Trace elements were not determined for olivine.

Primary **orthopyroxenes** (type 1) occur in lherzolites and websterites (both anhydrous and hydrated), whereas in clinopyroxenite, eclogite, and anhydrous websterite they are products of reaction (type 2) related to kelyphitic rims. Type 1 orthopyroxenes from lherzolites and anhydrous websterites contain strong enstatite endmember ($\text{En}_{0.88-0.90}$ $\text{Fs}_{0.08-0.10}$ $\text{Wo}_{0.02-0.03}$), while hydrated websterites comprise enstatite enriched in the ferrosilite component ($\text{En}_{0.73-0.78}$ $\text{Fs}_{0.21-0.26}$ $\text{Wo}_{0.00-0.01}$). Similarly, enstatites from lherzolites (90–92) and anhydrous websterites (90) have higher $\text{Mg\#}$ than those from hydrated websterites (74–78) (Supplementary Tab. S1). Hydrated websterites show higher Al_2O_3 (3.55–4.34 wt.%) coupled with lower CaO (0.23–0.50 wt.%) contents compared to lherzolites and anhydrous websterites (1.00–1.15 wt.%; and 1.13–1.34 wt.%, respectively) (Supplementary Tab. S1). Trace elements were not determined for orthopyroxenes.

Augite occurs in lherzolites (En_{56.2–58.7} Wo_{34.9–37.3} Fs_{5.7–7.1}), clinopyroxenites (En_{56.3} Wo_{36.6–36.7} Fs_{7.0–7.2}), and anhydrous websterites (En_{50.6–54.6} Wo_{37.9–43.4} Fs_{5.4–8.5}), while diopside occurs in hydrated websterites (En_{39.7–40.9} Wo_{48.0–39.5} Fs_{10.1–11.1}). In contrast, clinopyroxenes (En_{46.6} Wo_{46.6–47.6} Fs_{5.8–6.8}) from eclogite are omphacite with high Na₂O (>3.5 wt.%; Fig. 5.7a) and jadeite endmember (0.25–0.26). Most clinopyroxenes show intermediate to high Mg# (lherzolites = 0.89–0.90, clinopyroxenites = 0.86–0.91, anhydrous websterites = 0.89, and eclogite = 0.87–0.89) with hydrated websterites containing the lowest values (0.78–0.80) (Fig. 5.7). In general, lherzolites (CaO = 16.53–17.60 wt.%, Al₂O₃ = 1.74–2.03 wt.%), clinopyroxenites (CaO = 17.92–20.88 wt.%, Al₂O₃ = 1.66–2.22 wt.%), and anhydrous websterites (CaO = 17.17–17.22 wt.%, Al₂O₃ = 1.86–1.90 wt.%) display lower CaO and Al₂O₃ contents than hydrated websterites (CaO = 20.99–21.90 wt.%, Al₂O₃ = 5.59–6.39 wt.%) and eclogites (CaO = 18.32–18.34 wt.%, Al₂O₃ = 6.23–5.46 wt.%). In the same way, lherzolites (9.67–12.91), clinopyroxenites (8.57–13.22), and anhydrous websterites (8.41–8.57) have higher Ca/Al (molar) compared to hydrated websterites (5.06–8.49) and eclogites (2.90–3.07) (Supplementary Tables S1 and S2). In Fig. 5.7, the Mg# decreases accompanied by Na₂O (a) content while CaO (b) and TiO₂ (c) increase from lherzolites to clinopyroxenites and anhydrous websterites.

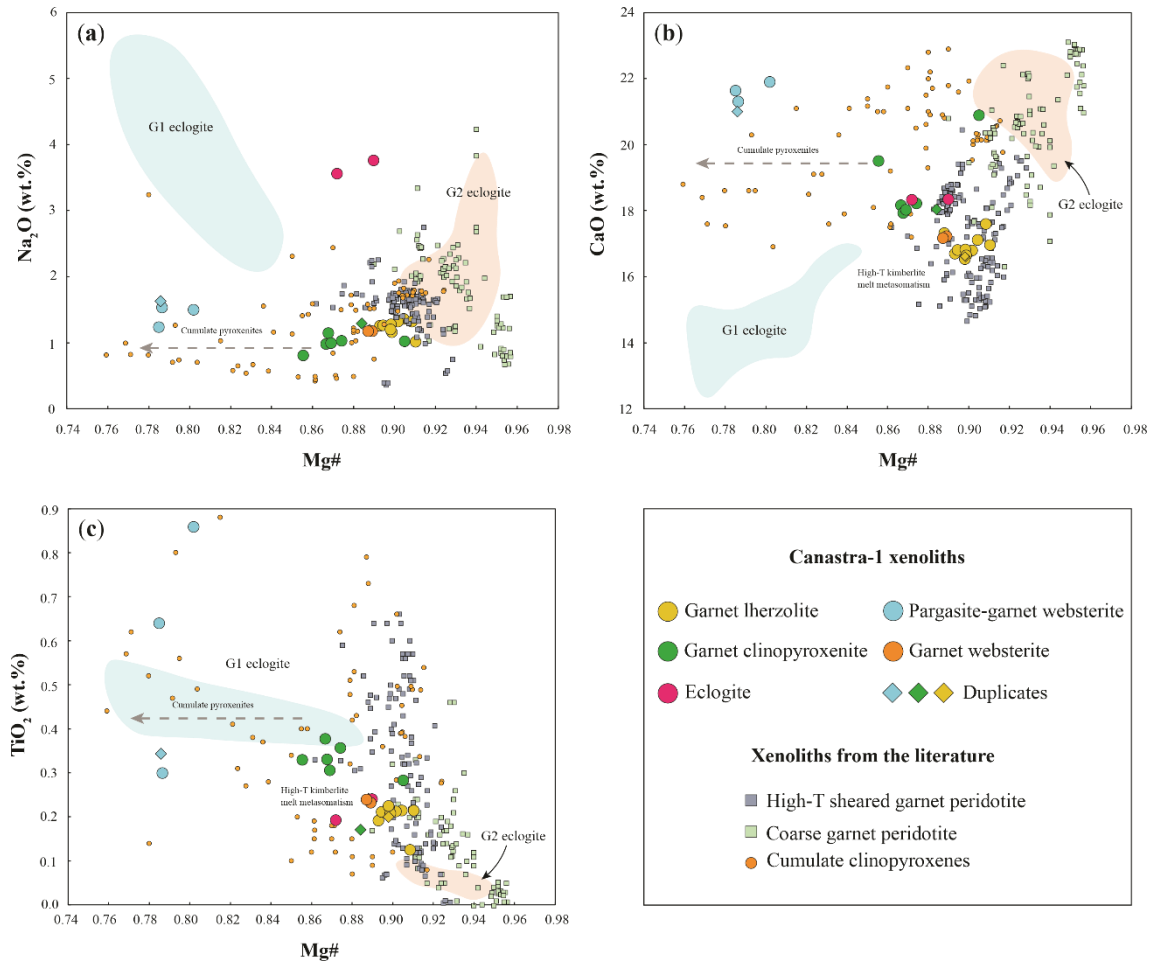


Fig. 5.7. Clinopyroxene major element compositions from Canastra-1 kimberlite mantle xenoliths. Eclogites plot between Group I and Group II eclogites (Viljoen *et al.*, 2005), whereas sheared lherzolites, anhydrous websterites, and clinopyroxenites show strong affinity with high-T sheared peridotites (Viljoen *et al.*, 2009; Ionov *et al.*, 2010; Baptiste *et al.*, 2012; Agashev *et al.*, 2013; Kargin *et al.*, 2017; Tappe *et al.*, 2021). Although clinopyroxenites are compositionally similar to sheared lherzolites, they have lower Mg#. Low-T coarse-grained peridotites were plotted for comparison (Viljoen *et al.*, 2009; Ionov *et al.*, 2010; Baptiste *et al.*, 2012; Kargin *et al.*, 2016; Fitzpayne *et al.*, 2020). Pargasite websterites show compositional affinity with cumulate pyroxenites from Cascade Cordillera (Müntener *et al.*, 2001), Southeastern Australia (Lu *et al.*, 2018), Sierra Nevada (Lee *et al.*, 2006), and Cameroon Volcanic Line (Puziewicz *et al.*, 2023).

In the primitive mantle (PM, Sun & McDonough, 1989) normalized diagram, clinopyroxenes from Canastra-1 mantle xenoliths show variable enrichment in light-REE (LREE) compared to heavy-REE (HREE) (i.e., $Ce/Yb_N = 10.52\text{--}93.63$, where N = normalized values) (Fig. 5.8a, c, e, g). In general, hydrated websterites ($Ce/Yb_N = 10.52\text{--}50.61$, usually >41) and eclogites ($Ce/Yb_N = 60.90\text{--}93.63$) are even more enriched in LREE over HREE than lherzolites ($Ce/Yb_N = 12.06\text{--}29.44$), clinopyroxenites ($Ce/Yb_N = 24.32\text{--}48.02$), and anhydrous websterites ($Ce/Yb_N = 13.41\text{--}18.67$) (Fig. 5.8 a, c, e, g). Clinopyroxenes have convex-upward LREE patterns caused by strong fractionation between LREE and HREE ($Ce/Yb_N = 10.52\text{--}93.63$) with a relatively flat slope from La

to Nd ($\text{La}/\text{Sm}_\text{N} = 0.57\text{--}2.74$, average of 1.24) (Fig. 5.8). In variable extents, all rock types have positive anomalies of U (except for clinopyroxenites), La-Ce, and Sr (except for hydrated websterites) coupled with negative anomalies of Nb-Ta-Ti, Pb and Zr-Hf in the PM-normalized multielement diagram (Fig. 5.8 b, d, f, h).

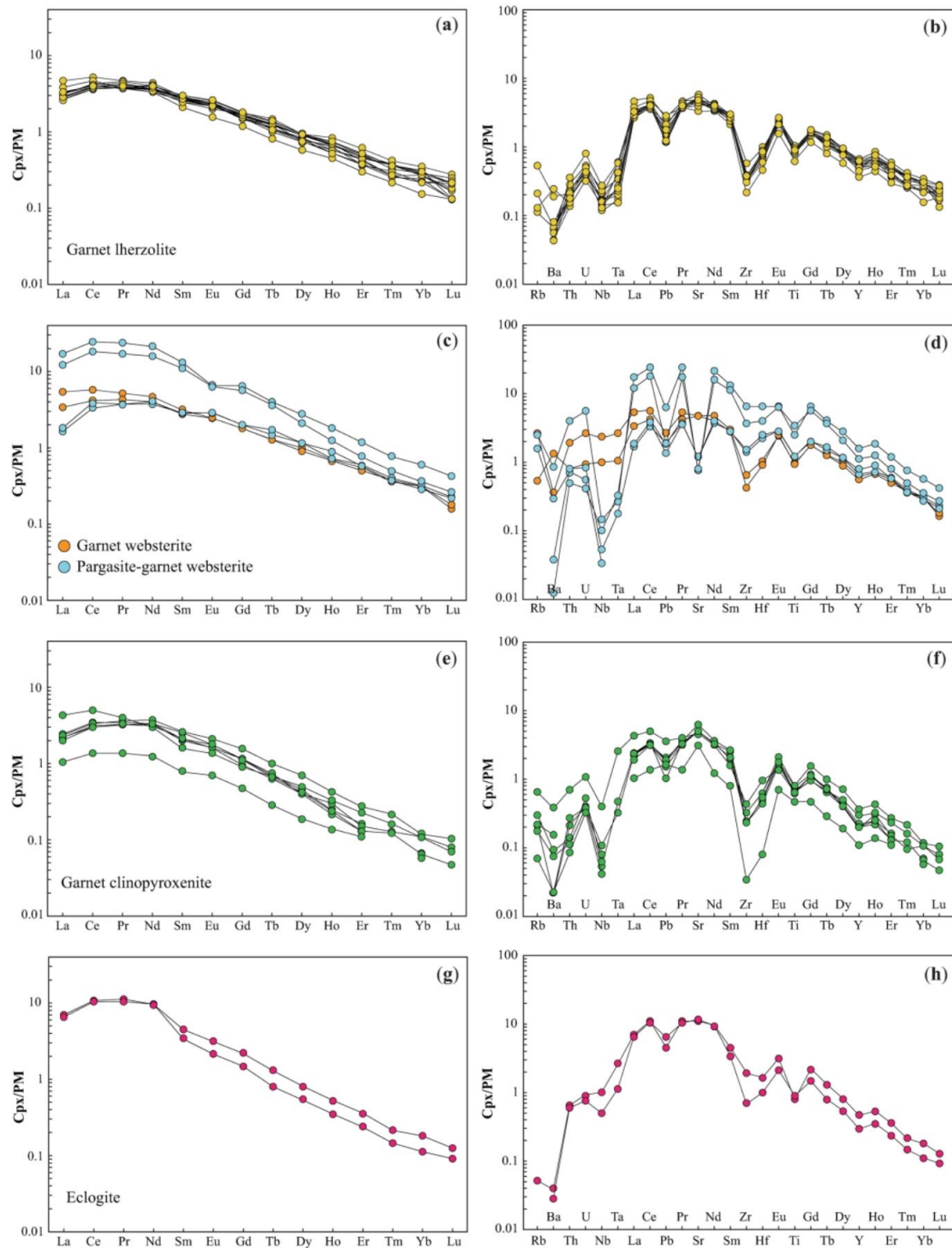


Fig. 5.8. Primitive mantle (PM; Sun & McDonough, 1989) (a) normalized rare earth and (b) multielement diagrams of clinopyroxenes from Canastra-1 mantle xenoliths.

Garnets from the Canastra-1 mantle xenoliths are mainly pyrope, in which this endmember decreases from dunite (Py_{72.2–77.3}) toward lherzolites (Py_{70.9–75.6}), anhydrous websterites (Py_{70.5–72.4}), clinopyroxenites (Py_{62.3–68.5}), eclogites (Py_{49.3–56.5}), and hydrated websterites (Py_{42.0–49.7}). Eclogites (Alm_{25.6–27.9}) and hydrated websterites (Alm_{34.3–41.7}) have strong almandine endmember compared to dunite (Alm_{8.2–13.3}), lherzolites (Alm_{11.7–16.2}), clinopyroxenites (Alm_{12.6–20.2}) and anhydrous websterites (Alm_{15.1–16.7}). Regarding the grossular endmember, eclogite garnets have the highest grossular content (Gros_{16.6–24.4}), whereas the other mantle xenoliths contain uniform composition (Gros_{10.8–17.7}). Dunite (Mg# = 0.87), lherzolites (Mg# = 0.83), anhydrous websterites (Mg# = 0.82), and clinopyroxenites (Mg# = 0.79) show higher Mg# than eclogites (Mg# = 0.66) and hydrated websterites (Mg# = 0.54). The Al₂O₃ contents are relatively uniform among all rock types (20.16–22.96 wt.%) while Cr₂O₃ contents are higher in dunite (3.23 wt.%), lherzolites (2.69 wt.%) and anhydrous websterites (2.12 wt.%) compared to clinopyroxenites (0.39 wt.%), hydrated websterites (0.22 wt.%) and eclogites (0.10 wt.%). According to their CaO and Cr₂O₃ contents, garnets from Canastra-1 are classified as lherzolitic (G9: lherzolites, anhydrous websterites, and dunite), pyroxenitic (G4: most clinopyroxenites and hydrated websterites), and eclogitic (G3: eclogites and two clinopyroxenites) (Fig. 5.9). Note that although lherzolites, anhydrous websterites, and dunite plot within the G5 pyroxenitic field, these samples are classified as belonging to the G9 due to their high Mg# (>0.7; Grütter *et al.*, 2004).

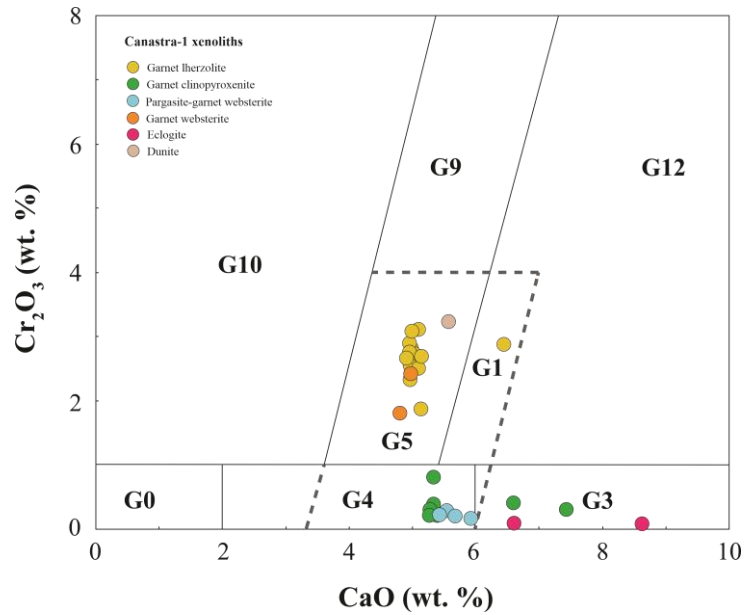


Fig. 5.9. Classification diagram of garnet considering CaO and Cr₂O₃ contents (Grütter *et al.*, 2004). Garnets from sheared lherzolites, anhydrous websterites, and sheared dunite are classified as lherzolitic (G9) due to their high Mg# (>0.7). Most clinopyroxenites and hydrated websterites are classified as pyroxenitic (G4), whereas eclogites and two clinopyroxenites are classified as eclogitic (G3).

In the REE diagram, in contrast to clinopyroxenes that are enriched in LREE/HREE, all garnets display normal “depleted” pattern characterized by LREE<HREE (Ce/Yb_N <0.32, Fig. 5.10a, c, e, g). In the PM-normalized multielement diagram (Fig. 5.10b, d, f, h), garnets from all rock types show incipient enrichment in U accompanied by depletion of LREE (i.e., La-Ce) and Sr (pronounced). Lherzolites, clinopyroxenites, and hydrated websterites show positive anomalies of Pb (pronounced in lherzolites). In different extents, lherzolites, anhydrous websterites, and clinopyroxenites are characterized by positive Zr-Hf anomalies. Controversially, clinopyroxenites show concomitant enrichment and depletion of Zr-Hf. Except for clinopyroxenites, garnets from other rock types have negative anomalies of Ti.

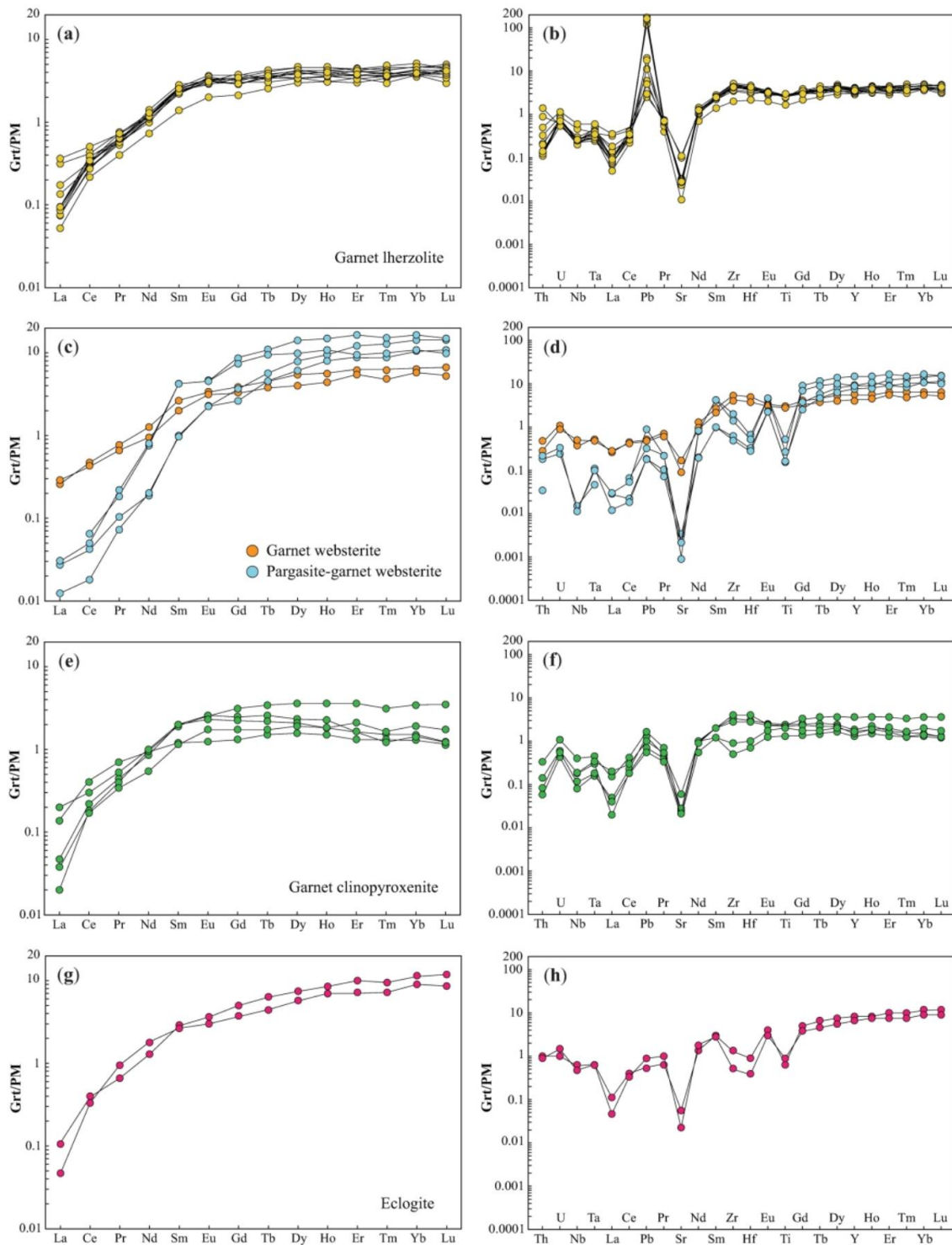


Fig. 5.10. Primitive mantle (PM; Sun & McDonough, 1989) (a) normalized rare earth and (b) multielement diagrams of garnets from Canastra-1 mantle xenoliths.

The occurrence of **amphibole** is restricted to the hydrated websterites. It is classified as pargasite with average $Mg\# = 0.80$, $TiO_2 = 2.03$ wt.%, $Al_2O_3 = 14.38$ wt.%, $Na_2O = 2.38$ wt.%, and $CaO = 11.28$ wt.%. Pargasite is characterized by the same convex-upward REE pattern observed in the coexisting clinopyroxene with fractionated

LREE/HREE ($\text{Ce/Yb}_N = 10.26\text{--}57.06$) and almost flat slope from La to Nd ($\text{La/Sm}_N = 0.61\text{--}1.35$, average of 0.98) (Supplementary Fig. S2a). In the PM-normalized multielement diagram (Supplementary Fig. S2b), these samples present positive anomalies of Nb as well as negative anomalies of Th-U, Ta, Sr, and Zr-Hf.

The mineral phases identified in kelyphitic rims around garnets from Canastra-1 xenoliths are type 2 orthopyroxene, type 2 clinopyroxene, phlogopite, spinel, rutile, and ilmenite (Supplementary Table S3). Due to the small size of these minerals, only measurements carried out on garnets with well-developed kelyphitic rims were achieved. Thus, these minerals are from lherzolite (CAN1-86), clinopyroxenites (CAN1-94 and CAN1-174), and anhydrous websterites (CAN1-182 and CAN1-209). **Phlogopite** laths present in garnet kelyphitic rims from lherzolite (CAN1-86: $\text{TiO}_2 = 1.29\text{--}2.47$ wt.% and $\text{Cr}_2\text{O}_3 = 0.91\text{--}1.71$ wt.%), clinopyroxenite (CAN1-174: $\text{TiO}_2 = 2.64\text{--}4.63$ wt.% and $\text{Cr}_2\text{O}_3 = 0.80\text{--}1.34$ wt.%), and anhydrous websterite (CAN1-209: $\text{TiO}_2 = 2.04\text{--}3.78$ wt.% and $\text{Cr}_2\text{O}_3 = 0.93\text{--}1.91$ wt.%) show high- TiO_2 (high-Ti) and high- Cr_2O_3 (high-Cr) contents (Giuliani *et al.*, 2014, 2016; Kargin *et al.*, 2019) (Fig. 5.11 and Supplementary Table S3). Phlogopite crystals from these three rock types have similar average variation of K_2O (8.10–10.39 wt.%), Al_2O_3 (12.78–15.97 wt.%), and FeO (5.05–7.05 wt.%), as well as relatively low Mg# (0.83–0.90 wt.%) (Fig. 5.11 and Supplementary Table S3). Type 2 orthopyroxene averages from garnet kelyphitic rims of samples CAN-86, CAN1-182, and CAN1-209 are enriched in TiO_2 (0.47–0.67 wt.%), Cr_2O_3 (0.33–0.55 wt.%), Al_2O_3 (10.72–11.93 wt.%), and CaO (1.34–1.79 wt.%) contents but depleted in Na_2O (<0.06 wt.%) and Mg# (0.82–0.84) compared to type 1 orthopyroxenes ($\text{TiO}_2 = 0.22\text{--}0.23$ wt.%, $\text{Cr}_2\text{O}_3 = 0.17\text{--}0.20$ wt.%, $\text{Al}_2\text{O}_3 = 1.00\text{--}1.04$ wt.%, CaO = 1.22–1.28; $\text{Na}_2\text{O} = 0.17\text{--}0.19$ wt.%, and Mg# = 0.90) (Supplementary Tables S1 and S3). Except for lherzolite CAN1-86, the composition of type 2 clinopyroxenes (from garnet kelyphitic rims) for the other xenoliths was obtained (CAN1-94, CAN1-174, CAN1-182, and CAN1-209). These secondary clinopyroxenes have higher contents of TiO_2 (1.50–1.72 wt.%), Al_2O_3 (11.55–13.77 wt.%), and CaO (19.29–20.09 wt.%), with lower Na_2O (0.21–0.53 wt.%) and Mg# (0.78–0.83) compared to those from type 1 ($\text{TiO}_2 = 0.26\text{--}0.36$ wt.%, $\text{Al}_2\text{O}_3 = 1.83\text{--}1.90$ wt.%, CaO = 17.17–18.22 wt.%, $\text{Na}_2\text{O} = 0.99\text{--}1.17$ wt.%, and Mg# = 0.87–0.89) (Supplementary Tables S1 and S3). **Spinel** averages are Al_2O_3 -rich (54.53–58.11 wt.%) with low TiO_2 (<0.35 wt.%), and variable MgO (18.58–20.49 wt.%), Cr_2O_3 (1.52–9.70 wt.%) and FeO (15.21–17.36 wt.%) contents. **Rutile** ($\text{TiO}_2 = 96.47\text{--}97.42$

wt.%) and Mg-rich **ilmenite** (picroilmenite: $\text{TiO}_2 = 53.90\text{--}54.35$ wt.%, $\text{FeO} = 32.57\text{--}32.94$, $\text{MgO} = 9.85\text{--}10.28$ wt.%, and $\text{Cr}_2\text{O}_3 = 0.70\text{--}0.98$ wt.%) were identified and analyzed only in the clinopyroxenite sample CAN1-174. Comparatively, ilmenites from garnet kelyphitic rims have similar composition to those from kimberlites (Mitchell, 1995; Wyatt *et al.*, 2004).

