ORIGIN AND COMPOSITION OF THE SUBCONTINENTAL LITHOSPHERIC MANTLE ALONG THE LINEAMENT OF 125° AZIMUTH, BRAZIL

by

LYNTHENER BIANCA TAKENAKA

Australian Research Council Centre of Excellence for
Core to Crust Fluid Systems (CCFS) and National Key Centre
for Geochemical Evolution and Metallogeny of Continents (GEMOC)

School of Natural Sciences
Faculty of Science and Engineering, Macquarie University, Australia
Supervisors: Suzanne Y. O'Reilly, William L. Griffin and Dorrit E. Jacob

Geosciences Institute
University of São Paulo, São Paulo, Brazil
Supervisors: Miguel Ângelo Stipp Basei and Carlos E. Ganade

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LYNTHENER BIANCA TAKENAKA OLIVEIRA

Orientador: Prof. Dr. Miguel Angelo Stipp Basei
Orientadora: Dra. Suzanne Yvette O'Reilly (Macquarie University)

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COMISSÃO JULGADORA

Dr. Miguel Angelo Stipp Basei
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DEDICATION

Dedicated to my parents Consolação and Elismar who are my daily inspiration.

Unconditional love and support make dreams come true.

“One, remember to look up at the stars and not down at your feet. Two, never give up work. Work gives you meaning and purpose and life is empty without it. Three, if you are lucky enough to find love, remember it is there and don't throw it away.”

Stephen Hawking

LIST OF ABBREVIATIONS

1D – Unidimensional
2D – Bidimensional
3D – Tridimensional
4D – Four-dimensional
APA – Alto Paranaíba Arch
APIP – Alto Paranaíba Igneous Province
AZ125 – Lineament of 125° Azimuth
BDL – Base of the Depleted Lithosphere
BRV – Bravo pipe
BSE – Backscattered-Electron
CAN – Canastra pipe
CARP – Cluster Analysis by Recursive Partitioning
CART – Classification and Regression Tree
CAT – Catalão pipe
CH – Canastra Highlands
CHN – Charneca pipe
CLIPPIR – Cullinan-like, Large, Inclusion-Poor, Pure, Irregular and Resorbed
Cpht – Carats per hundred tonnes
CRL – Craton Reference Line
D_i – Partition coefficient
$D_i^{cpx/gnt}$ – Partition coefficient of i (V, Sc, V/Sc) between garnet and clinopyroxene
DZ – Depleted Zone
EDS – Energy Dispersive Spectroscopy
EM – Enriched Mantle
EMP – Electron Microprobe
FER – Ferragem pipe
FMQ – Fayalite-Magnetite-Quartz
FOR – Forca pipe
fO_2 – Oxygen fugacity
FZ – Fertile Zone
GSB-CPRM – Geological Survey of Brazil
HFSE – High Field Strength Elements
HMI – Heavy-Mineral Indicator

HREE – Heavy Rare Earth Elements
IND – Indaiá pipe
IOCG – Iron-Oxide Copper-Gold
IR – Infrared
JAP – Japencanga pipe
JCO – Junco pipe
JOA – Joana pipe
KKAC – Kimberlitic, Kamafugitic, Alkaline-Carbonatitic
LAB/LAB_t – Lithosphere-Asthenosphere Boundary (thermal)
LA-ICP-MS – Laser Ablation Inductively Coupled Plasma Mass Spectrometry
LILE – Large-Ion Lithophile Elements
LIP – Large Igneous Province
LMA – Limeira pipe
LPZ – Limpeza pipe
LREE – Light Rare Earth Elements
MARID – Mica (phlogopite), Amphibole (K-richterite), Rutile, Ilmenite and Diopside
MM – Melt-Metasomatism trend
MORB – Mid-Ocean Ridge Basalts
MQGA – Macquarie GeoAnalytical laboratory
MT – Magnetotellurics
NNO – Nickel-NiO buffer
PAN – Paranaíba pipe
PB – Paranapanema Block
P_{Cr} – Cr-in-garnet barometer
PE-LIP – Paraná-Etendeka Large Igneous Province
PGE – Platinum-Group Elements
PM – Phlogopite-Metasomatism trend
PRA – Pratinha pipe
PVD – Poço Verde pipe
REE – Rare Earth Elements
RGR – Rio Grande Rise
SAAM23 – South American Adjoint Model (iteration 23)
SBO – Southern Brasília Orogen
SCL – Santa Clara pipe
SCLM – Subcontinetal Lithospheric Mantle
SEM – Scanning Electron Microscopy