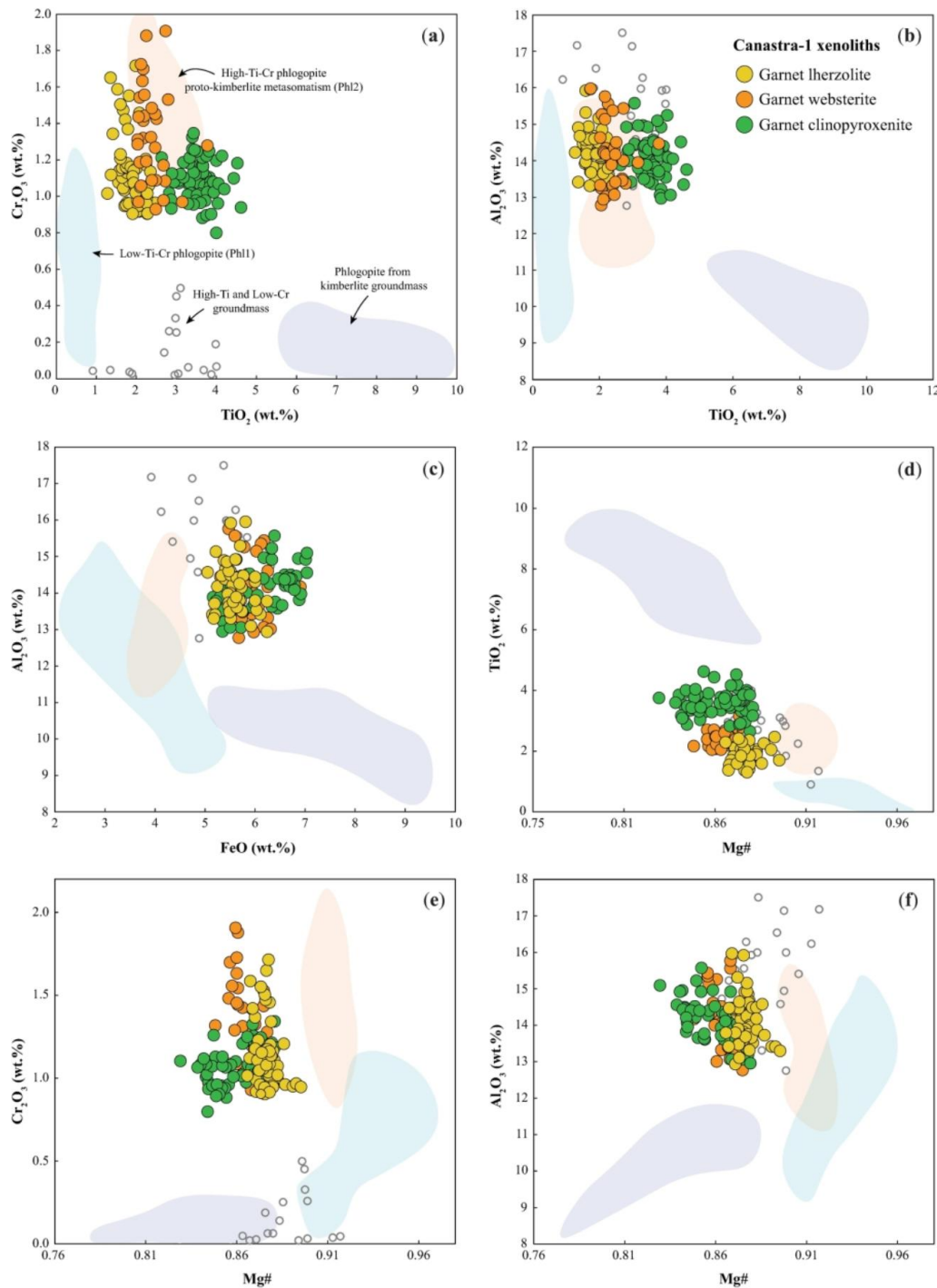


Fig. 5.11. Bivariate plots for major and minor elements of phlogopite from Canastra-1 mantle xenoliths. High-Ti-Cr phlogopite from mantle xenoliths (Giuliani *et al.*, 2016); type 1 phlogopites (Phl1) from mantle

xenoliths and kimberlite xenocrysts (Giuliani *et al.*, 2014; 2016; Kargin *et al.*, 2019); type 2 phlogopites (Phl2) (Kargin *et al.*, 2019); high-Ti and low-Cr groundmass phlogopites (Giuliani *et al.*, 2016; Kargin *et al.*, 2019); kimberlite phlogopites from the groundmass (Fritschle *et al.*, 2013).

5.4.3 Pressure and temperature estimates

The positive correlation between Al_2O_3 and Mg# accompanied by negative correlation of CaO shown by two pyroxenes indicates the equilibrium between these mineral phases (Supplementary Fig. S3). This equilibrium is corroborated by the well-defined positive correlations between the Mg# of olivine vs. orthopyroxene ($r^2 = 0.69$) and clinopyroxene ($r^2 = 0.89$) (not shown). Equilibrium temperature and pressure estimates were calculated assuming 4.0 GPa (garnet-facies) using several reliable geothermobarometers from the PTEXL Excel spreadsheet (created by T. Köhler in the 1990s and modified and updated by T. Stachel in 2024 at the University of Alberta, Canada: <https://doi.org/10.5683/SP3/IMYNCL>) (Supplementary Table S7). For this study, we used geothermometers based on two-pyroxenes (Krogh, 1988; Taylor, 1998; Brey & Köhler, 1990), garnet-clinopyroxene equilibrium (Sudholz *et al.*, 2022), Ca in orthopyroxene (Brey & Köhler, 1990), and single-clinopyroxene (Mercier, 1980; Nimis & Taylor, 2000). Selected geobarometers are based on garnet-orthopyroxene (Nickel & Green, 1985; Brey & Köhler, 1990; Taylor, 1998), single-pyroxene equilibrium (Nimis & Taylor, 2000; Nimis *et al.*, 2020), and Cr-in-clinopyroxene (Sudholz *et al.*, 2021). We additionally applied the REE-in-garnet-clinopyroxene thermometer for eclogites and garnet peridotites proposed by Sun & Liang (2015).

Note that the thermobarometry proposed for single-pyroxene could only apply to orthopyroxene-bearing mantle xenoliths (e.g., Nimis & Taylor, 2000; Nimis *et al.*, 2020). For this reason, we have decided to avoid the results obtained from these works for clinopyroxenites and eclogites. It is well-documented that accurate and precise pressure estimates for these xenoliths are generally not possible due to the absence of suitable coexisting minerals (i.e., orthopyroxene coexisting with garnet or clinopyroxene) (e.g., Viljoen *et al.*, 2005; Beyer *et al.*, 2015; Aulbach *et al.*, 2020).

Canastra-1 sheared lherzolites have high and uniform temperature (high-T) averages (1212–1290 °C), which are in the same range defined for anhydrous websterites (1239–1248 °C) and clinopyroxenites (1191–1237 °C) (Fig. 5.12a). Conversely, eclogites (978–982 °C) show the lowest temperatures (lower-T), which are slightly lower than

those from hydrated websterites (875–926 °C) (Fig. 5.12a). Consistent pressure estimates are restricted to lherzolites (5.3–5.6 GPa) and anhydrous websterites (5.4–5.5 GPa) (Fig. 5.12a). These pressure estimates correspond to depth ranges of 174–186 km (Fig. 5.12a). Pressure and temperature estimates constrained by lherzolites and anhydrous websterites correspond to the geotherm of 40 mW/m² (Fig. 5.12a). Thus, pressure estimates were extrapolated for clinopyroxenites (~5.3–5.5 GPa), eclogites (~4.0 GPa), and hydrous websterites (~3.4–3.8 GPa) based on their temperatures projected on the conductive geotherm of 40 mW/m² (Hasterok & Chapman, 2011) (Fig. 5.12a). It should be noted that although the temperature estimates of hydrated websterites are compatible with those obtained for eclogites, the geothermobarometers employed in this study were calibrated for anhydrous conditions. Considering the stability field defined for pargasite, in which temperature reaches around 1100 ± 50 °C at pressures from 1 to 3 GPa (Green, 2015), our pressure estimates (~3.4–3.8 GPa) are overestimated. Therefore, we can infer a maximum pressure estimate for our hydrated websterites at around ~3 GPa (probably between 2–3 GPa). When plotted in Fig. 5.12b, eclogites plot within the geotherm of 40 mW/m² while pargasite websterites in the stability field defined for pargasite (Green, 2015). These samples plot along with the tentative Archean subduction path, in which pargasite websterites plot close to the field defined for modern blueschists and eclogites (Aulbach & Smart, 2023 and references therein) (Fig. 5.12c).

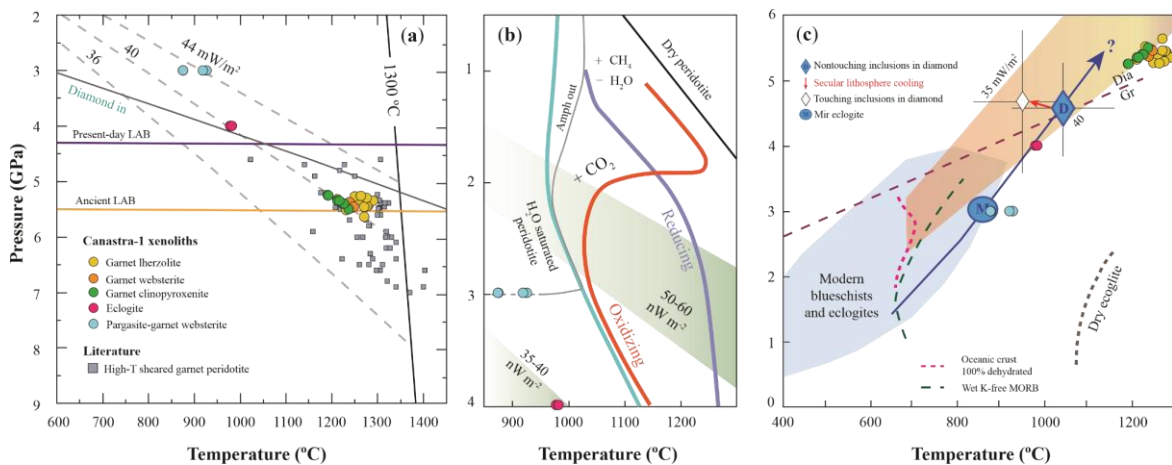


Fig. 5.12. (a) Pressure versus temperature diagram after Giuliani *et al.* (2023) containing the conductive model geotherms from Hasterok & Chapman (2011). Sheared lherzolites and anhydrous websterites from Canastra-1 show reliable geothermobarometers and plot within the geotherm of 40 mW/m² in the ancient lithosphere-asthenosphere boundary (LAB = 174–186 km). The present-day LAB occurs at 143 km depth (Ciardelli *et al.*, 2022), indicating extensive lithospheric thinning in the last 120 Ma. Due to the lack of precise pressure estimates for clinopyroxenites and eclogites, the temperature estimates of these samples were extrapolated to the geotherm of 40 mW/m² (Hasterok & Chapman, 2011), which represents that

defined by lherzolites and anhydrous websterites. Pressure estimate for pargasite websterites is assumed as 3.0 GPa (Green, 2015). Sheared lherzolites, anhydrous websterites, and clinopyroxenites overlap the field defined by high-T sheared peridotites from the Kaapval and Siberian cratons (Ionov *et al.*, 2010; Baptiste *et al.*, 2012; Agashev *et al.*, 2013; Tappe *et al.*, 2021). (b) Pressure versus temperature diagram after Green (2015) and Aulbach (2018). According with the pressure and temperature estimates of pargasite websterites, they plot within the amphibole stability field while eclogites plot within the geotherm of 40 mW/m². Shown for comparison are the nominally dry peridotite solidus (water undersaturated) and water-saturated peridotite solidus coupled with the effect of oxidizing versus reducing conditions (Green, 2015; Aulbach, 2018). (c) Pressure versus temperature diagram showing that sheared lherzolites, anhydrous websterites, and clinopyroxenites plot within the geotherm of 40 mW/m² (after Stachel *et al.*, 2022 and Aulbach & Smart, 2023). Pargasite websterites and eclogites plot within the tentative Archean subduction path (blue arrow). For comparison, modern blueschists and eclogites are plotted (blue field). Touching inclusions in diamonds record lower average temperatures, indicative of secular lithosphere cooling (orange arrow). Also shown are the solidus (dotted line) for dry (gray) and for K-free wet mid-ocean ridge basalt (MORB)-like eclogite (green); a curve (purple) for 100 % dehydration of oceanic crust.

5.4.4 Sm-Nd systematics and Sr-Nd isotopic ratios

Supplementary Table S5 displays the Sr-Nd isotopic ratios of lherzolites (n = 10), pargasite websterites (n = 2), clinopyroxenite (n = 1), and eclogite (n = 1). Selected clinopyroxene (n = 13) and garnet (n = 8) mineral separates had their Sr-Nd isotopic ratios determined, whereas the whole-rock samples have only Nd data (n = 10).

Lherzolites have clinopyroxenes ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51273\text{--}0.51293$, $\epsilon\text{Nd} = +1.8$ to $+5.7$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.70560\text{--}0.70770$; where $\epsilon\text{Nd} = (^{143}\text{Nd}/^{144}\text{Nd}_{\text{sample}}/^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}} - 1) \times 10000$) and garnets ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51287\text{--}0.51315$, $\epsilon\text{Nd} = +4.5$ to $+10.1$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.70704\text{--}0.70869$) with intermediate to high $^{143}\text{Nd}/^{144}\text{Nd}$ coupled with enriched $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios (Fig. 5.13 and Supplementary Table S5). In general, garnets show higher Sr and Nd isotopic ratios than clinopyroxenes (Fig. 5.13 and Supplementary Table S5). Whole-rock lherzolites have similar $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (0.51277–0.51292) and ϵNd (+2.5 to +5.6) compared to their clinopyroxene separates. The clinopyroxenite sample has the same pattern observed in the lherzolites (Fig. 5.13 and Supplementary Table S5) considering clinopyroxene ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51292$, $\epsilon\text{Nd} = +5.5$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.70753$), garnet ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51303$, $\epsilon\text{Nd} = +7.6$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.70831$) and whole-rock ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51292$, $\epsilon\text{Nd} = +5.4$) isotopic compositions. The Sr-Nd distribution pattern defined by the lherzolitic and clinopyroxenite samples is scattered and near-horizontal with depleted (high) Nd at a given enriched (high) Sr isotopic ratio compared to the array formed by kimberlites (Fig. 5.13).

Pargasite websterites had only clinopyroxenes ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51196\text{--}0.51198$, $\epsilon\text{Nd} = -12.9$ to -13.3 , $^{87}\text{Sr}/^{86}\text{Sr} = 0.70894\text{--}0.71003$) and whole-rocks ($^{143}\text{Nd}/^{144}\text{Nd} =$

0.51196–0.51227, $\epsilon\text{Nd} = -7.2$ to -13.2) successfully analyzed (Fig. 5.13 and Supplementary Table S5). They represent the most enriched samples among all rock types with the lowest Nd and the highest Sr isotopic ratios (Fig. 5.13 and Supplementary Table S5). Likewise, clinopyroxene ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51232$, $\epsilon\text{Nd} = -6.3$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.70912$) and garnet ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51226$, $\epsilon\text{Nd} = -7.3$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.70842$) separates, as well as the whole-rock ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51235$, $\epsilon\text{Nd} = -5.6$) from the eclogite sample are slightly less enriched compared to the hydrated websterites (Fig. 5.13 and Supplementary Table S5). Thus, as observed in the mineral chemistry data, these xenoliths are considerably enriched with respect to the lherzolites, clinopyroxenites, and anhydrous websterites. Note that in this case, the term enriched consists in low-Nd and high-Sr isotopic ratios. For comparison, in Fig. 5.13 were plotted the worldwide Group I or archetypal kimberlites (Nowell *et al.*, 2004; Becker & le Roex, 2006; Becker *et al.*, 2007; Tappe *et al.*, 2017; Tappe *et al.*, 2020 and references therein), transitional kimberlites (Nowell *et al.*, 2004; Becker *et al.*, 2007), and lamproites (former micaceous Group II kimberlites or orangeites; Nowell *et al.*, 2004; Becker & le Roex, 2006; Coe *et al.*, 2008; Tappe *et al.*, 2022, 2023), as well as the garnet xenocrysts from the Carolina kimberlite (Gervasoni *et al.*, 2022).

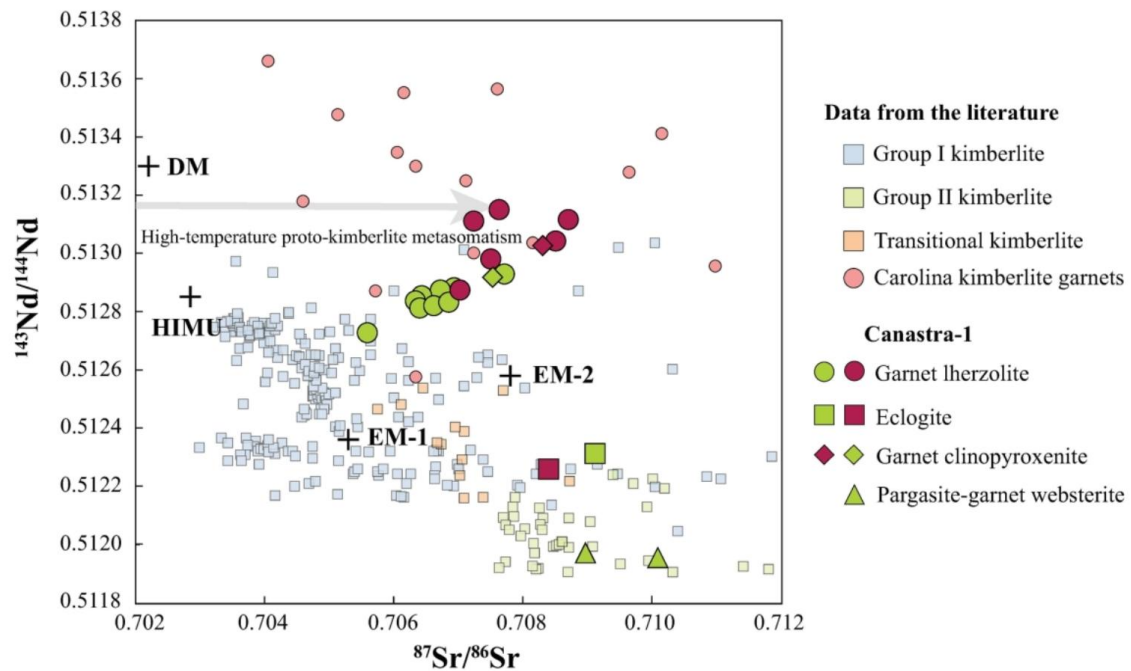


Fig. 5.13. Sr-Nd isotopic composition of clinopyroxene (green symbols) and garnet (purple symbols) from Canastra-1 xenoliths. For comparison, the depleted mantle (DM), HIMU, enriched mantle 1 (EM1) and enriched mantle 2 (EM2) mantle end-members (Hart *et al.*, 1992), worldwide kimberlites from Group 1,

Group 2 (orangeites) and Transitional kimberlites (Nowell *et al.*, 2004; Becker & Le Roex, 2006; Becker *et al.*, 2007; Coe *et al.*, 2008; Tappe *et al.*, 2017, 2020, 2021a, and references therein), and Carolina kimberlite garnets (Gervasoni *et al.*, 2022) are plotted.

Based on the ^{147}Sm - ^{143}Nd systematics, consistent isochron ages were calculated based on sheared lherzolites and clinopyroxenite isotopic compositions (Supplementary Fig. S4 and Supplementary Table S5). In contrast, coherent ages for eclogites and pargasite websterites were not achieved. Thus, four ages were determined using (1) clinopyroxene, garnet and whole-rock of lherzolite xenoliths [$n = 21$; 146.1 ± 8.2 Ma, initial $^{143}\text{Nd}/^{144}\text{Nd} = 0.51273$, MSWD = 5.8] (Supplementary Fig. S4a), (2) clinopyroxene and garnet of lherzolite xenoliths [$n = 14$; 149.6 ± 9.4 Ma, initial $^{143}\text{Nd}/^{144}\text{Nd} = 0.51272$, MSWD = 7.7] (Supplementary Fig. S4b), (3) clinopyroxene, garnet and whole-rock for lherzolite and clinopyroxenite xenoliths [$n = 24$; 139.8 ± 7.9 Ma, initial $^{143}\text{Nd}/^{144}\text{Nd} = 0.51274$, MSWD = 6.5] (Supplementary Fig. S4c), and (4) clinopyroxene and garnet for lherzolite and clinopyroxenite xenoliths [$n = 16$; 143.2 ± 9.0 Ma, initial $^{143}\text{Nd}/^{144}\text{Nd} = 0.51273$, MSWD = 8.6] (Supplementary Fig. S4d). This Cretaceous age is slightly older than the age proposed for the emplacement of the host kimberlite (120 Ma; Read *et al.*, 2004 after personal communication of Martin Doyle, De Beers). It is important to consider that the mentioned report does not detail essential information regarding radiogenic dating, such as what material was used, and the analytical method applied.

However, aiming to avoid the compositional influence of the host kimberlite in the whole-rock Sm/Nd isochrons, we plotted two-point clinopyroxene-garnet isochrons (Shu *et al.*, 2014) considering the measured $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios (Supplementary Tab. S5) while the $^{147}\text{Sm}/^{144}\text{Nd}$ ratios were calculated using the Sm and Nd concentrations (in ppm) of clinopyroxene and garnet (Supplementary Tab. S1). Based on the available results, six two-point isochrons were constructed for high-T sheared lherzolites (samples CAN1-89, 96, 97, 99, 100, and 101). Three of them (CAN1-96 = 121 ± 39 Ma, CAN1-99 = 115 ± 26 Ma, and CAN1-101 = 125 ± 17 Ma) present ages resembling the kimberlite emplacement age (120 Ma) (Fig. 5.14). Conversely, sample CAN1-100 shows an older age (195 ± 31 Ma) while the others have younger results relative to 120 Ma. The initial $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios for samples CAN1-96, CAN1-99, and CAN1-101 are, respectively, 0.51271, 0.51284, and 0.51278. Remarkably, the two-point isochrons from high-T sheared lherzolites (Fig. 5.14) reflect either cooling ages or emplacement of the

kimberlite magma (Shu *et al.*, 2014). Considering the whole-rock, the obtained age is slightly older (average of 145 ± 4 Ma) than that of the clinopyroxene-garnet two-point isochron age (average of 120 ± 5 Ma). Hence, for further discussion, we will adopt the two-point isochron age as representative of the kimberlite emplacement and probably the proto-kimberlite metasomatism (see details below).

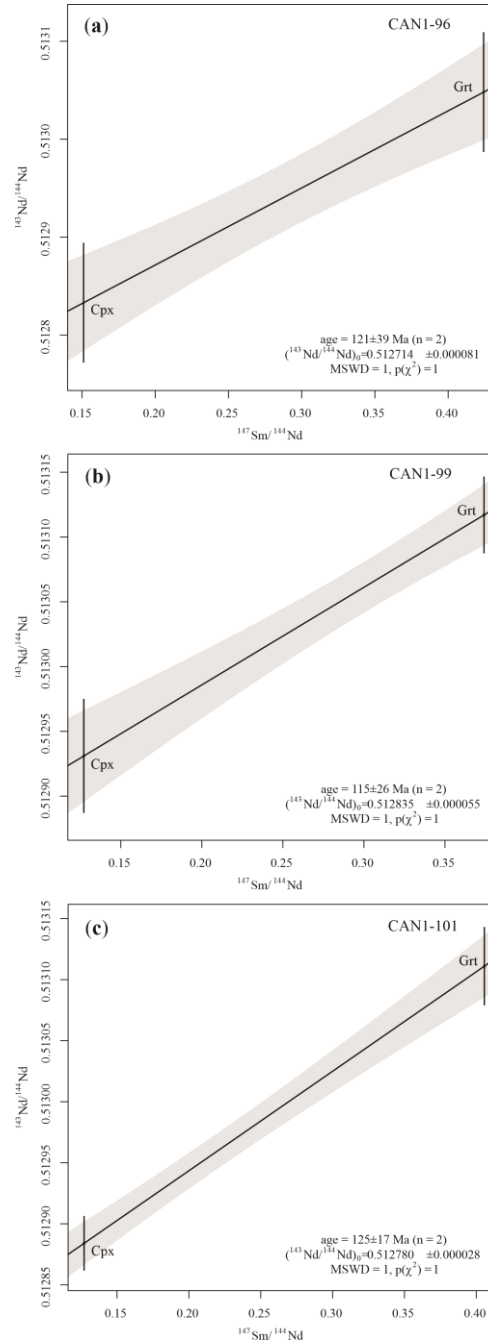


Fig. 5.14. Two-point clinopyroxene-garnet Sm–Nd isochron ages for sheared lherzolites from Canastra-1 kimberlite, representing the emplacement age of the host kimberlite, which is coeval with the proto-kimberlite metasomatism. The ages are 121 ± 39 Ma (CAN1-96), 115 ± 26 Ma (CAN1-99), and 125 ± 17 Ma (CAN1-101), with average of 120 ± 5 Ma.

5.5 Discussion

The subcontinental lithospheric mantle underneath Canastra-1 kimberlite exhibits a complex geological history that may still be recovered based on petrography, mineral chemistry, and geochemistry. Based on the petrographic and chemical evidence, mantle xenoliths from Canastra-1 record cryptic and modal metasomatism (refertilization) (Dawson, 1984). Cryptic metasomatism involves enrichment in incompatible elements with no generation of new phases. In contrast, modal metasomatism leads to the change of the modal mineralogy (and composition) by the growth of new phases (e.g., clinopyroxene, amphibole, and phlogopite). Therefore, the mechanisms responsible for triggering the enrichment of the upper mantle beneath the SW margin of the São Francisco Craton, and their temporal relationship, are discussed below.

5.5.1 *Constraining the refertilization in the lithosphere beneath the SW margin of the São Francisco Craton*

The identification of mantle **eclogites** within Canastra-1 kimberlite represents undoubtable evidence of recycling and metamorphism of an ancient oceanic crust beneath the SW margin of the São Francisco Craton. Eclogites are high-pressure biminerallitic rocks, essentially composed of garnet (usually 55 %) and omphacite (45 %) in subequal proportions, with rutile and ilmenite as the main accessory phases (Jacob, 2004; le Roex *et al.*, 2020). Two origins have been ascribed to eclogite xenoliths hosted by kimberlites in Archean cratonic regions (e.g., Jacob, 2004; Viljoen *et al.*, 2005; Aulbach & Smart, 2023). The first, defined as Group I eclogites, is formed of prograde metamorphism of recycled oceanic crust (basalt or gabbro), with a heterogeneous protolith related to dehydration and partial melting of a mixed subducted oceanic slab with basaltic composition and seafloor sediments. Conversely, Group II eclogites are derived from the crystallization of a small volume of primary mantle melt at high pressure within conduits in old, enriched subcontinental lithosphere. Although eclogite usually has mid-ocean ridge basalt (MORB) protolith, which would confer on its depleted geochemical and isotopic characters, several later metasomatic agents may overprint its original composition (Viljoen *et al.*, 2005). The selected major element diagrams (Mg# vs. Na₂O,

CaO, and TiO₂) of clinopyroxenes from Canastra-1 eclogites demonstrate their transitional affinity compared to Groups I and II eclogites from the Kaalvallei Kimberlite, South Africa (Viljoen *et al.*, 2005) (Fig. 5.7).

Based on the garnet composition, the Canastra-1 eclogites are classified as high-Mg (garnet Mg# = 0.64–0.69) and low-Ca (Ca# = 0.17–0.22, where Ca# = Ca/Ca+Mg+Mn+Fe⁺² molar), indicating a less differentiated crustal protolith (Aulbach & Jacob, 2016; Aulbach *et al.*, 2020; Aulbach & Smart, 2023) (Supplementary Fig. S5). According to the Mg# (0.87–0.89) and Na# (0.26–0.27, where Na# = Na/Na+Ca molar) (Supplementary Fig. S5), clinopyroxenes are defined as eclogitic (Aulbach *et al.*, 2020). These minerals show remarkable cryptic metasomatism during their residence in the cratonic lithospheric mantle, which is evidenced by the pronounced LREE-enrichment (Ce/Yb_N = 60.90–93.63). In contrast, the REE pattern of garnets defines smooth positive slopes from LREE to middle-REE (MREE) (La/Eu_N <0.02) accompanied by less fractionated MREE/HREE ratios (Dy/Lu_N = 0.62–0.64) (Fig. 5.10g). Hence, clinopyroxene represents the main carrier of the metasomatic signature in Canastra-1 eclogites while garnet maintained its original and unmetasomatized composition (Aulbach *et al.*, 2020).

Based on the modal percentages of the eclogites, the whole-rock compositions for samples CAN1-147 (garnet = 40 % and clinopyroxene = 60 %) and CAN1-206 (garnet = 48 % and clinopyroxene = 52 %) were reconstructed. The spoon-like REE pattern of the eclogite whole-rock (La/Sm_N = 1.60–2.06, Dy/Yb_N = 0.71) reinforces the metasomatism ascertained by clinopyroxenes (Supplementary Fig. S6). The REE pattern of Canastra-1 eclogites is incompatible with undisturbed mantle-derived mafic magmas (i.e., depleted MORB-like composition). Garnets are characterized by “normal” REE pattern (Fig. 5.10) but the clinopyroxenes are enriched (Fig. 5.8), defining an unusual whole-rock composition (Supplementary Fig. S6). This unexpected REE patterns would be related to the clinopyroxene, which apparently was pervasively generated, as indicated by its spongy (reacted) nature. Although inclusion-rich spongy margins are a common feature observed in all rock types of this study, this texture is more pervasive in eclogites, covering up to 50 % of the mineral (Fig. 5.5b). This texture has been interpreted as evidence for incipient partial melting near to the LAB in the North Atlantic Craton (Kopylova *et al.*, 2019) and Kaapvaal Craton (Tappe *et al.*, 2021).

As the reconstructed whole-rock composition was achieved considering only clinopyroxene and garnet, the negative anomalies of high field strength elements (HFSE) such as Nb-Ta-Ti and Zr-Hf in the PM-normalized multielement diagram are expected, reflecting the absence of rutile and/or ilmenite as a part of the considered mineral assemblage (Aulbach *et al.*, 2007; Aulbach & Stachel 2022) (Supplementary Fig. S6). In this context, rutile significantly contributes to the Zr (and Hf) budget in eclogites (up to 35 %) and controls that of Nb (and Ta) (95–100 %). This implies that whole-rock reconstruction without accounting rutile leads to minimum concentrations of these elements and that this deficit is highest at low temperatures where the highest rutile modes are expected (Aulbach *et al.*, 2011; Aulbach, 2020).

The high-Mg (Mg# = 0.46–0.54, MgO = 13.23–14.41 wt.%), Σ REE (Tb–Lu), and the lack of positive Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.92\text{--}0.95$, where $\text{Eu}/\text{Eu}^* = \text{Eu}_\text{N}/(\text{Sm}_\text{N} \times \text{Gd}_\text{N})^{1/2}$) (Supplementary Fig. S5) of the Canastra-1 eclogites indicate a more primitive, olivine-rich basaltic protolith (“non-gabbroic”; Aulbach *et al.*, 2007, 2020). In addition, these features, accompanied by the enrichment of LREE and Cr_2O_3 in the reconstructed whole-rocks may suggest the addition of a small volume of a kimberlite-like melt (Aulbach *et al.*, 2020). However, their low concentration of strong mobile elements (i.e., U, and Pb) relative to the ocean crust protolith (White & Klein, 2014), suggest that these elements may have been lost during prograde metamorphism in subduction zones (Supplementary Fig. S6). An enriched component is further supported by the Sr–Nd isotope compositions of the mineral phases (clinopyroxene and garnet) and whole-rock of eclogites, as indicated by high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (clinopyroxene = 0.70842, garnet = 0.70912) and negative ϵNd values (–5.6 to –7.3). Therefore, we suggest that the high-Mg eclogites from Canastra-1 could originate from subducted oceanic crust, which was metasomatized later on by fluids/melts liberated from the underlying oceanic mantle (fresh or serpentinized) and overlying sediments (Aulbach *et al.* 2020; Aulbach & Smart, 2023).

The origin of the olivine-free **hydrated (pargasite-bearing) websterites** from Canastra-1 kimberlite is strongly linked to the high-pressure (>2–3 GPa) cumulates from an evolved (SiO_2 -rich) and hydrated basaltic andesitic magma. The reconstructed whole-rock compositions of pargasite websterites were determined using mineral data and point-counted modes (Supplementary Tabs. S1 and S6). Compared to the trend defined by the experimental pyroxenite cumulates from hydrous basalt and basaltic andesite (Müntener

et al., 2001), our samples plot within the endmembers defined for the higher contents of CaO (>10 wt.%), Al₂O₃ (>10 wt.%), FeO (>11 wt.%), Na₂O (>0.7 wt.%), and TiO₂ (>0.4 wt.%) at a given MgO content (>15 wt.%) (Fig. 5.15). In general, these major element compositions are similar to those of high-MgO pyroxenite cumulates from Cascades Cordillera (Müntener *et al.*, 2001), NE Tibet (Xiong *et al.*, 2004), Sierra Nevada (Lee *et al.*, 2006), and Southeastern Australia (Lu *et al.*, 2018), which are interpreted as cumulates from mantle wedge-derived hydrous basalt or basaltic andesite (Fig. 5.15). Comparatively, cumulate pyroxenites from the Cameroon Volcanic Line (Puziewicz *et al.*, 2023) show distinctive composition marked by their higher MgO coupled with lower FeO contents (Fig. 5.15). Although the pargasite websterites from Canastra-1 would be defined as high-MgO cumulates, their Mg# is low (51–58) due to the enrichment of FeO.

We also have estimated the trace element compositions of melts in equilibrium with the clinopyroxene (Supplementary Fig. S7). The partition coefficients used in the calculations are taken from Ionov *et al.* (2002). Calculated melts show trace element pattern typical of arc-related lavas, with moderate to strong enrichment of LREE over HREE (i.e., Ce/Yb_N = 53–253), and prominent depletion of Nb-Ta-Ti (Supplementary Fig. S7). The radiogenic isotopes of clinopyroxenes support these results, with pargasite websterites showing enriched ⁸⁷Sr/⁸⁶Sr (0.70894–0.71003) coupled with negative εNd (-12.9 to -13.3) ratios (Fig. 5.13).

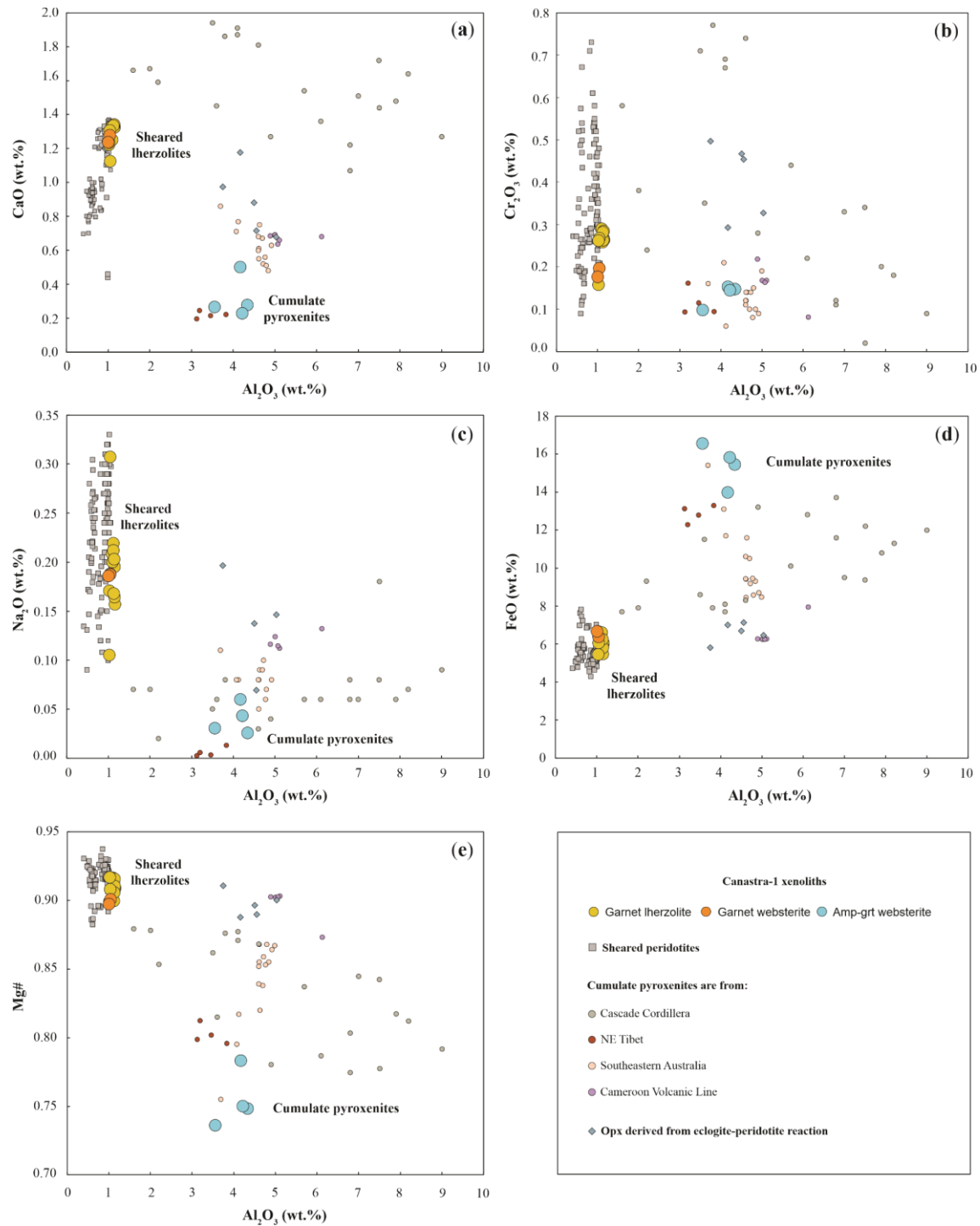


Fig. 5.15. Selected major elements (CaO , Al_2O_3 , FeO , Na_2O , TiO_2 , and SiO_2) versus MgO (wt.%) showing the compositional affinity of the reconstructed whole-rock pargasite websterites from Canastra-1 with cumulate pyroxenites. For comparison, cumulate pyroxenites from Cascade Cordillera (Müntener *et al.*, 2001), NE Tibet (Xiong *et al.*, 2014), Southeastern Australia (Lu *et al.*, 2018), Cameroon Volcanic Line (Puziewicz *et al.*, 2023), and Sierra Nevada continental arc (Lee *et al.*, 2006) are plotted. High-T sheared peridotites were plotted for comparison (Viljoen *et al.*, 2009; Ionov *et al.*, 2010; Baptiste *et al.*, 2012; Agashev *et al.*, 2013; Kargin *et al.*, 2017; Tappe *et al.*, 2021). The gray line represents the fractional crystallization trend defined by experimentally derived pyroxenite cumulates from hydrous basaltic andesite at 1.2 GPa (Müntener *et al.*, 2001). Fields of pyroxenites from metamorphosed oceanic crust and melt-rock reaction are from Xiong *et al.* (2014).

This assumption is supported by the occurrence of Al_2O_3 -rich orthopyroxene (~ 4 wt.%), which is considerably higher than those observed in lherzolites and anhydrous websterites (both ~ 1 wt.%) (Fig. 5.16). This Al_2O_3 -rich orthopyroxene demonstrates strong compositional similarities especially with cumulate pyroxenes from NE Tibet (Xiong *et al.*, 2004) and Southeastern Australia (Lu *et al.*, 2018) (Fig. 5.16). Clinopyroxenes from pargasite websterites are also enriched in Al_2O_3 (>5 wt.%) and CaO (>21 wt.%) compared to other Canastra-1 xenoliths (~ 2 wt.% Al_2O_3 and CaO dominantly <18 wt.%), corroborating the role of an Al_2O_3 -rich melt as the metasomatic agent. Based on the discussion above, we conclude that the pargasite websterites studied here are cumulates from a hydrous basaltic andesite.

In an alternative scenario, the origin of the pargasite websterites from Canastra-1 would be related to mantle hybridization promoted by melt-rock interaction, in which a peridotitic mantle reacted with a hydrous Al- and Si-rich melt potentially formed by melting of eclogites, either in subduction zones or from relicts of subducted crust buried in the mantle. Experimental studies of melt-rock reactions simulating metasomatism of the mantle wedge caused by partial melting of subducted slab have shown that hydrous Al- and Si-rich melts react with peridotite and form a new assemblage composed of orthopyroxene and amphibole. The metasomatic assemblage follows the reaction: $\text{ol} + \text{cpx} + \text{opx}_{(1)} + \text{sp} + \text{melt} = \text{amp} + \text{opx}_{(2)}$ (Sen & Dunn, 1994; Rapp *et al.*, 1999; Gervasoni *et al.*, 2017). These studies were conducted at pressures ($\sim 2\text{--}3$ GPa) and temperatures (~ 900 °C), like those assumed here for the pargasite websterites.

However, pyroxenites generated by this process usually inherit the chemical and isotopic compositions from low-P protolith (e.g., depleted gabbro and MORB). Clearly, based on the calculated melt in equilibrium (Supplementary Fig. S7) and Sr-Nd isotopic results (Supplementary Tab. S5), this is not the case. In general, pyroxenites generated by melt-rock interaction would have higher SiO_2 , FeO and TiO_2 but lower Al_2O_3 , CaO, and Na_2O contents than those from metamorphosed oceanic crust, which overlap most of the worldwide (“Global”) database of pyroxenite cumulates (Lu *et al.*, 2018). Comparatively, pargasite websterites from Canastra-1 display strong affinity with cumulate pyroxenites in terms of CaO, Na_2O , TiO_2 , and SiO_2 , but with higher FeO and lower Al_2O_3 contents (Fig. 5.15). Clinopyroxenes and garnets of pargasite websterites from Canastra-1 do not record the “ghost” effect (positive Eu and Sr anomalies) promoted by a protolith containing plagioclase (Lu *et al.*, 2018 and references therein) (Figs. 5.8c-d and 5.10c-d).

Besides whole-rock inference, the orthopyroxenes of Canastra-1 pargasite websterites show different compositions than pyroxenites formed by melt-rock reaction. For instance, our orthopyroxenes are characterized by distinctive lower contents of CaO, Cr_2O_3 , Na_2O , and Mg# coupled with higher FeO compared to experimental orthopyroxenes product of partial melting from eclogite-peridotite (Gervasoni *et al.*, 2017). Therefore, we preclude the origin of pargasite websterite as related to the melt-rock reaction products. Instead, they are defined as cumulate pyroxenites.

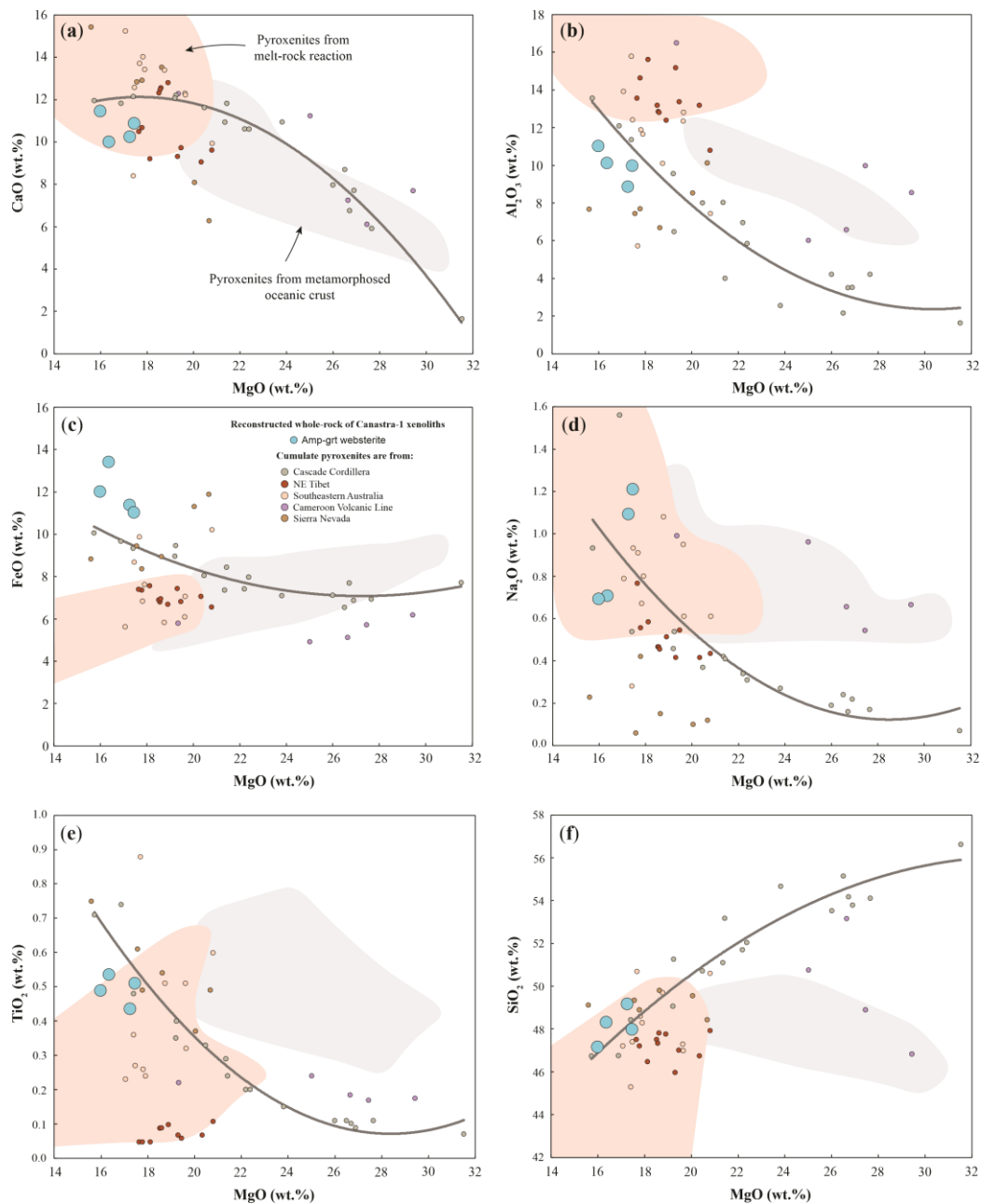


Fig. 5.16. Selected major elements (CaO, Cr_2O_3 , Na_2O , FeO) and Mg# versus Al_2O_3 of orthopyroxenes from Canastra-1 mantle xenoliths. For comparison, orthopyroxenes from cumulate pyroxenites from

Cascade Cordillera (Müntener *et al.*, 2001), NE Tibet (Xiong *et al.*, 2014), Southeastern Australia (Lu *et al.*, 2018), and Cameroon Volcanic Line (Puziewicz *et al.*, 2023) are plotted. Experimental orthopyroxenes from peridotite-eclogite reaction also are plotted (Gervasoni *et al.*, 2017).

Garnets from eclogites and pargasite websterites plot within the fields defined for mica-amphibole-rutile-ilmenite-diopside (MARID) metasomatism in the Zr–Y diagram (in ppm), that is, related with a hydrated metasomatic agent (Fig. 5.17a). On the other hand, these garnets show strong affinity with depleted samples in the Ti–Zr diagram (in ppm) (Fig. 5.17b). Moreover, based on classical diagrams (Ti/Eu vs. La/Yb_N and Sm/Er_N) (Griffin *et al.*, 1999), the compositional distribution of these garnets indicates the interaction of these xenoliths with silicate melt metasomatism, precluding any influence of carbonatite or CO₂-rich metasomatism (Fig. 5.17c, d). Here it is important to consider that the composition of eclogitic garnet alone cannot reliably constrain the nature of the metasomatic melt. This is because the partitioning of incompatible elements (i.e., LREE) into garnet strongly depends on temperature and grossular content (Aulbach *et al.*, 2020). These authors clearly demonstrate that the decreasing of Ca contents (or Ca#) in garnet is accompanied by the partitioning of LREE into clinopyroxene (see Fig. 2b and d of Aulbach *et al.*, 2020). Regarding our eclogitic garnets, their Ca# is low (0.17–0.22), indicating that these minerals are more susceptible to LREE partitioning. For this reason, LREE-enriched eclogites are characterized by garnets with few, or even non-trace element differences compared to depleted samples. Thus, it is evident that clinopyroxene is the main carrier of the metasomatic signature in LREE-enriched eclogites. This behavior is well-illustrated by enriched clinopyroxenes (Ce/Yb_N = 61–94) and depleted garnets of eclogites from Canastra-1 (Ce/Yb_N = 0.03–0.04). In the same way, Ti and therefore Zr concentrations reflect the temperature-dependent solubility of rutile into garnet (Aulbach, 2020). Considering that low-temperature eclogites should contain higher volumes of accessory rutile than high-temperature eclogites, a moderate temperature-dependent Ti solubility in garnet and clinopyroxene is expected for Canastra-1 eclogites (T = 978–982 °C). Hence, the deficiency of Nb-Ta-Ti and Zr-Hf observed in the eclogites from Canastra-1 is justified (Supplementary Fig. S6).