SFB – São Francisco Basin
SFC – São Francisco Craton
SFCP – São Francisco-Congo Paleoplate
SFPB – São Francisco Paleocontinental Block
SJU – Santa Juliana pipe
SRA – Santa Rosa pipe
SUC – Sucesso pipe
SW-SFC – Southwestern margin of the São Francisco Craton
TL – Tecton-Lherzolite trend
T_{Ni} – Ni-in-garnet thermometer
TRS – Três Ranchos pipe
TTG – Tonalite-Trondjemite-Granodiorite
T_{Zn} – Zn-in-chromite thermometer
UV – Ultraviolet
VNN – Viúva Nunes pipe
V/Sc_{gnt} – V/Sc in garnet
WDS – Wavelength-Dispersive X-ray Spectroscopy
XANES – X-ray Absorption Near-Edge Spectroscopy

ABSTRACT

The subcontinental lithospheric mantle (SCLM) plays an essential role in tectonic and metallogenetic processes affecting the continental lithosphere. Kimberlitic, kamafugitic and alkaline-carbonatitic (KKAC) magmas are probes of the SCLM; they may carry mantle xenoliths, xenocrysts and ore-forming elements. Over 700 KKAC intrusions are currently identified on the south-western margin of the São Francisco Craton (SW-SFC), within the NW-SE lineament of 125° Azimuth (AZ125). However, the ages of the KKAC rocks and the nature of the SCLM are not well established. Moreover, the diamond content in these rocks is very low, while large volumes and individual gems, commonly >100ct, occur in secondary sources. A re-evaluation of the history of the KKAC magmas combines geochronology with mineralogical/chemical characterization of geochronometers. A critical literature review and new ages demonstrate that inherited xenocrysts and primary minerals occur in the same pipes. The compositions of resistate minerals carry clues on their parental magmas, and microstructural/chemical/isotopic features distinguish maximum *vs* intrusion ages, refining the main KKAC magmatism at 88-76 Ma. Geochemical data from garnet and spinel xenocrysts in the KKAC magmas reveal a SCLM with typical cratonic model geotherms (37.5-42.5 mW/m^2) and a lithosphere 110-175 km thick; the mean depth for the Base of the Depleted Lithosphere (BDL) is *ca* 140 km. Ten unidimensional SCLM sections reveal that fertile lherzolites affected by varying degrees of melt-related metasomatism dominate the SCLM; a few depleted SCLM volumes remain both on- and off-craton. A newly recognized trace-element pattern, the Tecton-lherzolite trend, reflects physical mixing between asthenospheric and lithospheric materials in extensional and/or compressional regimes. The perovskite-based oxygen fugacity of KKAC magmas shows relatively low values, where perovskites with ΔFMQ -2 or below probably represent shallow cumulates from deep-seated magmas. A new oxybarometer based on V/Sc in pyrope garnets (V/Sc^{gnt}) was calibrated and key trends of fO_2 distribution in cratonic, reworked, and Tecton SCLM were defined. Below the SW-SFC, the V/Sc^{gnt} trend reflects a SCLM significantly more reduced than cratonic mantle. The chemical tomography is used for interpretation of seismic and MT data. Lithosphere-scale melt/fluid channels controlled the emplacement of magmas that sampled a relatively thin SCLM with large-scale short-range variability in degrees of depletion/fertility. Local differences in lithosphere thickness might explain the large variety of KKAC magmas in the area. The timing of KKAC magmatism in the AZ125, and perhaps in the Lucapa corridor (Angola), may represent a far-field response to the South Atlantic opening. The Archean SCLM below the SW-SFC was progressively modified by several tectonothermal events linked to intense metasomatism and refertilisation, representing craton-margin lithospheric erosion and asthenosphere-SCLM mixing during continental collision and post-rifting continental magmatism. Types I, II and CLIPPIR diamonds found in secondary sources are survivors of those processes, sampled by numerous low-grade, but potentially high-value, KKAC pipes. These findings imply new exploratory paradigms for diamond exploration and perhaps exploration for magmatic ores in the SW-SFC.