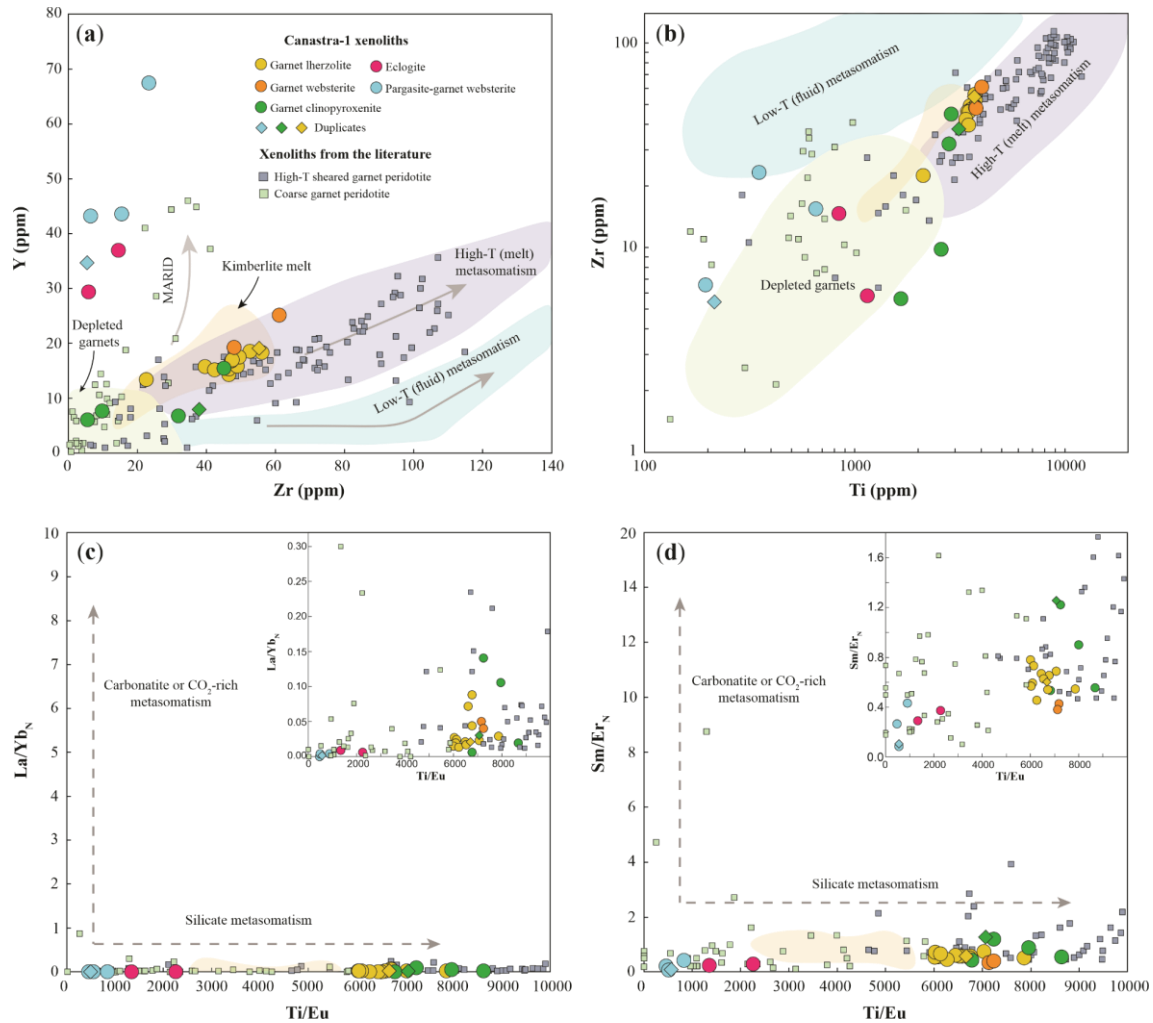


Fig. 5.17. Variation diagrams of trace elements. (a) Plots of Y versus Zr (ppm); (b) Zr versus Ti (ppm), (c) La/Yb_N ($N = \text{PM-normalized}$) versus Ti/Eu , and (d) Sm/Er_N ($N = \text{PM-normalized}$) versus Ti/Eu of garnets from Canastra-1 kimberlite mantle xenoliths. For comparison, high-T sheared peridotites (Viljoen *et al.*, 2009; Agashev *et al.*, 2013; Ionov *et al.*, 2010; Tappe *et al.*, 2021) and low-T coarse peridotites (Viljoen *et al.*, 2009; Ionov *et al.*, 2010; Kargin *et al.*, 2016; Fitzpayne *et al.*, 2020) from the Siberian, Kaapvaal, and East European cratons were plotted.

5.5.2 Decratonization of the São Francisco Craton caused by lithospheric thinning triggered by high-temperature refertilization at the LAB

The decratonization of the São Francisco Craton was previously discussed based on the rifting mechanism that promoted the orogenic reworking of the limit between the north São Francisco Craton and the Borborema Province, which is a late Neoproterozoic orogen mosaic formed during the amalgamation of Gondwana during the Brasiliano/Pan-African Orogeny (Ganade *et al.*, 2021). These authors combined radiometric data (U-Pb and Sm-Nd model ages) to conclude that the Borborema Province consists of ancient and strongly sheared crustal rocks related to the São Francisco Craton, being separated by major transcurrent shear zones, with small amount of juvenile material during the

Neoproterozoic orogeny. Similarly, Neves (2021) discussed an intense process of decratonization and crustal reworking in the Borborema Province during the Brasiliano-Pan-African Orogeny. This author indicates that the recurrent late Paleoproterozoic to early Neoproterozoic extension-related magmatism in the São Francisco Craton differs from the worldwide occurrence of orogenic episodes. In this work, the author suggests that the São Francisco Craton did not participate to the amalgamation of the Columbia supercontinent, its fragmentation, and the Rodinia consolidation. Additional discussion concerning the decratonization of the lithospheric mantle of the São Francisco Craton was given by Caxito & Alkmim (2023), who related this process to the opening (rifting) of V-shaped oceanic basins in the São Francisco-Congo Craton. They also support the hypothesis that this cratonic nucleus represents a single landmass isolated from the Rodinia Supercontinent. Recently, Rodrigues *et al.* (2023) discussed for the first time the effect of pervasive metasomatism/refertilization in a wide mantle column (spinel and garnet facies) beneath Catalão, SW margin of the São Francisco Craton, which resulted in cratonic rejuvenation.

Available geophysical data demonstrate that the São Francisco Craton extends further in depth than its geological boundaries at surface with the neighboring Neoproterozoic Brasília Belt (Pinto *et al.*, 2010; Assumpção *et al.*, 2017; Rocha *et al.*, 2019a, b) (Fig. 5.1 and Supplementary Fig. S8). For instance, the Canastra-1 mantle xenoliths have cratonic nature (on-craton) despite the kimberlite being emplaced in rocks of a Neoproterozoic belt. This feature is commonly observed in the edge of Archean cratons, where the ancient SCLM underlies younger collisional belts demonstrating contemporaneity and a possible genetic link (Lin *et al.*, 2022). Furthermore, geophysical studies indicate that a strong low-velocity seismic anomaly occurs within the lithospheric to asthenospheric mantle from ~100 to 250 km depth (Rocha *et al.*, 2019a, b) (Supplementary Fig. S8). However, this result needs to be carefully interpreted due to the limited number of seismographic stations in the studied area. Based on the S-wave propagation (V_s), a significant reduction of velocity is recognized at ~150 km depth (Assumpção *et al.*, 2013), which coincides with the current LAB (143 km, Ciardelli *et al.*, 2022). In this region, the V_s is 3.73 km/s (Assumpção *et al.*, 2013), implying a reduction of 17.2 % compared to the reference value of 4.75 km/s (Rader *et al.*, 2015). This anomaly appears to be the result of hot asthenospheric upwelling toward the shallower lithospheric mantle in the SW margin of the São Francisco Craton. This process

allows the thermo-mechanical erosion of the LAB at the base of the cratonic lithosphere through small-scale mantle convections (edge-driven convection) (King & Anderson, 1998; King & Ritsema, 2000; Foley *et al.*, 2008). However, the thermal influence of the Tristan da Cunha mantle plume cannot be excluded, especially due to the two-point Sm-Nd isochron ages (120 ± 5 Ma) obtained for Canastra-1 sheared lherzolites (see details below). In any case, the deformation observed in the sheared lherzolites, anhydrous websterites (and dunite) might have been caused by the intense heating due to Gondwana break-up and the consequent opening of the Atlantic Ocean. Because of such erosion, the lithospheric mantle in the SW limit between the São Francisco Craton and the Paranapanema Block has been rejuvenated by refertilization at least since the Neoproterozoic (Brasiliano Orogeny).

The heating source for the generation of alkaline lavas from the Alto Paranaíba Igneous Province (i.e., kimberlite and kamafugite) has been linked to lithospheric extension and incipient rifting during opening of the South Atlantic Ocean (e.g., Gibson *et al.*, 1995; Read *et al.*, 2004). The relationship between the rift systems and the formation of sheared peridotites is well-documented by sheared garnet-bearing lherzolites from the East African Rift (Henjes-Kunst & Altherr, 1992; Kaeser *et al.*, 2006; Baptiste *et al.*, 2015). These sheared peridotites are associated to deep-seated shear zones near to the LAB, which coincides with the presence of anomalously low-velocity material related to a rift zone. The origin of the high-T sheared garnet-peridotites hosted by kimberlites and equilibrated at pressures ranging from 4.5 to >6.5 GPa was also discussed by Grégoire *et al.* (2006). These authors suggested that although cratonic mantle xenoliths are assumed as lithospheric (O'Reilly & Griffin, 2010), their plastic state when they were captured by the kimberlite magmas suggests that they do not belong to the “typical” lithospheric mantle but to the underlying “asthenosphere”. Here it is important to consider that porphyroclastic and mosaic-porphyroclastic textures cannot be preserved for long periods in the LAB, keeping stable for a short period before the entrainment of xenoliths in the host kimberlite (e.g., Grégoire *et al.*, 2006 and references therein). For this reason, it was defined that sheared peridotites result from plastic deformation at the top of melt pockets due to the high-pressure condition imposed in this tectonic context. Thus, the hot geotherm (40 mW/m^2) defined by sheared lherzolites from Canastra-1 results from strain heating. This heating occurred during the plastic deformation in the early stages of the South Atlantic Ocean opening, shortly predating kimberlite emplacement. This

assumption is supported when we compare this geotherm with the intact thick cratonic lithosphere characterized by geotherms corresponding to 35–38 mW/m² surface heat flow. Further evidence of the effective replacement of the cratonic mantle is the absence of high-Cr₂O₃ coupled with CaO-undersaturated garnets (harzburgitic - G10 garnets, Grütter *et al.*, 2004), as typically observed in intact cratons. It is well-demonstrated in the plot of CaO vs. Cr₂O₃ (in wt.%) (Fig. 5.9, Grütter *et al.*, 2004), which confirms the classification of Canastra-1 mantle xenoliths accordingly.

Advected heat, likely related to kimberlite magmatism (proto-kimberlite melt), generates high-T refertilization and is especially common at the base of the continental lithosphere (Grütter, 2009). Proto-kimberlite melt metasomatism consists of interaction between fluid of kimberlitic affinity with mantle wall rocks at different depths in cratonic regions and that takes place immediately prior to kimberlite entrainment (Giuliani *et al.*, 2013). Therefore, this rejuvenation may be confirmed due to the shallow present-day LAB observed beneath Canastra-1 kimberlite (143 km; Ciardelli *et al.*, 2022). The difference in depth between current and ancient (174–186 km) LABs represents strict evidence of lithospheric thinning produced by the refertilization caused by proto-kimberlite melts from the asthenospheric upwelling (Fig. 5.12). For this reason, the occurrence of abundant sheared peridotites, anhydrous websterites (and a completely recrystallized dunite) in the LAB beneath Canastra-1 indicates that they are former “normal” coarse-granular peridotites. It further indicates that these rocks underwent extensive dynamic and static recrystallization, resulting in a bimodal grain size with large porphyroclasts immersed in a fine-grained, strongly deformed neoblastic matrix partially or totally recrystallized (e.g., Boyd & Nixon, 1975; Harte, 1977; Nixon *et al.*, 1981; Baptiste *et al.*, 2012; Agashev *et al.*, 2013; Tappe *et al.*, 2021). In the literature, it is widely accepted that these types of xenoliths are characterized by mosaic-porphyroclastic texture (Harte, 1977) and by high equilibration temperatures (usually between 1000 and 1300 °C) and pressures (usually >4.5 GPa) (i.e., 40–45 mW/m² geotherms) (e.g., Harte, 1977; Nixon *et al.*, 1981; Baptiste *et al.*, 2012; Tappe *et al.*, 2021). In general, these deformed rocks have fertile compositions associated with the melt-related metasomatism at the LAB shortly before the kimberlite eruption (e.g., Boyd & Nixon, 1975; Nixon *et al.*, 1981; Kennedy *et al.*, 2002; Grégoire *et al.*, 2006; O'Reilly & Griffin, 2010).

The development of garnet crystals surrounded by kelyphitic rims is a common feature of these xenoliths (Figs. 5.2f-h; 5.3a, c; 5.4a, c; 5.5a, d; 5.6b-i), usually containing

small crystals of phlogopite, secondary ortho- and clinopyroxenes (types 1 and 2), spinel, rutile, ilmenite, and Fe-Ni sulfides (with absence of olivine or low-pressure phases). Minerals product of alteration, such as serpentine, chlorite, carbonates, or even amphibole and sodalite, were not identified in kelyphitic rims from Canastra-1. Two main mechanisms have been proposed to decipher the origin of kelyphites, which are related to the conditions under which the kelyphite minerals were formed (Sharygin *et al.*, 2023). They are: (1) during xenolith transport to the surface, involving solid-state reaction between garnet and olivine during decompression, or reaction between garnet and kimberlite melt or fluid, and (2) mantle metasomatism promoted under the mantle residence P-T conditions of lherzolite before its entrainment into the ascending kimberlite magma. As reported for the Udachnaya pipe (Siberian Craton) mantle xenoliths (Sharygin *et al.*, 2023), those from Canastra-1 are also fresh (free of secondary alteration). Our mantle xenoliths were sampled from large drill-holes, and they are not in contact with the host kimberlite.

Considering the first scenario, solid-state reaction between garnet and olivine during decompression seems to be improbable due to the lack of compositional zonation among mineral phases within the rock-forming or kelyphitic rims, as well as there is no compositional variation between grains within kelyphite from Canastra-1 (i.e., they are in equilibrium). It is important to note that low-pressure minerals, such as sodalite and amphibole (as reported by Sharygin *et al.*, 2023) were not identified in Canastra-1 mantle xenoliths, precluding the formation of kelyphitic rims through magma ascent. Based on the pressure and temperature estimates of our deeper samples (5.3-5.6 GPa and 1191-1290 °C), they plot within the stability field defined for phlogopite instead of amphibole (see Fig. 16a of Sharygin *et al.*, 2023), supporting our interpretation. We also discard the reaction between garnet and kimberlite melt during their ascent to the surface because garnets from Canastra-1 do not show veinlets crosscutting these minerals or contain chemical zonation. In addition, we do not find kelyphite shells covering garnet grains either near the contact with kimberlite or even near the xenolith core, as well as there is no clear evidence of the effective role of a CO₂-rich melt (or carbonatite melt) in the mineral chemistry of garnet. Thus, after comparing our results with those reported by Sharygin *et al.* (2023), we are convinced that kelyphitic rims were formed by metasomatism (high-T proto-kimberlite) at the LAB before xenolith entrainment into the

ascending kimberlite magma, as it is not possible to keep this type of texture for a long time in such conditions.

Additional evidence that the kelyphitization process has been triggered under the mantle residence P-T conditions is provided by the lack of significant garnet breakdown based on the occurrence of very fine-grained spinel + orthopyroxene + clinopyroxene symplectites. It is important to note that among all studied samples from Canastra-1, vermicular lamellae of spinel forming a fine-scale pyroxene-spinel symplectite was only observed in sample CAN1-209 (anhydrous websterite). This feature was invoked to exemplify the effective decompression and cooling event and the consequently lithospheric thinning recorded by mantle peridotites of the garnet-spinel transition zone from the Marsabit Volcanic Field (Northern Kenya) (Kaesler *et al.*, 2006). These authors also reported significant chemical zonation that indicates the changing of P-T conditions, deformation, and variable styles of metasomatism, which was not revealed by mantle xenoliths from Canastra-1.

Phlogopites in kelyphitic rims from lherzolite (CAN1-86), clinopyroxenite (CAN1-174), and anhydrous websterite (CAN1-209) are classified as high-Ti -Cr ($\text{TiO}_2 = 1.29\text{--}4.63$ wt.% and $\text{Cr}_2\text{O}_3 = 0.80\text{--}1.91$ wt.%) due to their close affinity with type 2 phlogopites (Phl2) from proto-kimberlite metasomatism (Kargin *et al.*, 2019) (Fig. 5.11). However, the analyzed phlogopites show enrichment in FeO implying lower Mg# compared to Phl2 (Fig. 5.11c-f). According to the relation between TiO_2 and Cr_2O_3 (Fig. 5.11a), the studied crystals do not have any influence of type 1 phlogopites (Phl1) from mantle xenoliths and kimberlite xenocrysts (Giuliani *et al.*, 2014, 2016; Kargin *et al.*, 2019) or even of typical kimberlite phlogopites from the groundmass (Fritschle *et al.*, 2013) (Fig. 5.11). However, except for Cr_2O_3 contents, the xenolithic phlogopites from Canastra-1 and the high-Ti and low-Cr groundmass phlogopites have similar composition (Giuliani *et al.*, 2016; Kargin *et al.*, 2019) (Fig. 5.11). In this case, it is important to consider the peculiar and complex origin of these high-Ti and low-Cr groundmass phlogopites as they are interpreted as a mixing between magmatic minerals (with high-Ti and low-Cr) and xenocrystic material, including mantle-derived antecrysts (with high-Ti-Cr) (Giuliani *et al.*, 2016; Kargin *et al.*, 2019).

Compared with primary pyroxenes (type 1), both type 2 orthopyroxene and clinopyroxene (secondary) from the kelyphitic rims demonstrate selective enrichment in TiO_2 , Cr_2O_3 , CaO, and Al_2O_3 accompanied by depletion in Na₂O and Mg#

(Supplementary Tables S1–S3). This suggests the role of a common metasomatic agent (proto-kimberlite melt) reacting with the garnet xenocrysts from Canastra-1, which favored the development of kelyphitic rims. In addition, spinel crystals with kimberlite affinity were identified in these kelyphitic rims, as well as rutile and ilmenite that are typical mineral phases found in kimberlites. Therefore, the presence of well-developed kelyphitic halos around garnets from the deep cratonic samples of Canastra-1, with hydrated silicate and oxide minerals rich in Ti and Cr, indicates the interaction of these xenocrysts with the proto-kimberlite melt at mantle depths (e.g., Giuliani *et al.*, 2014, 2016; Bussweiler *et al.*, 2016; Kargin *et al.*, 2019).

The textures of peridotites usually show correlation with the estimated depth of origin and can be grouped into low- and high-temperature peridotites (Boyd & Nixon, 1975). The low-temperature suite is coarse-grained and has depleted composition, whereas the high-temperature peridotites (>1000 °C) have deeper origin, a fertile composition, and are deformed in varying degrees from coarse to porphyroclastic and fluidal mosaic textures (Boyd & Nixon, 1975, 1978). The high-T estimates (1191–1290 °C) of Canastra-1 xenoliths provide additional evidence of their interaction with a proto-kimberlite melt, reinforced by garnet crystals containing elevated Ti, Zr, and Y concentrations that indicate high-T melt metasomatism (Fig. 5.17a, b). In these plots (Zr vs. Ti and Y; Fig. 5.17), they show strong affinity with garnets from high-T sheared peridotites (~1000–1400 °C; Fig. 5.12) from the Siberian, Kaapvaal, and East European cratons (Viljoen *et al.*, 2009; Agashev *et al.*, 2013; Ionov *et al.*, 2010; Tappe *et al.*, 2021). Conversely, low-T coarse-grained peridotites from the cratonic areas mentioned above (Viljoen *et al.*, 2009; Ionov *et al.*, 2010; Kargin *et al.*, 2016; Fitzpayne *et al.*, 2020) clearly show different distribution patterns than Canastra-1 lherzolites, clinopyroxenites, and anhydrous websterites (Fig. 5.17). In addition, according to the Ti/Eu vs. La/Yb_N and Sm/Er_N diagrams, the garnets from these Canastra-1 xenoliths interacted with a high-T silicate melt, as they fall within the high-T sheared peridotites (Fig. 5.17c, d).

Clinopyroxenes endorse the dominance of a high-T silicate melt (proto-kimberlite) at the LAB beneath the SW margin of the São Francisco Craton through the Ti/Eu vs. La/Yb_N and Sr, and by Zr/Hf vs. Ti/Nb (Supplementary Fig. S9). Besides all clinopyroxenes plotting close to the typical enrichment trend proposed for silicate melt, they have strong affinity with clinopyroxenes of high-T sheared peridotites (Agashev *et al.*, 2013; Ionov *et al.*, 2010; Kargin *et al.*, 2017; Tappe *et al.*, 2021). It is interesting that,

in general, the typical compositional trends proposed for silicate and carbonatite melts coincide, respectively, with the high-T sheared and low-T coarse-grained peridotites (Ionov *et al.*, 2010; Kargin *et al.*, 2016; Fitzpayne *et al.*, 2020) (Supplementary Fig. S9a, b). It is important to emphasize that although lherzolites, anhydrous websterites, and clinopyroxenites have high Ca/Al ratios (7.56–10.69) (Supplementary Tables S1 and S2), which would be indicative of carbonatite metasomatism, the diagrams above exclude any evidence of this type of metasomatism (Supplementary Fig. S9). In the Mg# vs. Na₂O, CaO, and TiO₂ diagrams (Fig. 5.7), clinopyroxenes from lherzolites and anhydrous websterites fall within the compositional field of high-T sheared peridotites similar to those from the Siberian (Ionov *et al.*, 2010; Agashev *et al.*, 2013), Kaapvaal (Viljoen *et al.*, 2009; Baptiste *et al.*, 2012; Fitzpayne *et al.*, 2020; Tappe *et al.*, 2021), and East European (Kargin *et al.*, 2017) cratons.

Regarding the anhydrous websterites, their SiO₂-rich composition is defined by the large modal content of pyroxenes (ortho- and clinopyroxenes). For this reason, the genesis of this rock type cannot be explained by crystallization from kimberlite or silica-poor melts (Rehfeldt *et al.*, 2008). Thus, they are formed by reaction between peridotite and silica-rich melt (>60 wt.% SiO₂) derived by partial melting of eclogite, which implies the conversion of olivine into orthopyroxene (Rehfeldt *et al.*, 2008). Alternatively, the origin of olivine-free anhydrous websterites can be attributed to the interaction between mantle xenoliths with a H₂O-poor, alkaline silicate melt that triggered the formation of orthopyroxene at the expense of clinopyroxene (Koornneef *et al.*, 2009). Considering the context of the cratonic LAB beneath Canastra-1, we propose that the infiltration of a proto-kimberlite melt (~120 Ma) would favor the localized partial melting of an eclogitized subducted oceanic crust that induces the formation of orthopyroxene-rich lithologies (Kelemen *et al.*, 1992; Rehfeldt *et al.*, 2008; Koornneef *et al.*, 2009). Rudnick *et al.* (1994) proposed a similar process to explain the orthopyroxene enrichment in Kaapvaal peridotites. In our set of samples, CAN1-209 is a good example of this reaction process with 78 % orthopyroxene (Supplementary Tab. S6).

The Canastra-1 clinopyroxenites appear to represent a mafic eclogite protolith that was destabilized at the base of the cratonic lithosphere through the interaction with proto-kimberlite melt in a system containing insufficient Na₂O (i.e., low modal plagioclase) to allow the formation of omphacitic pyroxene (le Roex *et al.*, 2020).

Considering the Sr-Nd isotopic ratios of clinopyroxenes and garnets from lherzolites and clinopyroxenites, these samples show selective enrichment of Sr ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70560\text{--}0.70869$) at intermediate to high Nd isotopic ratios ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51273\text{--}0.51315$; $\epsilon\text{Nd} = +1.8$ to $+10.10$) (Fig. 5.13). The Nd results of whole-rocks ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51277\text{--}0.51292$, $\epsilon\text{Nd} = +2.5$ to $+5.6$) are consistent with those from their minerals. Although less scattered and with slightly lower Nd ratios, this distribution pattern is similar to that observed in the garnet xenocrysts from the Carolina kimberlite, Amazonian Craton (Gervasoni *et al.*, 2022) (Fig. 5.13). This behavior is explained by the high incompatibility (and mobility) of Sr compared to Nd, which confer a sensitive character to Sr isotopic ratios, susceptible to perturbation that increases $^{87}\text{Sr}/^{86}\text{Sr}$ values while $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios remain constant.

Although there are no details about the method and material employed to determine the emplacement age of the Canastra-1 kimberlite, the only available age is Cretaceous (120 Ma, Read *et al.*, 2004). Therefore, based on the Sr-Nd isotopic compositions, as well as on the Sm-Nd isochron ages (average of 120 ± 5 Ma), it is assumed that lherzolites, clinopyroxenites, and anhydrous websterites (although there are no isotopic data for the latter) record the isotopic equilibrium at the time of the proto-kimberlite melt percolation and refertilization at the LAB beneath the São Francisco Craton, which precedes the subsequent eruption of the Canastra-1 host kimberlite. It is important to observe that this premise is plausible due to the higher equilibrium temperatures of these xenoliths (1191–1290 °C) compared to the closure temperature for the Sm-Nd system in clinopyroxene (1000–1150 °C) and garnet (750–900 °C) (Ganguly & Tirone, 1999; Van Orman *et al.*, 2001, 2002). Hence, the two-point Sm-Nd isochrons constructed based on clinopyroxenes and garnets from sheared lherzolites (Fig. 5.14) represent cooling/emplacement ages that are product of proto-kimberlite melt metasomatism, as similarly proposed by Gervasoni *et al.* (2022) for Carolina mantle xenoliths.

5.6 Conclusion

Mantle xenoliths hosted by the Canastra-1 kimberlite, exposed in the SW edge of the São Francisco Craton, are equilibrated within the garnet stability field. Sheared lherzolites, granuloblastic dunite, coarse clinopyroxenites and anhydrous websterites are

deeper xenoliths within the lithosphere-asthenosphere boundary (LAB). On the other hand, eclogites and pargasite websterites are representative of the shallower cratonic lithosphere.

The deeper xenoliths are characterized by high-T estimates (1191–1290 °C) and were affected by metasomatism near the LAB shortly before the eruption of the host kimberlite (174–186 km). The high-T proto-kimberlite melt metasomatism is corroborated by strong compositional affinity with high-T sheared peridotites from other cratons worldwide (i.e., Siberian, North Atlantic, Kaapvaal, and East European). This metasomatism is exemplified by high Ti, Zr, and Y concentrations in garnets, as well as by clinopyroxene selected major (e.g., Mg# vs. Na₂O, CaO, and TiO₂) and trace elements (e.g., Ti/Eu vs. La/Yb_N and Sr; Ce/Yb_N = 12.06–48.02). Well-developed kelyphitic rims reinforce the interaction between garnet and proto-kimberlite metasomatic agent. Isotopically, they display selective enrichment of ⁸⁷Sr/⁸⁶Sr (0.70560–0.70869) coupled with intermediate to high Nd isotopic ratios (εNd = +1.8 to +10.10). The two-point Sm-Nd isochron age average obtained considering clinopyroxene and garnet from sheared lherzolites is 120 ± 5 Ma, which records the percolation of a proto-kimberlite melt into the LAB beneath the São Francisco Craton immediately before the eruption of the Canastra-1 kimberlite. This refertilization event is coeval with the early stages of the Gondwana break-up and the opening of the Atlantic Ocean. In this tectonic context, lithospheric thinning, extensive extensional deformation, and intense thermal activity are common.

Eclogites are classified as high-Mg (garnet Mg# = 0.64–0.69) and low-Ca (garnet Ca# = 0.17–0.22) and demonstrate transitional affinity between Groups I and II eclogites. These xenoliths represent a more primitive, olivine-rich basaltic protolith within the shallower cratonic lithosphere beneath Canastra-1 (~130 km). Eclogitic clinopyroxene shows cryptic metasomatism (Ce/Yb_N = 60.90–93.63), reinforced by the spoon-like REE pattern of reconstructed whole-rock. On the other hand, eclogitic garnet maintained its depleted character based on REEs (Ce/Yb_N < 0.32). The Sr-Nd isotope composition of eclogite suggests the role of an enriched component (⁸⁷Sr/⁸⁶Sr clinopyroxene = 0.70842, garnet = 0.70912; εNd = -5.6 to -7.3).

The partial melting of ancient oceanic slab fragments, which generates SiO₂- and Al₂O₃-rich hydrous melts, favored the formation of pyroxenite cumulates exemplified by olivine-free pargasite websterites. This is mainly corroborated by the Al-rich

orthopyroxene and reconstructed whole-rock compositions ($\text{Al}_2\text{O}_3 = 3.55\text{--}4.34$ and $8.88\text{--}11.03$ wt.%, respectively), low Mg# of orthopyroxene and reconstructed whole-rock ($0.74\text{--}0.78$ and $0.51\text{--}0.58$, respectively), and the formation of amphibole. These samples also evidence cryptic metasomatism as shown by LREE-enriched clinopyroxenes ($\text{Ce}/\text{Yb}_\text{N} = 10.52\text{--}50.61$), as well as by high-Sr isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}$ clinopyroxene = $0.70894\text{--}0.71003$) and pronounced negative ϵNd values (-12.9 to -13.3). Although we do not achieved chronological ages for eclogites and pargasite websterites, we attribute their formations to the Gondwana amalgamation in the Neoproterozoic (Brasiliano Orogeny).

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Data Availability

The data underlying this article are available in the article and in its online supplementary material (<https://doi.org/10.1093/petrology/egae087>).

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CAPÍTULO 6

ARTIGO II

6 ARTIGO II

O segundo manuscrito encontra-se em fase de elaboração para ser submetido na revista *Nature Communications*.

Archean to Paleoproterozoic subduction-derived noble gases in the lithospheric mantle beneath the São Francisco Craton

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Abstract

While mid-ocean ridge basalts (MORB) and ocean island basalts (OIB) are well characterized in terms of helium, neon, argon, and xenon isotopes, the continental lithosphere, especially cratonic domains and subduction settings, remain poorly constrained. We report new noble gas (He, Ne, Ar, Kr, and Xe) isotope ratios in peridotite, pyroxenite, and eclogite xenoliths from the SW margin of the São Francisco Craton. Helium isotopes reveal a strong radiogenic component, while neon shows MORB-like and nucleogenic signatures. This indicates the recycling of subduction-derived materials within the stratified cratonic mantle (2.0–5.5 GPa). Xenon reveals a cratonic lithosphere

where air and fissiogenic (crustal) components variably mix with a MORB source. The recycling of ancient hydrated oceanic crust and overlying sediments, characterized by high $(U+Th)/(^3He, ^{22}Ne, ^{132}Xe)$ ratios, is associated with a complex and long-lived subduction system established along the SW margin of the São Francisco Craton since the Archean-Paleoproterozoic.

Keywords

Mantle xenoliths

Metasomatized cratonic lithosphere

São Francisco Craton

Noble gas isotopes

Archean to Paleoproterozoic

6.1 Introduction

The longevity and unmodified nature of Archean to Proterozoic cratonic lithospheric mantle turn these regions into tectonically stable and highly depleted mantle domain, isolated from the convective mantle and characterized by cold geotherms on the order of $35\text{--}40\text{ mWm}^{-2}$ ¹⁻⁵. However, chemical and isotopic heterogeneities, particularly observed in mantle xenoliths from cratonic margins, indicate that these mantle domains have been affected by effective recycling of subduction-derived materials, including oceanic crust and overlying sediments⁶⁻²⁰.

Noble gas isotopes are crucial for understanding degassing (partial melting) and regassing (volatile recycling) processes in the Earth's mantle, owing to their chemical inertness and the contributions from both extinct and extant radionuclides. Helium isotopic ratios are used as the main noble gas tracer to define mantle heterogeneity due to the negligible atmospheric contamination^{21,22}. In contrast, due to their low abundances, reliable results of neon, argon, and especially xenon remain scarce, especially for mantle xenoliths.

Mantle-derived samples show increasing of radiogenic isotopes (i.e., ^4He , ^{21}Ne , ^{40}Ar , and ^{136}Xe) from primordial and undegassed/deep ocean island basalts (OIB²³⁻²⁶) towards depleted and degassed/shallower mid-ocean ridge basalts (MORB²⁷⁻³⁰), subcontinental lithospheric mantle (SCLM^{31,32}), and arc-related metasomatism in mantle

xenoliths^{19,33-35}. However, only oceanic domains (OIB and MORB) are well-constrained regarding helium, neon, argon, and xenon isotopic compositions. Conversely, the cratonic lithosphere has very limited noble gas isotope data (Fig. 6.1). For instance, mainly helium, but also some neon results are available for cratonic xenoliths from Siberia³⁶⁻³⁸, South Africa³⁸, Canada³⁸, Northern Tanzania³⁹, and China⁴⁰⁻⁴².

This study presents the first helium, neon, argon, krypton, and xenon isotope ratios for a cratonic lithosphere. It reveals remarkably radiogenic helium, MORB-like and nucleogenic neon, and fissiogenic/MORB-like xenon components recorded by garnet-bearing mantle xenoliths from the stratified lithosphere ($T = 875\text{--}1290\text{ }^{\circ}\text{C}$; $2.0\text{--}5.5\text{ GPa}$) beneath the São Francisco Craton. These xenoliths were sampled by the diamond-bearing Canastra-1 kimberlite (*ca.* 120 Ma⁶) placed at the SW margin of the craton. The noble gas components with high U+Th/primordial ratios were recycled into the cratonic lithosphere through a complex orogenic system, which records at least two collisional episodes during the Minas-Bahia (2.2–1.9 Ga) and Brasiliano (640–510 Ma) orogenies.

6.2 Results and discussion

We present the first helium, neon, argon, krypton, and xenon isotope ratios for garnet-bearing mantle xenoliths from the SW margin of the São Francisco Craton (Supplementary Data 1). We have analyzed clinopyroxene (cpx), garnet (grt), orthopyroxene (opx), pargasite (amp), and whole-rock (wr) samples from sheared lherzolites (cpx = 2, grt = 3, opx = 1, and wr = 1), clinopyroxenites (cpx = 5, grt = 5), olivine-free anhydrous websterite (cpx = 1 and grt = 1), olivine free pargasite websterite (cpx = 1, grt = 1, and amp = 1), and eclogite (cpx = 1 and grt = 1) (Supplementary Data 1).

Noble gas isotope ratios and concentrations of mantle xenoliths were extracted from trapped fluid inclusions by stepwise crushing method (100, 500, 1000, and 2000 strokes) under high vacuum condition, which avoid the cosmogenic or radiogenic contributions from the mineral matrix. To constrain the contribution of crystal-lattice-hosted component to the radiogenic signature of Canastra-1 mantle xenoliths, we have also analyzed their rock powders (after stepwise crushing) by heating extraction. For most xenoliths, heating extraction resulted in slightly lower $^3\text{He}/^4\text{He}$ ratios when compared to crushing extraction. Although this would indicate post-eruptive addition of ^4He to the

crushing experiments, the contribution from this component is negligible (<5 %) (Supplementary Information and Supplementary Data 1). Excluding the first extraction (100 strokes), the contribution of radiogenic component is <1 %. Given the lack of significant isotope variation with the number of crushing strokes, we adopt the helium total crushing isotope ratios for the discussion. Estimations for the atmospheric and radiogenic contributions to the helium isotope ratios of Canastra-1 xenoliths are detailed in Supplementary Information. For comparison, we used only helium data from literature with analytical uncertainties < 1 R_A (where R_A corresponds to atmospheric ratio of 1.4×10^{-6} ⁴³).

6.2.1 Radiogenic helium beneath the São Francisco Craton

Mantle-derived total crushing ³He/⁴He isotope ratios vary from 0.19 to 4.48 R_A (19 of 23 measurements <1 R_A) (Figs. 6.1 and 6.2). Higher ³He/⁴He individual ratios (6.12–9.77 R_A) were obtained in the first extraction (100 strokes), suggesting preferential release of noble gases from well-developed kelyphitic (garnet) and spongy (cpx) rims⁶. These ratios are consistent with proto-kimberlite melt metasomatism occurring within the lithosphere-asthenosphere boundary (LAB)⁶, which contains ³He/⁴He compatible with those expected for the convective mantle. Although this effect is present in other samples, it is observed in a lesser extent and can be considered negligible. Heating analyzes show significantly higher ⁴He concentration than the amount obtained by crushing (Fig. 6.2 and Supplementary Data 1), indicating that the helium in these samples resides in small inclusions and/or mineral lattice that remained closed systems during crushing. No difference in ³He/⁴He ratios is noted for deep (5.3–5.6 GPa; 1191–1290 °C) and shallow (2.0–4.0 GPa; 875–982 °C) mantle xenoliths⁶, as well as among cpx, grt, opx, prg, and wr samples (Fig. 6.2).

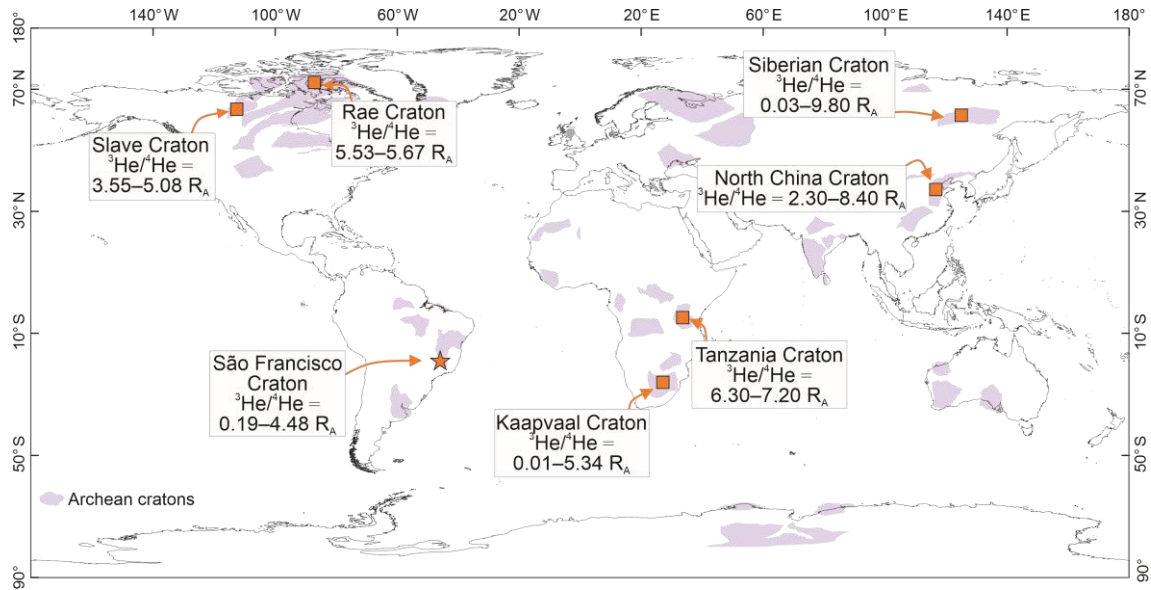


Fig. 6.1. World map showing the compositional variation in helium isotope ratios of mantle xenoliths overlaid on cratonic domains⁴⁴. Mantle xenoliths from the SW margin of the São Francisco Craton exhibit a highly radiogenic composition, similar to those found in the Kaapvaal (South Africa³⁸) and Siberian (Russia^{36-38,45}) cratons. These regions contrast with other cratonic lithospheres worldwide (Canada³⁸, China⁴⁰⁻⁴², and Northern Tanzania³⁹), which typically display less radiogenic compositions.

In cratonic regions, mantle xenoliths and diamonds are characterized by large variation in $^3\text{He}/^4\text{He}$ ratios, usually varying from the SCLM ($6 \pm 1 R_A$ ^{31,32}) to a more radiogenic reservoir ($<5 R_A$) (Fig. 6.2a). Among the available results of helium isotope ratios for on-craton mantle xenoliths (or xenocrysts) worldwide (Fig. 6.1), radiogenic signatures are identified in the Kaapvaal (0.01–5.34 R_A , most $<4 R_A$ ³⁸) and Siberian (0.03–9.80 R_A , most $<5 R_A$ ^{36-38,45}) cratons (Fig. 6.2a). In contrast, mantle xenoliths from the China (2.30–8.40 R_A , most $>6 R_A$ ⁴⁰⁻⁴²), Canadian (i.e., Slave and Rae: 3.55–5.67 R_A ³⁸), and especially Northern Tanzania (6.30–7.20 R_A ³⁹) cratons are considerably less radiogenic (Fig. 6.2a). Diamond samples from the Siberian Craton exhibit less radiogenic helium compositions compared to mantle xenoliths (2.78–11.23 R_A , most $>6 R_A$ ⁴⁶), whereas those from the Kaapvaal Craton display a similar interval of values (0.07–4.43 R_A ⁴⁷) (Fig. 6.2a). In addition, superdeep (>300 km) diamonds from Juína, Amazonian Craton, also exhibit predominantly radiogenic helium isotopic ratios (0.65–4.93 R_A ²⁰) (Fig. 6.2a). A few samples, however, show $^3\text{He}/^4\text{He}$ ratios comparable to those found in the SCLM (5.11–6.30 R_A), MORB (8.25 R_A) and OIB (10.74–49.91 R_A)²⁰ (Fig. 6.2a).

Figure 6.2b compares the $^3\text{He}/^4\text{He}$ ratios of Canastra-1 mantle xenoliths (usually $<1 R_A$) with those from off-craton, arc-related regions worldwide. In general, our results are similar or slightly more radiogenic than those reported for mantle xenoliths from

Coyhaique, Patagonian back-arc (total crushing $^3\text{He}/^4\text{He} = 0.24\text{--}1.74 R_A^{34}$) and phenocrysts (olivine and pyroxene) from Northern ($^3\text{He}/^4\text{He} = 2.00\text{--}7.96 R_A$, most $>6 R_A^{48}$), Central ($^3\text{He}/^4\text{He} = 0.82\text{--}6.02 R_A$, most $<4 R_A^{48-50}$) and Southern ($^3\text{He}/^4\text{He} = 0.18\text{--}6.84 R_A$, most $>4 R_A^{50}$) volcanic zones of the Andean Cordillera (Fig. 6.2b). However, it is worthy to note that the SCLM beneath Patagonia, Southern South America, shows high compositional heterogeneity regarding $^3\text{He}/^4\text{He}$ ratios^{32,34,51}. Except for Coyhaique, which records radiogenic helium, other occurrences of mantle xenoliths from Patagonia reveal the existence of intrinsic SCLM ($5.33\text{--}6.99 R_A$), MORB-like ($7.17\text{--}7.60 R_A$), and primordial ($21.65\text{--}27.68 R_A$) components^{32,51}. The comparison established above for the Andean subduction system is also observed in exhumed mantle wedge peridotites from the Italian Alps ($^3\text{He}/^4\text{He} = 0.16\text{--}0.69 R_A^{52}$) and SW Japan ($^3\text{He}/^4\text{He} = 1.34\text{--}1.99 R_A^{45}$, only crushing experiments) (Fig. 6.2b). Furthermore, Canastra-1 mantle xenoliths are considerably more radiogenic than those from the Cascades Volcanic Arc ($^3\text{He}/^4\text{He} = 4.14\text{--}7.67 R_A$, most $>6 R_A^{53}$) (Fig. 6.2b).

In this context, we argue that the subducting input, dominated by hydrous oceanic crust and overlying sediments with high $(U+Th)/^3\text{He}$ ratios, is responsible for the strictly radiogenic helium observed in the lithospheric mantle beneath the São Francisco Craton.

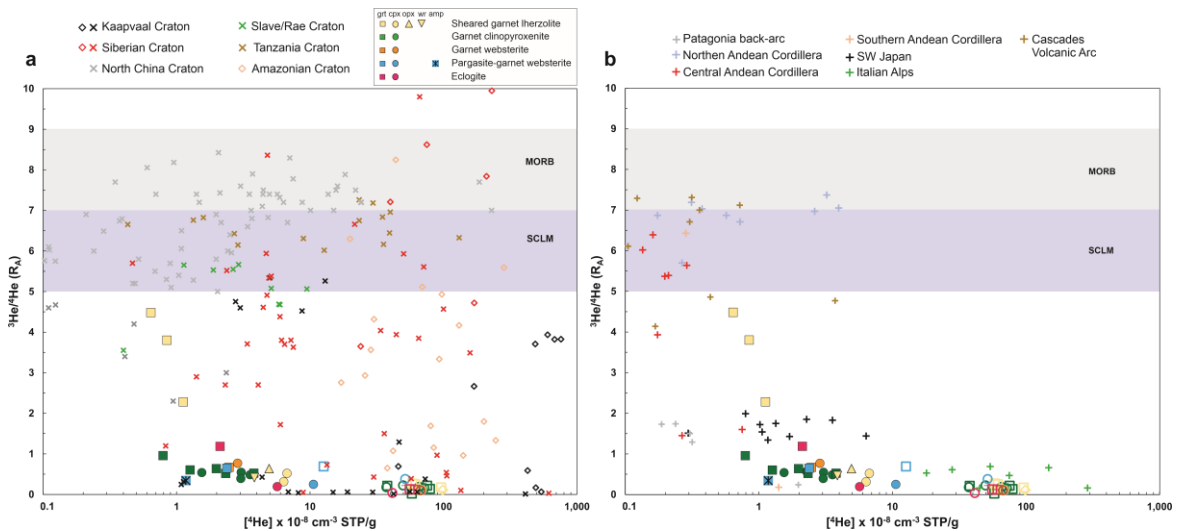


Fig. 6.2. Helium concentration versus $^3\text{He}/^4\text{He}$ of mineral separates (clinopyroxene, garnet, orthopyroxene, and pargasite) and whole-rocks from peridotites, pyroxenites, and eclogites hosted by the Canastra-1 kimberlite, SW margin of the São Francisco Craton. Analytical uncertainties (1σ) are smaller than the symbol size. Typical mid-ocean ridge basalt composition ($\text{MORB} = 8 \pm 1 R_A^{27-30}$) is represented by grey while typical subcontinental lithospheric mantle composition ($\text{SCLM} = 6 \pm 1 R_A^{31,32}$) is represented by purple. For comparison, helium isotope compositions of on- and off-cratonic regions were plotted (a and b, respectively). In (a), data are of mantle xenoliths and xenocrysts from Kaapvaal³⁸,

Siberian^{36-38,45}, North China⁴⁰⁻⁴², Canadian³⁸, and Tanzanian³⁹ cratons. In addition, diamond samples (diamond symbol) from the Amazonian Craton²⁰ are shown. In (b), arc-related mantle xenoliths are from Coyhaique (Patagonian back-arc³⁴), SW Japan⁴⁵, Italian Alps⁵², and Cascades Volcanic Arc⁵³, whereas olivine and pyroxene phenocrysts are from Andean Cordillera⁴⁸⁻⁵⁰. Abbreviations: grt: garnet; cpx: clinopyroxene; opx: orthopyroxene; wr: whole rock; amp: pargasite amphibole.

6.2.2 Neon isotopes indicate the recycling of an ancient hydrated oceanic crust and sediments within the São Francisco Craton

Neon isotope measurements with a strong contribution of blank, as well as high $^{40}\text{Ar}^{++}$ on $^{20}\text{Ne}^+$ and CO_2^{++} on $^{22}\text{Ne}^+$ (all >10 %) isobaric interferences, were not considered in the discussion due to their low analytical quality (Supplementary Data 1). Data that do not differ from air composition ($^{20}\text{Ne}/^{22}\text{Ne}_{\text{air}} = 9.80$; $^{21}\text{Ne}/^{22}\text{Ne}_{\text{air}} = 0.02924$ ⁴³) within 1σ analytical uncertainties were also discarded (Supplementary Data 1). In addition, only crushing measurements were used for the discussion.

Our data reveal that whilst the $^3\text{He}/^4\text{He}$ ratios are strongly radiogenic (usually <1 R_A), most neon isotopic data of Canastra-1 mantle xenoliths plot along with the air-MORB line²⁸ (Fig. 6.3). Eclogite xenolith is thought to come from recycled mafic oceanic crust protolith, whereas pargasite websterite xenoliths represent a water-rich cumulate⁶. Our eclogite (cpx = 0.19 and grt = 1.19 R_A) and pargasite websterite (cpx = 0.25, grt = 0.65, and amp = 0.34 R_A) xenoliths show low- $^3\text{He}/^4\text{He}$ ratios. They also represent low-temperature xenoliths (<1000 °C) within the lithospheric mantle beneath the SW margin of the São Francisco Craton⁶. As expected, the former plots within the air-MORB neon correlation line²⁸, whereas the latter demonstrates affinity with the air-Crustal line⁵⁴ (Fig. 6.3). On the other hand, the high-temperature xenoliths (>1200 °C) from Canastra-1 plot along with the air-MORB line²⁸ (Fig. 6.3). The pargasite separates of websterite (CAN1-95) unexpectedly revealed that the only representative result indicates contribution from a plume component²⁶ (Fig. 6.3). We interpret this as evidence of an ancient thermal anomaly. The contemporaneity between the Tristan da Cunha mantle plume and the emplacement age of the Canastra-1 host kimberlite (*ca.*120 Ma⁶) rules out the involvement of this event. This interpretation is further supported by the expectation that the Tristan da Cunha mantle plume would have a greater influence at greater depths (>5 GPa⁶) rather than the shallower cratonic lithosphere, where the pargasite websterite was stable (2–3 GPa⁶). However, this is not observed. In the neon three isotope plot ($^{20}\text{Ne}/^{22}\text{Ne}$ vs. $^{21}\text{Ne}/^{22}\text{Ne}$), the limited available data in the literature are of diamonds and mantle

xenoliths from the Siberian Craton^{36,45,46}, in which they demonstrate a mixing between plume (air-OIB line²⁶) and depleted mantle (air-MORB line²⁸) (not shown).

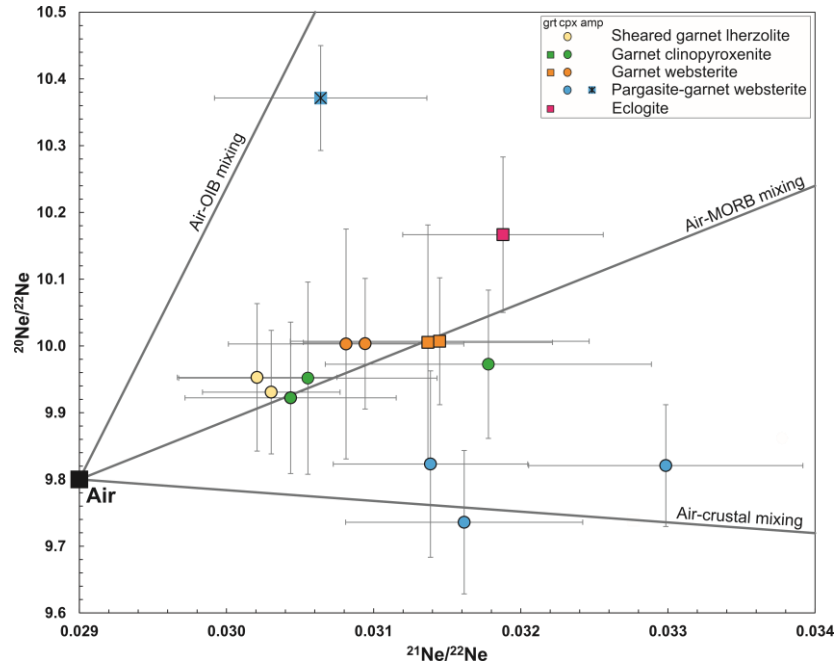


Fig. 6.3. Neon three-isotope diagram showing individual stepwise crushing measurements from the SW margin of the São Francisco Craton. Analytical uncertainties are 1σ . Mantle xenoliths from Canastra-1 mainly plot within the air-MORB mixing line²⁸. As expected, the eclogite sample is characterized by a MORB-like component. In contrast, clinopyroxene separate from the pargasite-websterite shows nucleogenic composition and plot along with the air-Crustal mixing line⁵⁴. Remarkably, pargasite separate has primordial neon, plotting within the air-OIB mixing line²⁶. Abbreviations: grt: garnet; cpx: clinopyroxene; amp: pargasite amphibole.

Concerning the existence of MORB-like and Crustal neon components, we propose two different models as possible candidates to explain the decoupling between helium and neon observed in our samples: (1) we envisage the contribution of different sources, such as hydrated oceanic crust and overlying sediments or (2) the replacement of a strong nucleogenic signature (i.e., crustal) by a MORB-like component due to the proto-kimberlite metasomatism during the Cretaceous. Except for the higher helium isotope ratios observed in the first extraction (100 strokes), where a few samples were variably affected by proto-kimberlite metasomatism, this pattern is not replicated in subsequent crushing extractions (Fig. 6.2). Based on this pattern, it seems unlikely that the interaction between the cratonic lithosphere and the proto-kimberlite melt shortly before the emplacement of the Canastra-1 kimberlite could have significantly modified the neon composition without also affecting the helium isotope ratios. Therefore, our

preferred model suggests the recycling of different slab-derived volatile components into the cratonic lithosphere.

6.2.3 *Atmospheric contribution to argon and krypton isotopes*

Argon extracted by crushing experiments shows lower $^{40}\text{Ar}/^{36}\text{Ar}$ isotope ratios (304–1250, average 514) than those extracted by heating (381–8464, average 1452) (Supplementary Data 1). These values represent mantle-derived gases strongly affected by atmospheric contribution ($^{40}\text{Ar}/^{36}\text{Ar} = 296^{43}$).

Krypton isotope ratios are indistinguishable from atmospheric compositions at analytical uncertainties of 1σ or demonstrate high blank contribution ($>10\%$) (Supplementary Data 1). For this reason, krypton isotope ratios have no geological significance.