RESUMO

O manto litosférico subcontinental (MLSC) tem um papel fundamental em processos tectônicos e metalogenéticos da litosfera. Magmas kimberlíticos, kamafugíticos e alcalino-carbonatíticos (KKAC) podem carregar xenólitos e xenocristais do manto, e elementos formadores de depósitos. Mais de 700 intrusões KKAC foram identificadas na margem sudoeste do Craton São Francisco (SW-CSF), parte do lineamento NW-SE do Azimute 125° (AZ125). Entretanto, as idades das rochas KKAC e a natureza do MLSC não são bem estabelecidas. Além disso, o conteúdo de diamantes nessas rochas é muito baixo, enquanto grandes volumes e gemas individuais, comumente >100 ct, ocorrem em fontes secundárias. Uma reavaliação da história dos magmas KKAC combina geocronologia com caracterização mineralógica/química de geocronômetros. Revisão bibliográfica e novas idades demonstram que xenocristais herdados e minerais primários ocorrem em mesmos corpos. A composição de minerais resistatos carrega pistas sobre seus magmas parentais, e feições microestruturais/químicas/isotópicas permitem a distinção entre idades máximas e de intrusão, refinando o intervalo do magmatismo KKAC para 88-76 Ma. Dados geoquímicos de xenocristais de granada e espinélio revelam um MLSC com geotermas modelo tipicamente cratônicas (37.5-42.5 mW/m^2) e litosfera de 110-175 km; a espessura média da Base da Litosfera Depletada (BLD) é *ca* 140 km. Dez seções unidimensionais do MLSC revelam que lherzolitos férteis afetados por variáveis graus de metassomatismo relacionado à *melts* são predominantes; pequenos volumes de MLSC depletado são encontrados *on-* e *off-craton*. Um novo padrão de elementos-traço foi reconhecido, o *trend* Tecton-lhezorlítico, reflete mistura física entre materiais litosféricos e astenosféricos em regimes extensionais e/ou compressionais. A fugacidade do oxigênio (fO_2) de magmas KKAC, baseada em perovskita, mostra valores relativamente baixos, onde ΔFMQ -2 ou abaixo representam acumulações de magmas profundos em porções mais rasas da litosfera. Um novo oxibarômetro de V/Sc em granadas piropo (V/Sc^{gnd}) foi calibrado e *trends* específicos de fO_2 em MLSC cratônico, retrabalhado, e Tecton foram definidos. No SW-SFC, o *trend* de V/Sc^{gnd} reflete um MLSC significativamente mais reduzido do que o manto cratônico. A tomografia química é usada para interpretação de dados de tomografia sísmica e magnetotelúrico. Canais de *melts*/fluidos em escala litosférica controlaram o encaixe dos KKAC magmas que amostraram um MLSC relativamente fino e com grande variabilidade espacial em larga escala, com relação à graus de depleção/fertilidade. Diferenças locais na BLD podem explicar a grande variedade de magmas KKAC na região. A cronologia e posicionamento do magmatismo KKAC no AZ125, e no corredor Lucapa (Angola), representam respostas intracontinentais distais relacionadas à abertura do Atlântico Sul. O MLSC Arqueano abaixo do SW-CSF foi progressivamente modificado por vários eventos tectonotermais ligados à intenso metassomatismo e refertilização, representando erosão litosférica na margem do cráton e mistura astenosfera-MLSC durante colisão e magmatismo continental pós-rifteamento. Diamantes tipos I, II e CLIPPIR encontrados em fontes secundárias sobreviveram à estes processos e foram amostrados por inúmeros corpos KKAC de baixo-grau, mas com potencial alto valor. Estas descobertas implicam em novos paradigmas exploratórios para diamantes e outros depósitos magmáticos no AZ125.