6.2.4 *Excess of ^{136}Xe produced by an enriched ^{238}U source*

Radiogenic ^{129}Xe was produced by radioactive decay of extinct ^{129}I ($t_{1/2} = 17$ Ma), while ^{136}Xe was produced by fission from extinct ^{244}Pu ($t_{1/2} = 80$ Ma) and extant ^{238}U ($t_{1/2} = 4.47$ Ga^{22,25-27}). In principle, if the lithosphere on the SW margin of the São Francisco Craton results from a mixture of air and mantle endmember, a regression line not forced to pass through the air composition should naturally intersect or include the air point within the analytical uncertainty. In contrast, the slope defined by our dataset in the $^{136}\text{Xe}/^{132}\text{Xe}$ versus $^{129}\text{Xe}/^{132}\text{Xe}$ indicates a pre-mixed air + fissiogenic/crustal component variably mixing with mantle MORB (Fig. 6.4). Remarkably, the Xe isotope ratios of Bravo Dome samples show the same systematics⁵⁵.

In this plot, samples enriched in Xe, exhibiting a compositional affinity with the MORB mantle, are derived from eclogite (Fig. 6.4). The MORB-source signature recorded in this sample corroborates the recycling of an ancient oceanic crust beneath the SW margin of the São Francisco Craton⁶.

The unambiguous evidence for a mixture of fissiogenic/radiogenic components and air with low He/Xe ratios due to the fractionation promoted by subduction is supported by $^{136}\text{Xe}/^{132}\text{Xe}$ versus $^3\text{He}/^4\text{He}$ (Fig. 6.5). In this plot, garnets from sheared lherzolites show the contribution of the MORB component at the LAB. In contrast, a

significant number of samples are characterized by variable degrees of He/Xe fractionation due to the high diffusion of He compared to Xe in subduction system⁵⁶ (Fig. 6.5). For instance, the $^4\text{He}^*/^{136}\text{Xe}^*_\text{U}$ ratio (Eq. 1 and 2) of *CAN1-206 CPX 500x* is 5.6×10^5 , several orders of magnitude lower than the mantle production ratio assuming all $^{136}\text{Xe}^*$ is derived from the fission of ^{238}U (4.5×10^8 ²²). In addition, the $^4\text{He}^*/^{136}\text{Xe}^*_\text{U}$ ratios of MORB-source worldwide vary from 8.8×10^7 to 2.6×10^{10} ⁵⁷. This sample was selected for comparison because it exhibits the highest degree of fractionation (Fig. 6.5).

$$^4\text{He}^* = \text{U} \times [8 \times (e^{\lambda_{238}t} - 1) + (1/137.88) \times (e^{\lambda_{235}t} - 1) + 6 \times \kappa \times (e^{\lambda_{232}t} - 1)]$$

(Equation 1)

$$^{136}\text{Xe}^* = (\lambda_{\text{sf}}/\lambda_{238}) \times ^{136}\text{y} \times ^{238}\text{U} \times (e^{\lambda_{238}t} - 1) \text{ (Equation 2)}$$

Where U is the whole-rock concentration (in ppm) of the primitive mantle (PM⁵⁸). This value was used due to the lack of available data for the Canastra-1 mantle xenoliths. λ_{238} , λ_{235} , and λ_{232} are the decay constants for ^{238}U , ^{235}U , and ^{232}Th (1.55×10^{-10} , 9.85×10^{-10} , and 4.95×10^{-11} , respectively)²²; 1/137.88 is the present canonical ratio of $^{235}\text{U}/^{238}\text{U}$; and κ is Th/U ratio of the whole-rock (PM) sample²². $\lambda_{\text{sf}}/\lambda_{238}$ is the ratio of fission to total decay (5.45×10^{-7}), while ^{136}y of 6.3 is the absolute yield of ^{136}Xe ²². Therefore, we propose that the air + fissiogenic + MORB components reflects the nature of subduction-affected cratonic lithosphere.

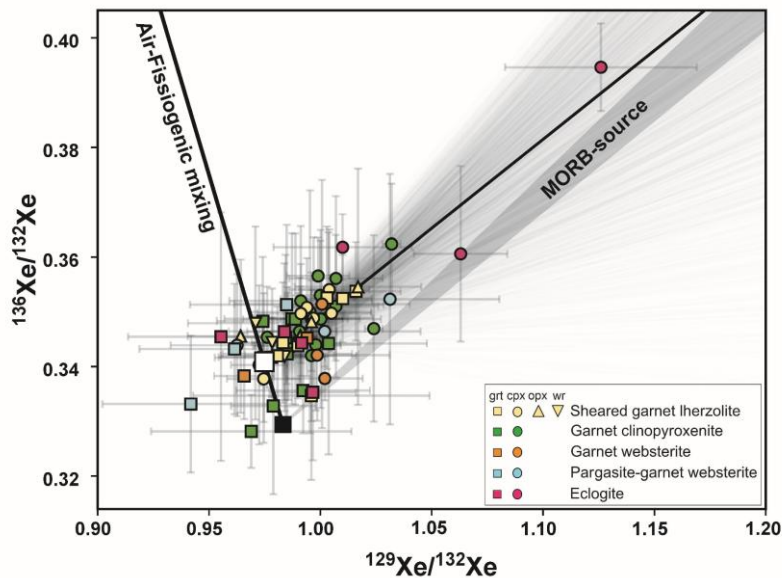


Fig. 6.4. Individual crushing measurements reveal the involvement of three components (air, fissiogenic, and MORB) in the cratonic lithosphere beneath Canastra-1. The solid black line through

Canastra-1 data is the uncertainty weighted best-fit, and the light grey solid lines represent the 1σ uncertainty envelope. This line intercepts the pre-mixed air (black square) and fissiogenic Xe component⁴³ at $^{129}\text{Xe}/^{132}\text{Xe} = 0.975$ and $^{136}\text{Xe}/^{132}\text{Xe} = 0.341$ (white square). The dark gray field represents the air-MORB mixing line, accounting for propagated uncertainties (1σ)³⁰. All analytical uncertainties are 1σ . Abbreviations: grt: garnet; cpx: clinopyroxene; opx: orthopyroxene; wr: whole rock.

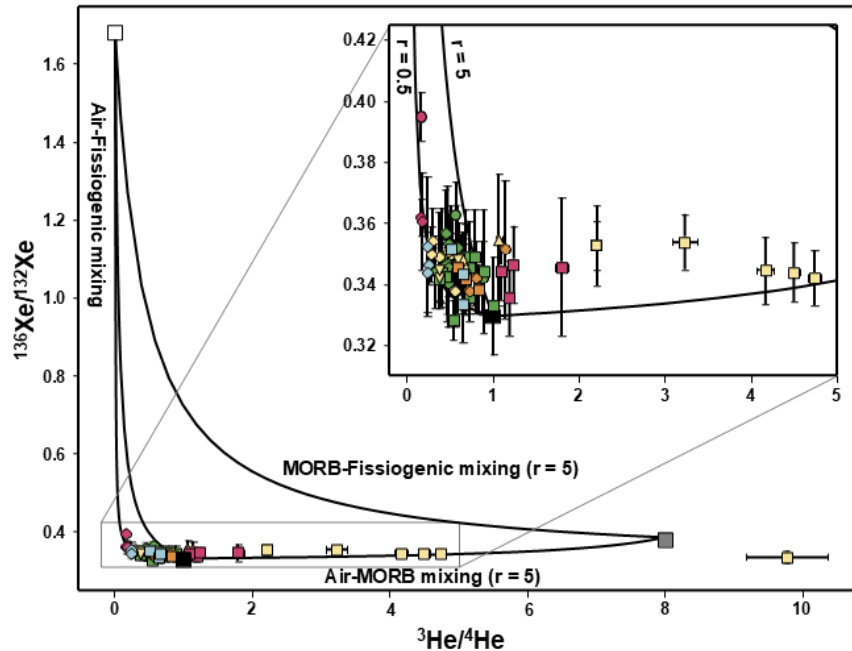


Fig. 6.5. The He-Xe systematics can be explained by mixing lines that represent a combination of air with fissiogenic/radiogenic and MORB endmembers. The mixing lines are defined for r values ranging from 5 to 0.5. Measurements with fissiogenic Xe and radiogenic He signatures are characterized by He/Xe fractionation to varying extents. In contrast, garnets from sheared lherzolites show a contribution from the MORB component. The endmembers are indicated as black (air⁴³), gray (MORB^{28,30}), and white (fissiogenic/crustal⁴³) squares. All analytical uncertainties are 1σ . Symbols as for Fig. 6.4.

6.2.5 Geodynamic evolution for the strong metasomatized SW margin of the São Francisco Craton

The Brasília Mobile Belt resulted from the subduction of a wide oceanic lithosphere named Goiás-Pharusian Ocean, forming an oceanic island arc (*ca.* 900–800 Ma), followed by the development of a continental arc (770–630 Ma) and the continental collision of the Amazonian, São Francisco, and Paranapanema paleocontinents (640–600 Ma^{59–63}). In this context, the Southern Brasília Belt represents the suture zone between the active margin of the Paranapanema Block and the passive margin of the São Francisco Craton⁶⁰. Besides the Brasília Belt (to the west), the São Francisco Craton is surrounded by several diachronous small continental masses (terrane or microplates), like the Ribeira Belt (to the south and southeast)^{60,64,65}. However, based on the subduction geometries of these successive collages of paleocontinents involved in the Gondwana

consolidation during the Brasiliano Orogeny⁶⁴⁻⁶⁶, we rule out their involvement in the highly metasomatized cratonic lithosphere beneath Canastra-1.

After the Neoproterozoic collisional events, the SW margin of the São Francisco Craton experienced an extended period of tectonic quiescence, with minimal relative plate motion up to the early stages of Pangea fragmentation and the subsequent opening of the Atlantic Ocean, which is coeval with the emplacement age of the Canastra-1 kimberlite (*ca.* 120 Ma⁶). Therefore, an ancient subduction component is necessary to account for the radiogenic helium, MORB-like and nucleogenic neon, and fissiogenic/MORB-like xenon signatures recorded in mantle xenoliths from the SW margin of the São Francisco Craton.

During the Paleoproterozoic, the São Francisco-Congo and Kalahari paleocontinents were connected to form the core of the Central African Block⁶⁷, which is a large continental block comprised of São Francisco-Congo, Kalahari, Rio de la Plata, and Borborema-Trans-Sahara. According to paleocontinent reconstructions, there is a consensus that the São Francisco-Congo Craton was located nearby or as an isolated landmass during the formation of Columbia (Nuna) or Rodinia supercontinents^{67,68}. It is supported by the lack of collisional tectonism affecting the São Francisco Craton from late Paleoproterozoic to the formation of Gondwana in Ediacaran/Cambrian times⁶⁷. Therefore, despite the Brasiliano Orogeny during the Neoproterozoic (*ca.* 600 Ma), the only candidate to account for the extensive noble gases recycling into the cratonic lithosphere is the Minas-Bahia orogeny (2.2–1.9 Ga⁶⁹). In the context of the Alto Paranaíba Igneous Province (APIP), where the Canastra-1 mantle xenoliths crop out, Archean to Paleoproterozoic Re-depletion model ages were reported for peridotites (3.17–1.92, average 2.4 Ga¹³), corroborating the preservation of an ancient cratonic lithosphere beneath the SW margin of the São Francisco Craton. However, given the high complexity of Neoproterozoic collisional events, we cannot entirely rule out the contribution of younger slab-derived noble gas components.

Based on the model above, we conclude that the extremely radiogenic helium (³He/⁴He usually <1 R_A) and fissiogenic/MORB-like xenon (high-¹³⁶Xe/¹³²Xe) signatures coupled with MORB-like and nucleogenic neon observed in the lithospheric mantle beneath the SW margin of the São Francisco Craton provide undoubtedly evidence for the preservation of a long-lived isolated reservoir since the Archean-Paleoproterozoic. These findings reveal that the proto-kimberlite melt metasomatism (*ca.* 120 Ma) shown

by mineral chemistry and Sr-Nd isotopes of Canastra-1 mantle xenoliths⁶ minimal resembled the ancient volatile-derived metasomatism. Therefore, these samples act as a “subduction-fingerprint” of volatile transport between the surface and mantle reservoirs over geological time. Moreover, the strong radiogenic $^3\text{He}/^4\text{He}$ ratios can be an important proxy for understanding the diamond formation and preservation processes in cratonic regions. This underscores the connection between mantle metasomatism promoted by ancient subduction events and the stability of diamond-bearing lithospheric roots.

6.3 Methods

Noble gas isotopes

Mantle xenoliths were mechanically disaggregated using an agate mortar. Separated minerals with incipient alteration were handpicked and discarded using a binocular microscope. Before crushing, the selected grains were washed with dilute HNO_3 in an ultrasonic bath for 5 minutes and heated at 70 °C for 30 minutes. They were then ultrasonicated twice in deionized water and ethanol (EtOH 99.5 %), respectively, for 5 minutes in each step.

The He-Ne-Ar-Kr-Xe analyses were carried out using a sector-type mass spectrometer (modified VG5400) at the Research Center for Advanced Science and Technology, University of Tokyo. Noble gases trapped in fluid/melt inclusions of clinopyroxene, garnet, orthopyroxene, and whole-rock separates (1–2 mm in size) were extracted by stepwise crushing under ultrahigh vacuum condition followed by single-step heating measurements of their recovered rock powders.

Twenty-four samples (0.55–1.57 g) were loaded into a stainless-steel tube. The entire extraction and purification line was baked under vacuum at 200 °C for 24 h to reduce atmospheric contamination. The gases were released by four crushing steps (100, 500, 1000, and 2000 strokes) for each sample using a nickel slug driven by an external solenoid magnet coil.

To determine whether the samples contain cosmogenic and radiogenic components from crystal lattices, sample powders recovered after the crushing measurements were wrapped in aluminum foil and placed in a stainless-steel holder attached to the top of the tantalum resistively heated furnace. After baking the system and

degassing the furnace to reduce adsorbed atmospheric noble gases, the samples were heated to 1800 °C to melt and completely extract the remaining gases.

The sensitivity and mass discrimination of the mass spectrometer were calibrated by measuring HESJ standard gas with $^3\text{He}/^4\text{He} = 20.415 \pm 0.029 R_A^{70}$ and known amounts of air aliquots for other noble gases. Experimental uncertainties in the noble gas concentrations were estimated to be 5 % for helium and argon and 10 % for neon, krypton, and xenon. Analytical uncertainties on isotopic ratios are one standard deviation (1σ), including those for mass discrimination and blank corrections. Before each analysis, blanks were determined using the same procedure applied to the samples. The highest blank values for crushing were $^4\text{He} = 1.2 \times 10^{-11}$, $^{20}\text{Ne} = 2.3 \times 10^{-12}$, $^{40}\text{Ar} = 1.9 \times 10^{-9}$, $^{84}\text{Kr} = 1.7 \times 10^{-13}$, and $^{132}\text{Xe} = 1.3 \times 10^{-13}$, all in cm^3 STP. Therefore, here we assume the higher contribution of blank to our samples.

The blank contribution for ^4He in crushing experiments is low and negligible (<0.7 %, except for CAN1-94 CPX with 2.5 % in 100 strokes). For neon, samples that showed isotope ratios indistinguishable from air and high blank contribution in the crushing experiments (>10 %) were discarded. In crushing and heating experiments, neon isotope ratios were corrected for isobaric interference of $^{40}\text{Ar}^{++}$ to ^{20}Ne and CO_2^{++} to ^{22}Ne . They vary from 0.3 to 24 % and 0.8 to 69 %, respectively. Only results with isobaric interference lower than 10 % were considered.

For ^{40}Ar , the blank contribution in the crushing analyses is commonly lower than 14 % ($n = 74$ of 92), reaching up to 63 % for a 100-strokes measurement (CAN1-149 GRT). Krypton isotope ratios do not differ from the air composition with 1σ uncertainty. The blank contribution for those samples is ≤ 3 %, except for CAN1-142 GRT (71 % in 100 strokes) and CAN1-149 GRT (25 % in 1000 strokes). Thus, krypton data do not have enough analytical quality to be used. Excluding samples with xenon isotope ratios indistinguishable from air, the blank contribution is usually ≤ 10 % ($n = 69$ of 92).

Heating blanks were: $^4\text{He} < 2.5 \times 10^{-12} \text{ cm}^3$ STP, $^{20}\text{Ne} = (2.5\text{--}6.3) \times 10^{-12} \text{ cm}^3$ STP, and $^{40}\text{Ar} = (3.8\text{--}5.5) \times 10^{-9} \text{ cm}^3$ STP. They represent less than 0.004 %, 17 % (except for CAN1-142 CPX and CAN1-95 GRT), and ≤ 30 % ($n = 19$ of 21).

Data availability

Source data file (Supplementary Data) used in this study and Supplementary Information are provided with this paper.

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Supplementary Information

Evaluation of atmospheric and radiogenic contributions to the $^3\text{He}/^4\text{He}$ isotope ratios

Atmospheric contamination

Here we evaluate the extent of atmospheric contribution to the helium isotope ratios of mantle xenoliths from Canastra-1, SW edge of the São Francisco Craton. This estimation was achieved using the $^4\text{He}/^{20}\text{Ne}$ ratios measured by crushing (33–6032) and heating (3925–15142) methods (Supplementary Data 1), as well as the $^4\text{He}/^{20}\text{Ne}$ ratio of the atmospheric component (0.319^{-1}). The $^3\text{He}/^4\text{He}$ ratios and the ^4He concentrations were corrected for the atmospheric contamination by applying the equations proposed by ref. 2 (Eq. 1) and ref. 3 (Eq. 2), respectively. These estimations reveal negligible atmospheric contribution to the $^3\text{He}/^4\text{He}$ ratios of most samples analyzed by crushing ($<1\%$, most $<0.01\%$) (Supplementary Data 1). Heating experiments show similar low atmospheric contribution ($<0.01\%$).

$$\left(\frac{^3\text{He}}{^4\text{He}}\right)_c = \frac{\left(\frac{(^3\text{He}/^4\text{He})_{\text{measured}}}{1.4 \times 10^{-6}} \times (^4\text{He}/^{20}\text{Ne})_{\text{measured}}\right) - 0.318}{(^4\text{He}/^{20}\text{Ne})_{\text{measured}} - 0.318} \times 1.4 \times 10^{-6} \quad (\text{Equation 1})$$

$$[^4\text{He}]_c = [^4\text{He}]_{\text{measured}} \times \left(\frac{(^4\text{He}/^{20}\text{Ne})_{\text{measured}}}{0.318} - 1\right) / \frac{(^4\text{He}/^{20}\text{Ne})_{\text{measured}}}{0.318} \quad (\text{Equation 2})$$

Post-eruptive processes

The post-eruptive radiogenic ^4He production⁴ (Eq. 3) was calculated using the U (0.021 ppm) and Th (0.085 ppm) of the primitive mantle⁵, as well as the eruption ages of Canastra-1 host kimberlite (120 Ma⁶). The primitive mantle values were used because there are no available U-Th concentrations determined for whole-rock mantle xenoliths from Canastra-1.

Thus, we defined a radiogenic ^4He production rate from the decay of U and Th of $6.3 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$, which indicates less than 1 % for most of the samples (usually $<0.3\%$) (Supplementary Data 1), which represent negligible contribution to the $^3\text{He}/^4\text{He}$ ratios of

Patagonian mantle xenoliths. However, the radiogenic contribution in the first extraction (100 strokes) is higher, reaching up to 5 % (usually <2 %). Regarding heating experiments, the radiogenic contribution is less than 0.01 %.

$$^4\text{He}^* = U \times [8 \times (e^{\lambda_{238}t} - 1) + (1/137.88) \times (e^{\lambda_{235}t} - 1) + 6 \times \kappa \times (e^{\lambda_{232}t} - 1)] \text{ (Equation 3)}$$

Where U is the whole-rock concentration (in ppm); λ_{238} , λ_{235} and λ_{232} are the decay constants for ^{238}U , ^{235}U and ^{232}Th (1.55×10^{-10} , 9.85×10^{-10} and 4.95×10^{-11} , respectively); 1/137.88 is the present canonical ratio of $^{235}\text{U}/^{238}\text{U}$; and κ is Th/U ratio of the whole-rock sample.

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Supplementary Data 1. He-Ne-Ar isotopic data for Canastra-1 mantle xenoliths.

Samples	Lithology	Weight (g)	[⁴ He] × 10 ⁻⁸ ccSTP/g	[⁴ He] × 10 ⁻⁸ ccSTP/g	[²⁰ Ne] × 10 ⁻⁸ ccSTP/g	[⁴⁰ Ar] × 10 ⁻⁸ ccSTP/g	³ He/ ⁴ He (R/R _A)			²⁰ Ne/ ²² Ne			²¹ Ne/ ²² Ne			⁴⁰ Ar/ ³⁶ Ar			Radiogenic contribution (%) in ³ He/ ⁴ He ratios	Atmospheric contribution (%) in ³ He/ ⁴ He ratios
CAN1-94 CPX 100x	Clinopyroxenite	1.15	0.04	0.039	0.0011	1.377	2.35	±	0.16	9.704	±	0.090	0.3562	±	0.004	303.50	±	0.64	1.596	0.852
CAN1-94 CPX 500x	Clinopyroxenite	1.15	0.14	0.137	0.0042	0.148	0.67	±	0.05	9.238	±	0.075	0.0286	±	0.000	312.01	±	0.59	0.454	0.961
CAN1-94 CPX 1000x	Clinopyroxenite	1.15	0.90	0.901	0.0049	17.324	0.57	±	0.01	9.695	±	0.078	0.0296	±	0.000	315.09	±	0.70	0.070	0.172
CAN1-94 CPX 2000x	Clinopyroxenite	1.15	1.19	1.194	0.0026	5.574	0.49	±	0.01	9.703	±	0.089	0.0299	±	0.001	329.72	±	0.80	0.053	0.068
Total crushing	Clinopyroxenite		2.27				0.57	±	0.01											
CAN1-94 CPX_Heating	Clinopyroxenite	0.54	49.89	49.887	0.0092	24.648	0.22	±	0.00	9.862	±	0.092	0.0338	±	0.000	789.13	±	1.60	0.001	0.006
CAN1-126 CPX 100x	Clinopyroxenite	1.21	0.16	0.157	0.0007	2.806	0.88	±	0.05	9.567	±	0.105	0.0291	±	0.001	312.85	±	0.74	0.399	0.136
CAN1-126 CPX 500x	Clinopyroxenite	1.21	0.59	0.592	0.0018	3.879	0.62	±	0.02	9.624	±	0.091	0.0293	±	0.001	321.67	±	0.64	0.106	0.096
CAN1-126 CPX 1000x	Clinopyroxenite	1.21	1.15	1.146	0.0019	4.032	0.53	±	0.01	9.548	±	0.081	0.0295	±	0.001	325.79	±	0.77	0.055	0.054
CAN1-126 CPX 2000x	Clinopyroxenite	1.21	1.16	1.156	0.0020	5.654	0.48	±	0.01	9.667	±	0.093	0.0295	±	0.001	331.90	±	0.57	0.054	0.055
Total crushing	Clinopyroxenite		3.05				0.55	±	0.01											
CAN1-126 CPX_Heating	Clinopyroxenite	0.59	65.62	65.622	0.0088	15.653	0.19	±	0.00	10.012	±	0.093	0.0343	±	0.001	843.17	±	1.46	0.001	0.004
CAN1-142 CPX 100x	Clinopyroxenite	1.20	0.04	0.042	0.0001	0.131	2.21	±	0.12	9.563	±	0.172	0.0298	±	0.002	370.33	±	0.90	1.494	0.066
CAN1-142 CPX 500x	Clinopyroxenite	1.20	0.35	0.348	0.0006	0.651	0.59	±	0.03	9.540	±	0.145	0.0305	±	0.001	412.46	±	0.84	0.181	0.055
CAN1-142 CPX 1000x	Clinopyroxenite	1.20	0.54	0.540	0.0005	0.919	0.46	±	0.02	9.983	±	0.145	0.0311	±	0.001	434.82	±	0.86	0.116	0.031
CAN1-142 CPX 2000x	Clinopyroxenite	1.20	0.62	0.616	0.0005	0.914	0.47	±	0.02	9.879	±	0.148	0.0307	±	0.002	475.70	±	0.80	0.102	0.025
Total crushing	Clinopyroxenite		1.55				0.54	±	0.01											
CAN1-142 CPX_Heating	Clinopyroxenite	0.64	37.39	37.389	0.0030	15.805	0.18	±	0.00	10.138	±	0.112	0.0410	±	0.001	1244.29	±	2.56	0.002	0.003
CAN1-149 CPX 100x	Clinopyroxenite	1.08	0.16	0.165	0.0004	0.539	7.39	±	0.06	10.057	±	0.217	0.0310	±	0.001	366.82	±	0.68	0.381	0.078
CAN1-149 CPX 500x	Clinopyroxenite	1.08	0.77	0.770	0.0017	2.133	0.40	±	0.02	9.775	±	0.093	0.0297	±	0.001	375.02	±	0.59	0.082	0.072
CAN1-149 CPX 1000x	Clinopyroxenite	1.08	1.03	1.025	0.0019	2.469	0.33	±	0.01	9.686	±	0.117	0.0299	±	0.001	396.11	±	0.95	0.061	0.058
CAN1-149 CPX 2000x	Clinopyroxenite	1.08	1.24	1.236	0.0015	2.256	0.45	±	0.01	9.922	±	0.113	0.0304	±	0.001	448.25	±	0.73	0.051	0.038
Total crushing	Clinopyroxenite		3.03				0.39	±	0.02											
CAN1-149 CPX_Heating	Clinopyroxenite	0.56	69.47	69.467	0.0059	41.517	0.12	±	0.00	9.733	±	0.093	0.0359	±	0.001	381.19	±	1.67	0.001	0.003
CAN1-174 CPX 100x	Clinopyroxenite	1.24	0.10	0.098	0.0001	0.328	1.09	±	0.07	10.172	±	0.180	0.0308	±	0.001	396.82	±	1.05	0.641	0.029
CAN1-174 CPX 500x	Clinopyroxenite	1.24	0.55	0.547	0.0005	1.592	0.48	±	0.02	9.838	±	0.136	0.0302	±	0.001	380.64	±	0.74	0.115	0.031
CAN1-174 CPX 1000x	Clinopyroxenite	1.24	1.26	1.255	0.0010	3.321	0.48	±	0.01	9.952	±	0.144	0.0306	±	0.001	390.05	±	0.76	0.050	0.027
CAN1-174 CPX 2000x	Clinopyroxenite	1.24	1.66	1.657	0.0009	3.012	0.46	±	0.01	9.973	±	0.111	0.0318	±	0.001	453.68	±	0.81	0.038	0.018
Total crushing	Clinopyroxenite		3.56				0.49	±	0.01											
CAN1-174 CPX_Heating	Clinopyroxenite	0.59	71.98	71.981	0.0057	33.251	0.15	±	0.00	10.149	±	0.079	0.0383	±	0.001	811.56	±	1.29	0.001	0.003
CAN1-94 GRT 100x	Clinopyroxenite	1.28	0.03	0.026	0.0001	0.339	2.94	±	0.24	9.500	±	0.286	0.0301	±	0.002	310.18	±	0.57	2.398	0.166