DECLARATION

This work was carried out in the Australian Research Council Centre of Excellence for Core to Crust Fluid Systems (CCFS) and National Key Centre for Geochemical Evolution and Metallogeny of Continents (GEMOC), School of Natural Sciences at Macquarie University, Australia, and in the Geosciences Institute at the University of São Paulo, Brazil. I hereby declare that all the data and interpretations presented in this thesis are from my own work, except for information cited from published or unpublished sources, which has been explicitly indicated and acknowledged. No part of this thesis has ever been submitted for any other degree in any university or education institute. This thesis is submitted to both Macquarie University, Australia and University of São Paulo, Brazil, under the conditions of a cotutelle agreement between these two universities for this PhD program.

September 5th, 2022

Lynthener Bianca de Oliveira

Lynthener B. Takenaka de Oliveira

COVID STATEMENT

Dear Examiner,

Many of our HDR candidates have had to make changes to their research due to the impact of COVID-19. Below you will find a statement from the candidate, approved by their Supervisory Panel, that indicates how their original research plan has been affected by COVID-19 restrictions. Relevant ongoing restrictions in place caused by COVID-19 will also be detailed by the candidate.

Thesis Title: Origin and composition of the Subcontinental Lithospheric Mantle (SCLM) along the lineament of 125° Azimuth, Brazil

Candidate Name: Lynthener Bianca Takenaka de Oliveira

Department: School of Natural Sciences, Faculty of Science and Engineering

This PhD thesis was written almost entirely during the COVID-19 pandemics. A few changes in the original schedule occurred because the restrictions came in and at least three periods of lockdown were faced, together with substantial modifications in the Faculty of Science and Engineering. The supervision of this work was performed mostly from distance, making it generally more difficult to discuss and interpret the data. Although many things were done online, such as the supervisors follow up and revisions, we persisted with laboratory work and personal meetings as much as possible in the periods between lockdowns. However, not all the analysis predicted in the original thesis plan could be completed, such as those for isotopes in diamonds. Instead, other approaches and new methodologies were presented, entirely based on the data obtained. Scientific articles were also planned and prepared within limitations, due to all the delays and issues linked to the pandemics impact, but it was not possible to deliver a thesis by publication. This was replaced by a volume containing nine comprehensive chapters, detailing all of the most important findings of this work which will be eventually published in the following months after the thesis submission; one of the articles is already submitted and under revision.

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This was certainly a very challenging PhD project, and I experienced many unpredictable issues made it much harder than it would be in a normal candidature. The COVID pandemic took control of the course of this work and led to extremely difficult situations with restrictions, cancellations, unexpected changes and more. I wouldn’t have overcome this without the help and kindness of my colleagues at Macquarie University that were like a family during the last 3 years. I would like to especially recognize Jinxiang, Montgarri, Yi-Jen, Yoan, Tim, Sean, Olivier, Peter, Michael, Lauren, Alanur, Hong-Kun, Elena, Steve, Juan Carlos for being so gentle and helpful. All other people I met in CCFS who I have not mentioned as well. To Sinan, I am extremely thankful for the extraordinary assistance with the programming, geophysics and production of 2D images which led to a unique improvement of this work. I would be very glad to work with you and all the others in the future again.

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other things regarding to my candidature, and also personal matters, Sally, Anna, Ana Borba, Louis and all the other MQ uni staff, you have my admiration and I really appreciate what you have done for me.