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Samples	Lithology	Weight (g)	⁴ He] × 10 ⁻⁸ ccSTP/g	⁴ He] × 10 ⁻⁸ ccSTP/g	²⁰ Ne] × 10 ⁻⁸ ccSTP/g	⁴⁰ Ar] × 10 ⁻⁸ ccSTP/g	³ He/ ⁴ He (R/R _A)			²⁰ Ne/ ²² Ne			²¹ Ne/ ²² Ne			⁴⁰ Ar/ ³⁶ Ar			Radiogenic contribution (%) in ³ He/ ⁴ He ratios	Atmospheric contribution (%) in ³ He/ ⁴ He ratios
CAN1-94 GRT 500x	Clinopyroxenite	1.28	0.15	0.151	0.0005	0.629	0.89	±	0.05	9.783	±	0.179	0.0298	±	0.001	341.48	±	0.72	0.414	0.108
CAN1-94 GRT 1000x	Clinopyroxenite	1.28	0.37	0.374	0.0013	1.836	0.72	±	0.02	9.692	±	0.113	0.0286	±	0.001	352.40	±	0.68	0.168	0.113
CAN1-94 GRT 2000x	Clinopyroxenite	1.28	1.78	1.782	0.0035	4.416	0.41	±	0.01	9.722	±	0.105	0.0294	±	0.001	371.35	±	0.86	0.035	0.063
Total crushing	Clinopyroxenite		2.34				0.52	±	0.02											
CAN1-94 GRT_Heating	Clinopyroxenite	0.53	58.00	57.993	0.0148	88.866	0.02	±	0.00	9.739	±	0.076	0.0328	±	0.001	831.97	±	1.48	0.001	0.008
CAN1-126 GRT 100x	Clinopyroxenite	1.24	0.05	0.049	0.0000	0.099	1.84	±	0.12	10.178	±	0.300	0.0336	±	0.003	450.90	±	0.92	1.275	0.030
CAN1-126 GRT 500x	Clinopyroxenite	1.24	0.32	0.319	0.0003	0.787	0.92	±	0.03	9.703	±	0.115	0.0298	±	0.001	515.81	±	1.11	0.197	0.028
CAN1-126 GRT 1000x	Clinopyroxenite	1.24	0.60	0.596	0.0005	1.499	0.69	±	0.02	9.722	±	0.136	0.0301	±	0.001	596.17	±	1.39	0.105	0.027
CAN1-126 GRT 2000x	Clinopyroxenite	1.24	1.02	1.020	0.0013	2.834	0.46	±	0.01	9.794	±	0.130	0.0299	±	0.001	747.08	±	1.60	0.062	0.039
Total crushing	Clinopyroxenite		1.98				0.64	±	0.01											
CAN1-126 GRT_Heating	Clinopyroxenite	0.63	37.98	37.974	0.0049	68.385	0.21	±	0.00	9.687	±	0.090	0.0375	±	0.001	1286.40	±	1.90	0.002	0.004
CAN1-142 GRT 100x	Clinopyroxenite	1.26	0.03	0.035	0.0000	0.076	2.45	±	0.17	9.830	±	0.505	0.0319	±	0.000	603.53	±	1.49	1.796	0.016
CAN1-142 GRT 500x	Clinopyroxenite	1.26	0.21	0.206	0.0002	0.450	0.72	±	0.03	10.019	±	0.076	0.0308	±	0.001	710.78	±	1.35	0.305	0.027
CAN1-142 GRT 1000x	Clinopyroxenite	1.26	0.49	0.489	0.0003	1.345	0.54	±	0.02	9.789	±	0.240	0.0306	±	0.001	952.60	±	1.81	0.128	0.021
CAN1-142 GRT 2000x	Clinopyroxenite	1.26	0.53	0.534	0.0004	2.180	0.49	±	0.02	9.726	±	0.224	0.0303	±	0.001	1249.69	±	3.23	0.118	0.023
Total crushing	Clinopyroxenite		1.26				0.60	±	0.01											
CAN1-142 GRT_Heating	Clinopyroxenite	0.52	79.35	79.344	0.0056	57.587	0.14	±	0.00	9.638	±	0.096	0.0360	±	0.001	951.37	±	1.55	0.001	0.002
CAN1-149 GRT 100x	Clinopyroxenite	1.30	0.04	0.037	0.0000	0.072	2.26	±	0.13	9.220	±	0.510	0.0278	±	0.002	541.63	±	1.49	1.688	0.022
CAN1-149 GRT 500x	Clinopyroxenite	1.30	0.15	0.145	0.0001	0.627	1.27	±	0.07	10.022	±	0.199	0.0304	±	0.002	574.63	±	1.52	0.432	0.028
CAN1-149 GRT 1000x	Clinopyroxenite	1.30	0.16	0.159	0.0002	0.517	1.01	±	0.04	9.829	±	0.213	0.0312	±	0.002	712.54	±	1.65	0.394	0.031
CAN1-149 GRT 2000x	Clinopyroxenite	1.30	0.45	0.450	0.0004	1.830	0.73	±	0.02	9.782	±	0.204	0.0307	±	0.001	915.70	±	2.12	0.140	0.030
Total crushing	Clinopyroxenite		0.79				0.96	±	0.01											
CAN1-149 GRT_Heating	Clinopyroxenite	0.56	75.49	75.487	0.0151	88.718	0.22	±	0.00	9.745	±	0.079	0.0316	±	0.000	584.09	±	0.86	0.001	0.006
CAN1-174 GRT 100x	Clinopyroxenite	1.35	0.10	0.100	0.0001	0.338	1.47	±	0.05	9.294	±	0.204	0.0291	±	0.002	445.87	±	1.08	0.627	0.037
CAN1-174 GRT 500x	Clinopyroxenite	1.35	0.50	0.498	0.0005	1.692	0.79	±	0.02	9.574	±	0.137	0.0299	±	0.001	512.34	±	1.20	0.126	0.032
CAN1-174 GRT 1000x	Clinopyroxenite	1.35	1.01	1.014	0.0019	2.404	0.61	±	0.01	9.636	±	0.104	0.0295	±	0.001	500.55	±	0.81	0.062	0.061
CAN1-174 GRT 2000x	Clinopyroxenite	1.35	2.18	2.180	0.0015	3.961	0.38	±	0.01	9.791	±	0.093	0.0300	±	0.001	765.65	±	1.41	0.029	0.021
Total crushing	Clinopyroxenite		3.79				0.53	±	0.03											
CAN1-96 CPX 100x	Sheared lherzolite	1.27	0.08	0.082	0.0001	0.143	1.39	±	0.06	9.72	±	0.17	0.03	±	0.00	422.07	±	0.90	0.765	0.034
CAN1-96 CPX 500x	Sheared lherzolite	1.27	1.02	1.018	0.0007	1.122	0.56	±	0.01	9.90	±	0.16	0.03	±	0.00	463.55	±	0.92	0.062	0.022
CAN1-96 CPX 1000x	Sheared lherzolite	1.27	2.50	2.504	0.0014	2.090	0.52	±	0.01	9.93	±	0.09	0.03	±	0.00	492.02	±	1.27	0.025	0.018
CAN1-96 CPX 2000x	Sheared lherzolite	1.27	3.12	3.119	0.0017	3.216	0.49	±	0.01	9.95	±	0.11	0.03	±	0.00	484.81	±	1.10	0.020	0.018

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Samples	Lithology	Weight (g)	[⁴ He] × 10 ⁻⁸ ccSTP/g	[⁴ He] × 10 ⁻⁸ ccSTP/g	[²⁰ Ne] × 10 ⁻⁸ ccSTP/g	[⁴⁰ Ar] × 10 ⁻⁸ ccSTP/g	³ He/ ⁴ He (R/R _A)			²⁰ Ne/ ²² Ne			²¹ Ne/ ²² Ne			⁴⁰ Ar/ ³⁶ Ar			Radiogenic contribution (%) in ³ He/ ⁴ He ratios	Atmospheric contribution (%) in ³ He/ ⁴ He ratios
Total crushing	Sheared lherzolite		6.72				0.52	±	0.02											
CAN1-96 CPX_Heating	Sheared lherzolite	0.57	59.39	59.389	0.0103	57.419	0.13	±	0.00	10.11	±	0.09	0.04	±	0.00	1093.22	±	1.43	0.001	0.006
CAN1-89 CPX 100x	Sheared lherzolite	1.40	0.21	0.215	0.0002	0.388	0.55	±	0.03	9.49	±	0.20	0.03	±	0.00	348.12	±	0.67	0.293	0.034
CAN1-89 CPX 500x	Sheared lherzolite	1.40	0.92	0.916	0.0007	1.242	0.37	±	0.01	9.85	±	0.12	0.03	±	0.00	368.31	±	0.70	0.069	0.026
CAN1-89 CPX 1000x	Sheared lherzolite	1.40	2.32	2.316	0.0015	2.190	0.30	±	0.01	9.83	±	0.07	0.03	±	0.00	386.74	±	0.85	0.027	0.021
CAN1-89 CPX 2000x	Sheared lherzolite	1.40	2.91	2.907	0.0015	2.558	0.29	±	0.00	9.85	±	0.10	0.03	±	0.00	412.08	±	1.07	0.022	0.017
Total crushing	Sheared lherzolite		6.36				0.32	±	0.06											
CAN1-89 CPX_Heating	Sheared lherzolite	0.48	68.71	68.713	0.0063	59.101	0.11	±	0.01	10.27	±	0.10	0.04	±	0.00	1190.26	±	3.16	0.001	0.003
CAN1-88 WR 100x	Sheared lherzolite	1.44	0.27	0.271	0.0002	0.194	1.66	±	0.11	9.62	±	0.14	0.03	±	0.00	336.54	±	0.69	0.231	0.021
CAN1-88 WR 500x	Sheared lherzolite	1.44	0.33	0.333	0.0007	1.375	0.59	±	0.02	9.81	±	0.11	0.03	±	0.00	340.20	±	0.71	0.188	0.071
CAN1-88 WR 1000x	Sheared lherzolite	1.44	1.19	1.194	0.0015	2.388	0.38	±	0.01	9.79	±	0.10	0.03	±	0.00	369.95	±	0.68	0.053	0.041
CAN1-88 WR 2000x	Sheared lherzolite	1.44	2.01	2.005	0.0015	3.784	0.38	±	0.01	9.85	±	0.08	0.03	±	0.00	415.26	±	0.87	0.031	0.024
Total crushing	Sheared lherzolite		3.80				0.49	±	0.03											
CAN1-88 WR_Heating	Sheared lherzolite	0.49	98.82	98.815	0.0065	68.584	0.11	±	0.00	9.92	±	0.08	0.04	±	0.00	816.61	±	1.17	0.001	0.002
CAN1-88 GRT 100x	Sheared lherzolite	1.05	0.08	0.085	0.0003	0.827	9.77	±	0.59	9.71	±	0.16	0.03	±	0.00	317.93	±	0.77	0.741	0.118
CAN1-88 GRT 500x	Sheared lherzolite	1.05	0.09	0.088	0.0024	3.848	3.21	±	0.15	9.67	±	0.09	0.03	±	0.00	320.98	±	0.64	0.708	0.865
CAN1-88 GRT 1000x	Sheared lherzolite	1.05	0.34	0.339	0.0040	7.731	2.20	±	0.05	9.66	±	0.08	0.03	±	0.00	331.22	±	0.64	0.185	0.378
CAN1-88 GRT 2000x	Sheared lherzolite	1.05	0.69	0.691	0.0052	11.948	2.20	±	0.03	9.65	±	0.08	0.03	±	0.00	352.36	±	0.72	0.091	0.237
Total crushing	Sheared lherzolite		1.12				2.28	±	0.05											
CAN1-88 GRT_Heating	Sheared lherzolite	0.55	96.15	96.145	0.0084	80.808	0.17	±	0.00	9.80	±	0.08	0.04	±	0.00	1130.36	±	1.74	0.001	0.003
CAN1-89 GRT 100x	Sheared lherzolite	0.90	0.04	0.037	0.0003	0.542	5.25	±	0.29	9.73	±	0.27	0.03	±	0.00	342.17	±	0.95	1.676	0.249
CAN1-89 GRT 500x	Sheared lherzolite	0.90	0.11	0.114	0.0009	1.656	4.13	±	0.14	9.69	±	0.15	0.03	±	0.00	348.97	±	0.92	0.550	0.240
CAN1-89 GRT 1000x	Sheared lherzolite	0.90	0.27	0.270	0.0014	2.980	3.79	±	0.09	9.76	±	0.12	0.03	±	0.00	373.32	±	0.85	0.232	0.166
CAN1-89 GRT 2000x	Sheared lherzolite	0.90	0.42	0.424	0.0014	3.376	3.59	±	0.05	9.87	±	0.14	0.03	±	0.00	428.53	±	0.90	0.148	0.106
Total crushing	Sheared lherzolite		0.85				3.80	±	0.06											
CAN1-89 GRT_Heating	Sheared lherzolite	0.54	61.63	61.625	0.0062	43.278	0.25	±	0.00	9.72	±	0.09	0.04	±	0.00	720.49	±	1.33	0.001	0.003
CAN1-96 GRT 100x	Sheared lherzolite	1.23	0.02	0.017	0.0003	0.662	9.57	±	0.45	9.52	±	0.17	0.03	±	0.00	321.11	±	0.60	3.652	0.599
CAN1-96 GRT 500x	Sheared lherzolite	1.23	0.15	0.148	0.0019	2.834	4.15	±	0.10	9.71	±	0.10	0.03	±	0.00	327.16	±	0.67	0.423	0.415
CAN1-96 GRT 1000x	Sheared lherzolite	1.23	0.20	0.198	0.0023	4.016	4.72	±	0.07	9.70	±	0.08	0.03	±	0.00	341.23	±	0.61	0.316	0.373
CAN1-96 GRT 2000x	Sheared lherzolite	1.23	0.29	0.294	0.0026	5.162	4.49	±	0.07	9.68	±	0.09	0.03	±	0.00	362.97	±	1.14	0.213	0.279
Total crushing	Sheared lherzolite		0.64				4.48	±	0.07											
CAN1-96 GRT_Heating	Sheared lherzolite	0.54	58.40	58.395	0.0098	47.434	0.27	±	0.00	9.71	±	0.10	0.03	±	0.00	671.33	±	1.02	0.001	0.005

UnB IG PPG Geologia																				
Samples	Lithology	Weight (g)	$[^4\text{He}] \times 10^{-8}$ ccSTP/g	$[^4\text{He}] \times 10^{-8}$ ccSTP/g	$[^{20}\text{Ne}] \times 10^{-8}$ ccSTP/g	$[^{40}\text{Ar}] \times 10^{-8}$ ccSTP/g	$^3\text{He}/^4\text{He}$ (R/R _A)			$^{20}\text{Ne}/^{22}\text{Ne}$			$^{21}\text{Ne}/^{22}\text{Ne}$			$^{40}\text{Ar}/^{36}\text{Ar}$			Radiogenic contribution (%) in $^3\text{He}/^4\text{He}$ ratios	Atmospheric contribution (%) in $^3\text{He}/^4\text{He}$ ratios
CAN1-96 OPX 100x	Sheared lherzolite	1.08	0.17	0.166	0.0001	0.461	1.07	±	0.04	9.87	±	0.24	0.03	±	0.00	363.46	±	0.88	0.378	0.021
CAN1-96 OPX 500x	Sheared lherzolite	1.08	1.07	1.066	0.0007	2.130	0.68	±	0.01	9.90	±	0.16	0.03	±	0.00	376.43	±	0.87	0.059	0.021
CAN1-96 OPX 1000x	Sheared lherzolite	1.08	1.95	1.952	0.0008	1.025	0.65	±	0.01	9.81	±	0.07	0.03	±	0.00	512.78	±	0.77	0.032	0.013
CAN1-96 OPX 2000x	Sheared lherzolite	1.08	1.76	1.755	0.0016	2.944	0.56	±	0.01	9.60	±	0.13	0.03	±	0.00	538.96	±	0.89	0.036	0.029
Total crushing	Sheared lherzolite		4.94				0.64	±	0.02											
CAN1-182 CPX 100x	Websterite	1.22	0.01	0.014	0.0001	0.081	6.12	±	0.37	9.59	±	0.18	0.03	±	0.00	405.66	±	1.90	4.553	0.141
CAN1-182 CPX 500x	Websterite	1.22	0.17	0.174	0.0006	0.891	1.13	±	0.05	9.87	±	0.13	0.03	±	0.00	396.90	±	1.09	0.361	0.110
CAN1-182 CPX 1000x	Websterite	1.22	0.58	0.583	0.0011	2.996	0.80	±	0.02	10.00	±	0.17	0.03	±	0.00	483.03	±	0.90	0.108	0.062
CAN1-182 CPX 2000x	Websterite	1.22	2.11	2.108	0.0031	2.733	0.73	±	0.01	10.00	±	0.10	0.03	±	0.00	492.06	±	0.85	0.030	0.047
Total crushing	Websterite		2.87				0.77	±	0.02											
CAN1-182 CPX_Heating	Websterite	0.51	67.47	67.472	0.0068	50.114	0.10	±	0.10	10.51	±	0.12	0.04	±	0.00	1367.78	±	2.39	0.001	0.003
CAN1-182 GRT 100x	Websterite	1.36	0.04	0.042	0.0000	0.097	2.29	±	0.13	9.85	±	0.29	0.03	±	0.00	560.60	±	1.11	1.489	0.026
CAN1-182 GRT 500x	Websterite	1.36	0.27	0.273	0.0002	1.202	0.84	±	0.03	9.90	±	0.16	0.03	±	0.00	564.25	±	1.13	0.230	0.025
CAN1-182 GRT 1000x	Websterite	1.36	0.70	0.699	0.0005	1.412	0.68	±	0.02	10.01	±	0.18	0.03	±	0.00	648.59	±	1.92	0.090	0.023
CAN1-182 GRT 2000x	Websterite	1.36	1.46	1.461	0.0009	1.431	0.59	±	0.01	10.01	±	0.10	0.03	±	0.00	698.20	±	1.46	0.043	0.019
CAN1-182 GRT_Heating	Websterite	0.51	61.29	61.286	0.0077	78.700	0.12	±	0.00	10.14	±	0.08	0.04	±	0.00	2421.31	±	7.01	0.001	0.004
Total crushing	Websterite		2.47				0.67	±	0.01											
CAN1-206 CPX 100x	Eclogite	0.55	0.34	0.344	0.0006	0.606	0.56	±	0.03	9.85	±	0.15	0.03	±	0.00	530.92	±	1.21	0.183	0.057
CAN1-206 CPX 500x	Eclogite	0.55	1.90	1.904	0.0025	2.779	0.17	±	0.01	9.82	±	0.14	0.03	±	0.00	616.37	±	1.11	0.033	0.042
CAN1-206 CPX 1000x	Eclogite	0.55	1.64	1.643	0.0017	2.444	0.18	±	0.01	9.83	±	0.11	0.03	±	0.00	558.60	±	1.33	0.038	0.034
CAN1-206 CPX 2000x	Eclogite	0.55	1.79	1.791	0.0017	2.572	0.17	±	0.01	9.90	±	0.13	0.03	±	0.00	523.19	±	1.15	0.035	0.030
Total crushing	Eclogite		5.68				0.19	±	0.03											
CAN1-206 CPX_Heating	Eclogite	0.52	41.41	41.407	0.0073	21.394	0.04	±	0.00	9.66	±	0.08	0.04	±	0.00	492.47	±	0.97	0.002	0.006
CAN1-206 GRT 100x	Eclogite	1.57	0.09	0.091	0.0002	0.368	1.80	±	0.08	9.96	±	0.25	0.03	±	0.00	637.48	±	1.17	0.692	0.064
CAN1-206 GRT 500x	Eclogite	1.57	0.44	0.440	0.0001	1.712	1.19	±	0.02	9.50	±	0.44	0.03	±	0.00	762.97	±	1.52	0.143	0.005
CAN1-206 GRT 1000x	Eclogite	1.57	0.62	0.616	0.0006	1.662	1.24	±	0.02	9.91	±	0.13	0.03	±	0.00	826.02	±	1.87	0.102	0.033
CAN1-206 GRT 2000x	Eclogite	1.57	0.97	0.973	0.0008	3.161	1.09	±	0.01	10.17	±	0.12	0.03	±	0.00	921.46	±	1.89	0.065	0.027
CAN1-206 GRT_Heating	Eclogite	0.58	55.92	55.916	0.0065	54.937	0.13	±	0.00	9.91	±	0.09	0.04	±	0.00	1814.92	±	3.99	0.001	0.004
Total crushing	Eclogite		2.12				1.19	±	0.05											
CAN1-95 CPX 100x	Pargasite websterite	1.12	0.31	0.309	0.0001	0.408	0.46	±	0.02	9.85	±	0.18	0.03	±	0.00	857.63	±	2.43	0.203	0.015
CAN1-95 CPX 500x	Pargasite websterite	1.12	3.05	3.052	0.0011	2.410	0.26	±	0.01	9.82	±	0.14	0.03	±	0.00	814.00	±	1.41	0.021	0.012
CAN1-95 CPX 1000x	Pargasite websterite	1.12	3.45	3.454	0.0012	2.621	0.24	±	0.01	9.74	±	0.11	0.03	±	0.00	1002.88	±	3.36	0.018	0.011

UnB IG PPG Geologia																			Radiogenic contribution (%) in ³ He/ ⁴ He ratios	Atmospheric contribution (%) in ³ He/ ⁴ He ratios
Samples	Lithology	Weight (g)	[⁴ He] × 10 ⁻⁸ ccSTP/g	[⁴ He] × 10 ⁻⁸ ccSTP/g	[²⁰ Ne] × 10 ⁻⁸ ccSTP/g	[⁴⁰ Ar] × 10 ⁻⁸ ccSTP/g	³ He/ ⁴ He (R/R _A)			²⁰ Ne/ ²² Ne			²¹ Ne/ ²² Ne			⁴⁰ Ar/ ³⁶ Ar				
CAN1-95 CPX 2000x	Pargasite websterite	1.12	3.79	3.788	0.0010	3.203	0.24	±	0.00	9.82	±	0.09	0.03	±	0.00	1211.11	±	3.16	0.017	0.008
Total crushing	Pargasite websterite		10.60				0.25	±	0.08											
CAN1-95 CPX_Heating	Pargasite websterite	0.60	51.69	51.687	0.0037	160.315	0.38	±	0.00	9.78	±	0.12	0.05	±	0.00	8464.46	±	128.17	0.001	0.002
CAN1-95 GRT 100x	Pargasite websterite	1.07	0.09	0.091	0.0001	0.128	1.71	±	0.08	9.05	±	0.15	0.03	±	0.00	551.50	±	1.31	0.686	0.018
CAN1-95 GRT 500x	Pargasite websterite	1.07	0.80	0.799	0.0002	0.854	0.51	±	0.02	9.58	±	0.31	0.03	±	0.00	821.41	±	2.39	0.079	0.010
CAN1-95 GRT 1000x	Pargasite websterite	1.07	0.72	0.717	0.0002	0.957	0.65	±	0.02	9.78	±	0.28	0.03	±	0.00	920.08	±	1.68	0.088	0.009
CAN1-95 GRT 2000x	Pargasite websterite	1.07	0.78	0.775	0.0003	1.368	0.66	±	0.02	9.52	±	0.18	0.03	±	0.00	1073.64	±	2.67	0.081	0.013
Total crushing	Pargasite websterite		2.38				0.65	±	0.01											
CAN1-95 GRT_Heating	Pargasite websterite	0.51	12.66	12.658	0.0012	24.053	0.689	±	0.008	9.02	±	0.07	0.04	±	0.00	2579.06	±	11.55	0.005	0.003
CAN1-95 AMP 100x	Pargasite websterite	0.84	0.58	0.572	0.0150	97.211	0.39	±	0.02	9.68	±	0.08	0.03	±	0.00	294.64	±	0.69	0.109	0.826
CAN1-95 AMP 500x	Pargasite websterite	0.84	0.07	0.070	0.0005	3.626	0.17	±	0.01	9.40	±	0.16	0.04	±	0.00	596.22	±	1.38	0.897	0.212
CAN1-95 AMP 1000x	Pargasite websterite	0.84	0.07	0.066	0.0009	15.831	0.21	±	0.01	10.37	±	0.08	0.03	±	0.00	354.64	±	0.94	0.943	0.419
CAN1-95 AMP 2000x	Pargasite websterite	0.84	0.07	0.066	0.0005	79.429	0.21	±	0.01	9.35	±	0.23	0.04	±	0.00	305.36	±	0.89	0.944	0.254
Total crushing	Pargasite websterite		1.18				0.34	±	0.00											
CAN1-95 AMP_Heating	Pargasite websterite	0.66	71.44	71.442	0.0051	647.867	0.30	±	0.00	9.47	±	0.10	0.06	±	0.00	12484	±	1373	0.001	0.002

Supplementary Data 1. Kr-Xe isotopic data for Canastra-1 mantle xenoliths.

Samples	Lithology	[⁸⁴ Kr] ccSTP/g	[¹³² Xe] ccSTP/g	⁸² Kr/ ⁸⁴ Kr		⁸⁶ Kr/ ⁸⁴ Kr		¹²⁹ Xe/ ¹³⁰ Xe		¹³⁶ Xe/ ¹³⁰ Xe		¹²⁹ Xe/ ¹³² Xe		¹³⁶ Xe/ ¹³² Xe			
CAN1-94 CPX 100x	Clinopyroxenite	2.0E-12	3.9E-13	0.202	± 0.005	0.305	± 0.005	6.858	± 0.351	2.591	± 0.161	1.001	± 0.033	0.375	± 0.020		
CAN1-94 CPX 500x	Clinopyroxenite	3.0E-13	3.1E-15	0.203	± 0.006	0.308	± 0.009	6.522	± 0.564	2.179	± 0.464	0.940	± 0.123	0.299	± 0.052		
CAN1-94 CPX 1000x	Clinopyroxenite	1.9E-11	1.3E-12	0.200	± 0.002	0.304	± 0.002	6.608	± 0.094	2.179	± 0.072	1.052	± 0.013	0.375	± 0.011		
CAN1-94 CPX 2000x	Clinopyroxenite	1.4E-11	1.2E-12	0.201	± 0.002	0.305	± 0.003	6.663	± 0.134	2.390	± 0.072	1.008	± 0.019	0.358	± 0.007		
CAN1-126 CPX 100x	Clinopyroxenite	5.4E-12	3.7E-13	0.205	± 0.002	0.304	± 0.003	6.532	± 0.159	2.305	± 0.086	1.006	± 0.023	0.348	± 0.012		
CAN1-126 CPX 500x	Clinopyroxenite	1.0E-11	7.6E-13	0.205	± 0.002	0.302	± 0.003	6.512	± 0.113	2.317	± 0.072	1.001	± 0.020	0.353	± 0.010		
CAN1-126 CPX 1000x	Clinopyroxenite	1.5E-11	1.2E-12	0.204	± 0.002	0.305	± 0.003	6.623	± 0.162	2.317	± 0.071	1.018	± 0.019	0.358	± 0.013		
CAN1-126 CPX 2000x	Clinopyroxenite	1.4E-11	9.1E-13	0.204	± 0.002	0.304	± 0.002	6.530	± 0.093	2.350	± 0.071	1.010	± 0.016	0.359	± 0.010		
CAN1-142 CPX 100x	Clinopyroxenite	2.2E-13	3.0E-14	0.200	± 0.006	0.299	± 0.010	6.457	± 0.430	2.269	± 0.196	0.975	± 0.062	0.340	± 0.039		
CAN1-142 CPX 500x	Clinopyroxenite	1.1E-12	1.7E-13	0.204	± 0.003	0.307	± 0.006	6.535	± 0.235	2.375	± 0.131	1.003	± 0.034	0.362	± 0.014		
CAN1-142 CPX 1000x	Clinopyroxenite	1.5E-12	2.2E-13	0.202	± 0.003	0.296	± 0.004	6.653	± 0.228	2.375	± 0.166	1.042	± 0.013	0.356	± 0.017		
CAN1-142 CPX 2000x	Clinopyroxenite	1.4E-12	2.3E-13	0.204	± 0.004	0.300	± 0.004	6.575	± 0.170	2.355	± 0.166	1.008	± 0.030	0.360	± 0.023		
CAN1-149 CPX 100x	Clinopyroxenite	9.2E-13	9.6E-14	0.202	± 0.003	0.295	± 0.005	6.622	± 0.262	2.469	± 0.229	1.001	± 0.029	0.366	± 0.030		

Samples	Lithology	[⁸⁴ Kr] ccSTP/g	[¹³² Xe] ccSTP/g	⁸² Kr/ ⁸⁴ Kr		⁸⁶ Kr/ ⁸⁴ Kr		¹²⁹ Xe/ ¹³⁰ Xe		¹³⁶ Xe/ ¹³⁰ Xe		¹²⁹ Xe/ ¹³² Xe		¹³⁶ Xe/ ¹³² Xe		
CAN1-149 CPX 500x	Clinopyroxenite	3.4E-12	3.6E-13	0.201	± 0.003	0.299	± 0.003	6.664	± 0.229	2.362	± 0.113	1.011	± 0.030	0.356	± 0.017	
CAN1-149 CPX 1000x	Clinopyroxenite	4.1E-12	4.2E-13	0.202	± 0.002	0.299	± 0.003	6.646	± 0.117	2.362	± 0.099	1.009	± 0.023	0.351	± 0.013	
CAN1-149 CPX 2000x	Clinopyroxenite	3.4E-12	3.9E-13	0.201	± 0.003	0.301	± 0.003	6.698	± 0.140	2.399	± 0.099	1.019	± 0.024	0.364	± 0.016	
CAN1-174 CPX 100x	Clinopyroxenite	6.6E-13	6.0E-14	0.202	± 0.007	0.299	± 0.006	6.586	± 0.335	2.326	± 0.118	0.988	± 0.039	0.345	± 0.019	
CAN1-174 CPX 500x	Clinopyroxenite	1.7E-12	2.9E-13	0.199	± 0.002	0.301	± 0.006	6.407	± 0.300	2.333	± 0.045	0.985	± 0.025	0.353	± 0.009	
CAN1-174 CPX 1000x	Clinopyroxenite	8.8E-12	7.6E-13	0.202	± 0.002	0.300	± 0.003	6.588	± 0.094	2.333	± 0.079	0.981	± 0.017	0.347	± 0.015	
CAN1-174 CPX 2000x	Clinopyroxenite	7.6E-12	7.3E-13	0.201	± 0.002	0.305	± 0.003	6.487	± 0.111	2.381	± 0.054	1.011	± 0.018	0.366	± 0.007	
CAN1-94 GRT 100x	Clinopyroxenite	4.1E-13	3.2E-13	0.204	± 0.007	0.292	± 0.006	6.300	± 0.404	2.090	± 0.131	0.982	± 0.034	0.325	± 0.032	
CAN1-94 GRT 500x	Clinopyroxenite	8.8E-13	8.2E-14	0.204	± 0.006	0.297	± 0.005	6.594	± 0.236	2.291	± 0.125	1.013	± 0.046	0.350	± 0.021	
CAN1-94 GRT 1000x	Clinopyroxenite	2.4E-12	1.8E-13	0.201	± 0.002	0.306	± 0.003	6.553	± 0.302	2.291	± 0.093	1.002	± 0.032	0.341	± 0.008	
CAN1-94 GRT 2000x	Clinopyroxenite	7.5E-12	7.5E-13	0.202	± 0.002	0.304	± 0.002	6.488	± 0.234	2.320	± 0.090	0.996	± 0.020	0.350	± 0.010	
CAN1-126 GRT 100x	Clinopyroxenite	-2.8E-14	1.5E-14	0.200	± 0.007	0.310	± 0.022	7.018	± 0.710	2.277	± 0.200	1.196	± 0.075	0.387	± 0.029	
CAN1-126 GRT 500x	Clinopyroxenite	7.6E-13	7.0E-14	0.203	± 0.003	0.306	± 0.007	6.477	± 0.612	2.280	± 0.171	1.012	± 0.085	0.356	± 0.039	
CAN1-126 GRT 1000x	Clinopyroxenite	1.5E-12	1.1E-13	0.201	± 0.004	0.305	± 0.005	6.468	± 0.286	2.368	± 0.107	0.999	± 0.033	0.361	± 0.016	
CAN1-126 GRT 2000x	Clinopyroxenite	1.9E-12	1.5E-13	0.200	± 0.003	0.302	± 0.004	6.642	± 0.193	2.411	± 0.091	0.997	± 0.032	0.353	± 0.012	
CAN1-142 GRT 100x	Clinopyroxenite	7.6E-14	1.1E-14	0.213	± 0.009	0.314	± 0.018	6.294	± 0.589	2.021	± 0.370	1.194	± 0.171	0.346	± 0.038	
CAN1-142 GRT 500x	Clinopyroxenite	3.4E-13	4.7E-14	0.203	± 0.003	0.291	± 0.008	6.887	± 0.747	2.419	± 0.113	1.014	± 0.064	0.348	± 0.025	
CAN1-142 GRT 1000x	Clinopyroxenite	8.4E-13	1.1E-13	0.200	± 0.003	0.296	± 0.004	6.501	± 0.234	2.268	± 0.072	0.971	± 0.047	0.332	± 0.007	
CAN1-142 GRT 2000x	Clinopyroxenite	1.1E-12	1.3E-13	0.201	± 0.002	0.303	± 0.005	6.657	± 0.189	2.438	± 0.144	1.025	± 0.022	0.374	± 0.029	
CAN1-149 GRT 100x	Clinopyroxenite	8.5E-14	1.5E-14	0.199	± 0.002	0.318	± 0.014	6.386	± 0.496	2.290	± 0.204	1.038	± 0.096	0.364	± 0.061	
CAN1-149 GRT 500x	Clinopyroxenite	9.5E-13	7.9E-14	0.198	± 0.003	0.302	± 0.006	6.421	± 0.253	2.518	± 0.165	0.972	± 0.053	0.376	± 0.023	
CAN1-149 GRT 1000x	Clinopyroxenite	4.0E-13	7.5E-14	0.206	± 0.003	0.307	± 0.004	6.545	± 0.250	2.272	± 0.151	0.988	± 0.022	0.339	± 0.016	
CAN1-149 GRT 2000x	Clinopyroxenite	1.3E-12	2.4E-13	0.200	± 0.003	0.307	± 0.003	6.578	± 0.259	2.401	± 0.075	0.996	± 0.023	0.359	± 0.015	
CAN1-174 GRT 100x	Clinopyroxenite	4.1E-13	3.8E-14	0.205	± 0.004	0.292	± 0.008	6.529	± 0.290	2.174	± 0.109	1.034	± 0.057	0.340	± 0.025	
CAN1-174 GRT 500x	Clinopyroxenite	1.6E-12	1.6E-13	0.201	± 0.004	0.300	± 0.004	6.776	± 0.425	2.460	± 0.209	1.000	± 0.026	0.358	± 0.016	
CAN1-174 GRT 1000x	Clinopyroxenite	5.1E-12	3.0E-13	0.202	± 0.002	0.300	± 0.003	6.467	± 0.142	2.378	± 0.111	0.983	± 0.024	0.358	± 0.012	
CAN1-174 GRT 2000x	Clinopyroxenite	4.3E-12	3.8E-13	0.202	± 0.002	0.301	± 0.002	6.552	± 0.298	2.325	± 0.038	0.987	± 0.027	0.350	± 0.008	
CAN1-96 CPX 100x	Sheared Iherzolite	2.1E-13	3.0E-14	0.208	± 0.010	0.305	± 0.011	6.725	± 0.416	2.391	± 0.282	1.016	± 0.014	0.361	± 0.046	
CAN1-96 CPX 500x	Sheared Iherzolite	1.7E-12	2.3E-13	0.202	± 0.002	0.300	± 0.003	6.575	± 0.092	2.319	± 0.103	0.984	± 0.020	0.345	± 0.012	
CAN1-96 CPX 1000x	Sheared Iherzolite	4.0E-12	5.6E-13	0.202	± 0.002	0.299	± 0.004	6.593	± 0.157	2.319	± 0.071	1.019	± 0.021	0.359	± 0.007	
CAN1-96 CPX 2000x	Sheared Iherzolite	7.0E-12	8.5E-13	0.202	± 0.002	0.306	± 0.003	6.498	± 0.143	2.369	± 0.071	1.005	± 0.017	0.360	± 0.010	
CAN1-89 CPX 100x	Sheared Iherzolite	6.6E-13	8.7E-14	0.204	± 0.005	0.300	± 0.004	6.447	± 0.410	2.307	± 0.117	0.992	± 0.028	0.351	± 0.029	
CAN1-89 CPX 500x	Sheared Iherzolite	2.1E-12	2.5E-13	0.203	± 0.002	0.298	± 0.003	6.634	± 0.144	2.381	± 0.101	1.008	± 0.029	0.356	± 0.015	
CAN1-89 CPX 1000x	Sheared Iherzolite	4.8E-12	6.6E-13	0.202	± 0.002	0.299	± 0.003	6.562	± 0.110	2.381	± 0.051	1.015	± 0.022	0.361	± 0.011	

Samples	Lithology	[⁸⁴ Kr] ccSTP/g	[¹³² Xe] ccSTP/g	⁸² Kr/ ⁸⁴ Kr		⁸⁶ Kr/ ⁸⁴ Kr		¹²⁹ Xe/ ¹³⁰ Xe		¹³⁶ Xe/ ¹³⁰ Xe		¹²⁹ Xe/ ¹³² Xe		¹³⁶ Xe/ ¹³² Xe		
CAN1-89 CPX 2000x	Sheared lherzolite	5.8E-12	2.1E-13	0.202	± 0.002	0.299	± 0.003	6.499	± 0.097	2.346	± 0.051	1.002	± 0.023	0.357	±	0.009
CAN1-88 WR 100x	Sheared lherzolite	3.5E-13	3.2E-14	0.205	± 0.005	0.296	± 0.007	6.682	± 0.688	2.196	± 0.157	0.958	± 0.075	0.314	±	0.023
CAN1-88 WR 500x	Sheared lherzolite	2.6E-12	2.3E-13	0.203	± 0.002	0.297	± 0.004	6.426	± 0.114	2.360	± 0.125	0.979	± 0.033	0.357	±	0.018
CAN1-88 WR 1000x	Sheared lherzolite	5.0E-12	4.9E-13	0.201	± 0.003	0.298	± 0.003	6.623	± 0.132	2.360	± 0.061	0.994	± 0.012	0.350	±	0.011
CAN1-88 WR 2000x	Sheared lherzolite	7.8E-12	7.8E-13	0.204	± 0.003	0.303	± 0.002	6.537	± 0.088	2.356	± 0.083	0.988	± 0.015	0.353	±	0.010
CAN1-88 GRT 100x	Sheared lherzolite	1.3E-12	9.1E-14	0.202	± 0.003	0.299	± 0.006	6.762	± 0.334	2.321	± 0.123	1.006	± 0.055	0.341	±	0.016
CAN1-88 GRT 500x	Sheared lherzolite	7.7E-12	5.1E-13	0.201	± 0.002	0.299	± 0.003	6.583	± 0.150	2.344	± 0.051	1.029	± 0.024	0.361	±	0.009
CAN1-88 GRT 1000x	Sheared lherzolite	1.4E-11	7.9E-13	0.201	± 0.002	0.299	± 0.003	6.527	± 0.128	2.344	± 0.092	1.015	± 0.017	0.360	±	0.013
CAN1-88 GRT 2000x	Sheared lherzolite	2.1E-11	1.6E-12	0.200	± 0.002	0.299	± 0.003	6.587	± 0.069	2.345	± 0.072	1.022	± 0.018	0.360	±	0.008
CAN1-89 GRT 100x	Sheared lherzolite	6.4E-13	5.3E-14	0.201	± 0.005	0.305	± 0.004	6.398	± 0.568	2.148	± 0.185	1.001	± 0.070	0.331	±	0.035
CAN1-89 GRT 500x	Sheared lherzolite	2.1E-12	3.1E-14	0.200	± 0.003	0.305	± 0.007	6.230	± 0.357	2.136	± 0.153	0.973	± 0.051	0.323	±	0.025
CAN1-89 GRT 1000x	Sheared lherzolite	3.8E-12	1.6E-13	0.202	± 0.002	0.306	± 0.003	6.402	± 0.190	2.136	± 0.102	0.996	± 0.035	0.330	±	0.017
CAN1-89 GRT 2000x	Sheared lherzolite	6.1E-12	3.4E-13	0.201	± 0.002	0.305	± 0.004	6.345	± 0.135	2.208	± 0.070	0.996	± 0.021	0.336	±	0.009
CAN1-96 GRT 100x	Sheared lherzolite	9.1E-13	7.1E-14	0.204	± 0.004	0.306	± 0.006	6.649	± 0.311	2.368	± 0.158	1.025	± 0.061	0.359	±	0.028
CAN1-96 GRT 500x	Sheared lherzolite	5.4E-12	4.2E-13	0.201	± 0.002	0.304	± 0.003	6.509	± 0.244	2.326	± 0.073	0.993	± 0.025	0.352	±	0.011
CAN1-96 GRT 1000x	Sheared lherzolite	8.3E-12	6.3E-13	0.203	± 0.002	0.305	± 0.003	6.562	± 0.124	2.326	± 0.067	0.991	± 0.028	0.349	±	0.009
CAN1-96 GRT 2000x	Sheared lherzolite	1.1E-11	8.8E-13	0.201	± 0.002	0.305	± 0.002	6.573	± 0.106	2.334	± 0.086	1.001	± 0.023	0.351	±	0.010
CAN1-96 OPX 100x	Sheared lherzolite	1.4E-12	1.7E-13	0.203	± 0.003	0.307	± 0.006	6.782	± 0.352	2.400	± 0.104	1.027	± 0.031	0.361	±	0.022
CAN1-96 OPX 500x	Sheared lherzolite	5.2E-12	7.7E-13	0.201	± 0.003	0.302	± 0.004	6.394	± 0.126	2.342	± 0.082	0.973	± 0.027	0.352	±	0.014
CAN1-96 OPX 1000x	Sheared lherzolite	7.7E-12	1.4E-12	0.201	± 0.002	0.305	± 0.004	6.604	± 0.140	2.342	± 0.084	1.008	± 0.019	0.355	±	0.010
CAN1-96 OPX 2000x	Sheared lherzolite	6.8E-12	1.1E-12	0.203	± 0.002	0.303	± 0.004	6.554	± 0.069	2.334	± 0.074	1.002	± 0.016	0.352	±	0.009
CAN1-182 CPX 100x	Websterite	1.1E-13	1.9E-14	0.202	± 0.010	0.307	± 0.008	6.373	± 0.653	2.325	± 0.271	1.050	± 0.062	0.376	±	0.039
CAN1-182 CPX 1000x	Websterite	3.6E-12	4.4E-13	0.203	± 0.003	0.304	± 0.003	6.709	± 0.191	2.411	± 0.039	1.014	± 0.035	0.351	±	0.012
CAN1-182 CPX 2000x	Websterite	1.3E-11	1.5E-12	0.200	± 0.002	0.299	± 0.003	6.636	± 0.108	2.261	± 0.039	1.019	± 0.021	0.346	±	0.004
CAN1-182 GRT 100x	Websterite	1.9E-13	3.2E-14	0.201	± 0.006	0.288	± 0.008	6.492	± 0.248	2.338	± 0.195	0.975	± 0.057	0.349	±	0.026
CAN1-182 GRT 500x	Websterite	1.2E-12	1.7E-13	0.203	± 0.004	0.298	± 0.005	6.425	± 0.180	2.305	± 0.099	0.973	± 0.018	0.345	±	0.008
CAN1-182 GRT 1000x	Websterite	2.5E-12	3.4E-13	0.202	± 0.002	0.298	± 0.004	6.470	± 0.183	2.305	± 0.074	0.983	± 0.025	0.350	±	0.012
CAN1-182 GRT 2000x	Websterite	4.5E-12	5.8E-13	0.202	± 0.002	0.299	± 0.003	6.590	± 0.072	2.352	± 0.060	1.006	± 0.017	0.354	±	0.007
CAN1-206 CPX 100x	Eclogite	5.9E-13	5.5E-14	0.204	± 0.010	0.302	± 0.015	6.527	± 0.514	2.134	± 0.274	1.033	± 0.085	0.336	±	0.042
CAN1-206 CPX 500x	Eclogite	2.7E-12	2.9E-13	0.201	± 0.004	0.306	± 0.004	6.440	± 0.418	2.323	± 0.084	1.157	± 0.045	0.410	±	0.008
CAN1-206 CPX 1000x	Eclogite	2.6E-12	2.7E-13	0.203	± 0.003	0.300	± 0.005	6.667	± 0.250	2.323	± 0.098	1.085	± 0.024	0.371	±	0.016
CAN1-206 CPX 2000x	Eclogite	2.9E-12	2.9E-13	0.206	± 0.003	0.304	± 0.005	6.596	± 0.259	2.435	± 0.098	1.023	± 0.033	0.372	±	0.006
CAN1-206 GRT 100x	Eclogite	4.0E-13	4.5E-14	0.203	± 0.002	0.293	± 0.004	6.378	± 0.316	2.339	± 0.116	0.965	± 0.044	0.352	±	0.023
CAN1-206 GRT 500x	Eclogite	1.6E-12	1.9E-13	0.201	± 0.003	0.297	± 0.003	6.631	± 0.139	2.288	± 0.060	1.008	± 0.023	0.341	±	0.013

Samples	Lithology	⁸⁴ Kr ccSTP/g	¹³² Xe ccSTP/g	⁸² Kr/ ⁸⁴ Kr		⁸⁶ Kr/ ⁸⁴ Kr		¹²⁹ Xe/ ¹³⁰ Xe		¹³⁶ Xe/ ¹³⁰ Xe		¹²⁹ Xe/ ¹³² Xe		¹³⁶ Xe/ ¹³² Xe		
CAN1-206 GRT 1000x	Eclogite	2.3E-12	2.8E-13	0.200	± 0.002	0.298	± 0.003	6.487	± 0.122	2.288	± 0.079	0.994	± 0.020	0.353	±	0.013
CAN1-206 GRT 2000x	Eclogite	3.9E-12	4.8E-13	0.202	± 0.003	0.298	± 0.003	6.497	± 0.116	2.307	± 0.059	1.002	± 0.021	0.351	±	0.010
CAN1-95 CPX 100x	Pargasite websterite	2.2E-13	2.9E-14	0.209	± 0.007	0.298	± 0.005	6.874	± 0.672	2.518	± 0.431	0.999	± 0.058	0.367	±	0.044
CAN1-95 CPX 500x	Pargasite websterite	1.8E-12	2.1E-13	0.204	± 0.003	0.300	± 0.003	6.685	± 0.216	2.374	± 0.076	1.015	± 0.045	0.354	±	0.007
CAN1-95 CPX 1000x	Pargasite websterite	2.3E-12	2.8E-13	0.204	± 0.003	0.304	± 0.003	6.715	± 0.216	2.374	± 0.086	1.048	± 0.051	0.361	±	0.023
CAN1-95 CPX 2000x	Pargasite websterite	2.3E-12	3.3E-13	0.201	± 0.002	0.299	± 0.004	6.478	± 0.148	2.370	± 0.086	0.970	± 0.032	0.352	±	0.013
CAN1-95 GRT 100x	Pargasite websterite	1.2E-13	2.0E-14	0.193	± 0.009	0.289	± 0.011	6.346	± 0.600	2.241	± 0.296	1.042	± 0.087	0.348	±	0.017
CAN1-95 GRT 500x	Pargasite websterite	6.1E-13	1.1E-13	0.202	± 0.005	0.295	± 0.003	6.478	± 0.272	2.383	± 0.076	0.996	± 0.045	0.362	±	0.015
CAN1-95 GRT 1000x	Pargasite websterite	6.2E-13	1.2E-13	0.199	± 0.008	0.294	± 0.009	6.477	± 0.229	2.383	± 0.148	0.942	± 0.042	0.339	±	0.013
CAN1-95 GRT 2000x	Pargasite websterite	8.1E-13	1.5E-13	0.203	± 0.006	0.294	± 0.004	6.384	± 0.235	2.359	± 0.141	0.966	± 0.045	0.352	±	0.012

CAPÍTULO 7

CONSIDERAÇÕES FINAIS

7 CONSIDERAÇÕES FINAIS

Os xenólitos mantélicos hospedados pelo kimberlito diamantífero Canastra-1 pertencem à fácies granada e foram classificados como lherzolitos cisalhados, websteritos, clinopiroxenitos, eclogitos e dunito. Três amostras de websterito são hidratadas e contêm anfibólio (pargasita). Os resultados obtidos indicam que o manto litosférico na borda sudoeste do Cráton do São Francisco registra metassomatismo críptico e modal.

Eclogitos e websteritos hidratados (com pargasita) são provenientes da porção mais rasa da litosfera (~100-130 km). Eclogitos são classificados como alto-Mg e baixo-Ca, além de exibirem afinidade transitória entre os Grupos I e II. As composições isotópicas Sr-Nd sugerem a presença de um componente enriquecido. Os websteritos hidratados são cumulos gerados a partir da fusão parcial de fragmentos de placas oceânicas. Essas amostras apresentam altas razões isotópicas de Sr e valores negativos de ϵNd . O metassomatismo críptico, registrado pelos eclogitos e websteritos hidratados, é evidenciado pelo enriquecimento pronunciado de elementos terras raras leves em relação aos pesados no clinopiroxênio e pargasita.

Os lherzolitos, clinopiroxenitos e websteritos anidros são caracterizados por altas estimativas de temperatura (1191–1290 °C) e profundidades entre 174 e 186 km. Essas amostras são provenientes do limite litosfera-astenosfera (LAB) e são produto do processo de refertilização promovido pelo metassomatismo proto-kimberlítico. Esse metassomatismo ocorreu imediatamente antes da erupção do kimberlito. Isócronas Sm-Nd fornecem uma idade média de 120 ± 5 Ma, indicando que a refertilização ocorreu durante os estágios iniciais da separação de Gondwana.

As análises de He-Ar-Ne-Kr-Xe revelam um complexo processo de reciclagem de antiga crosta oceânica hidratada e sedimentos sobrepostos derivados de ambientes de subducção. Os isótopos de hélio e xenônio mostram componentes fortemente radiogênicos e fissiogênicos, enquanto o neônio apresenta características semelhantes às do MORB e nucleogênicos. As razões isotópicas de argônio e criptônio evidenciam forte contribuição atmosférica.

Nesse cenário, é provável que componentes voláteis derivados da placa e de diferentes fontes foram reciclados. Esses componentes seriam derivados de um sistema de subducção complexo e de longa duração desde o Arqueano-Paleoproterozoico.

A interação entre a litosfera cratônica e o *melt* proto-kimberlítico pouco antes da erupção do Kimberlito Canastra-1, fortemente registrado pela química mineral e isótopos Sr-Nd, afetou minimamente a assinatura de gases nobres proveniente de um metassomatismo antigo, em que os voláteis são derivados. Desta forma, os xenólitos mantélicos do Kimberlito Canastra-1 fornecem uma "impressão digital de subducção" do transporte de voláteis entre a superfície e os reservatórios do manto. Portanto, pode-se concluir que a margem sudoeste do Cráton do São Francisco revela uma história complexa de metassomatismo/refertilização relacionada a eventos tectônicos sobrepostos desde a consolidação cratônica.

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