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Lastly, I had also essential personal support from my family which always believed in me and invested their time and affection to help me achieve my dreams. Mom, dad and sis Júlia, without your love I would not be here. My grandma Conceição and the several aunts, uncles and cousins were always cheering for me. Also, thanks to my wonderful friends in Brazil and Australia, especially my girls Ana, Maris, Vivi, Carol, Juliana, Marina, Mari, Lu, Bruna, Lorena, Olga, Aline, Alyne, Sá, Alice, Aluine, Isa, Ana C., Roberta and Tobi, Rick, Matthew, together with many other countless nice people who have lifted me up. Obrigada!

CHAPTER I. GENERAL INTRODUCTION

1.1. Why Study the SCLM?

The subcontinental lithospheric mantle (SCLM) plays an essential role in tectonic, geodynamic and metallogenic processes affecting the continental crust. Acting as a non-convective layer of the uppermost mantle, the SCLM preserves thermal, chemical and chronological information, and hosts potential ore-forming elements. Therefore, understanding the characteristics of the SCLM is important to investigations of the lithosphere, mineral deposits and the evolution of Earth cycles (biosphere, atmosphere and hydrosphere) from Earth formation to present times. Since the SCLM along the lineament of 125° Azimuth (AZ125) is not extensively mapped to date, the following scientific questions inspired the present study:

A. What is the nature, composition and structure of the SCLM?: More than 70% by volume of the SCLM was likely generated between 3.5 and 3.0 Ga, as residues of a relatively short episode of massive high-degree partial melting (e.g. Griffin et al., 1999a, 2014). Throughout its evolution, the SCLM has been subjected to tectonic and metasomatic processes which gradually made it geochemically more complex and heterogeneous. The major rock types composing the SCLM are peridotites, followed by pyroxenites and eclogites (e.g., O’Reilly and Griffin, 2013 and references therein). The SCLM is generally more depleted than the underlying convective mantle and thus is buoyant and dynamically more stable. However, major disturbances such as rifting and collisional events may disrupt the lithosphere causing discrepancies in the heat flow, density and thickness of terrains with distinct tectonothermal ages. Thus, the nature and degree of the processes affecting the SCLM control the geothermal gradient, rheology and the distribution of lithotypes and ore-forming elements laterally and vertically.

B. What stories can the SCLM tell?: The generation of the Archean SCLM is chronologically coincident with the formation of more than 60% of continental crust before 2.5 Ga (Belousova et al., 2010; Dhuime et al., 2011; Arndt, 2013; Griffin et al., 2014). The onset of a plate tectonics regime sometime after this period (e.g., Hawkesworth and Kemp, 2006; Griffin et al., 2014 and references therein) modified the SCLM structure and composition and led to uplift, magmatism and the generation of important mineral resources such as diamonds, Ni-Cu-(PGE) and Cu-Au (Griffin et al., 2013) in the continental crust. Mantle-derived magmatism, especially the emplacement of kimberlites, kamafugites and alkaline-carbonatite (KKAC) complexes, commonly transports SCLM samples (mantle xenoliths and xenocrysts) to the surface, allowing investigation of the rock types in the deeper layers of the lithosphere. Robust sections of the SCLM over time in a diverse range of tectonic settings can be used to constrain geodynamic and tectonic models, geophysical interpretations and to open new mineral-exploration frontiers. The SCLM along the AZ125 was sampled by a significant number of KKAC magmas, bearing testimony to the breakup of Gondwana and the birth of numerous regions favourable to concentrate diamonds and other mineral deposits. An integrated picture of the lithosphere along this lineament could reveal the timing, mechanisms and composition – including potential resources – related to its evolutionary history.

C. How to investigate the SCLM?: Several methods were developed to investigate the SCLM and in this context, mapping techniques using xenocryst phases (e.g., O'Reilly and Griffin, 1996) stand out. The availability of materials such as kimberlite heavy-mineral indicators (HMI), mostly from diamond exploration campaigns, could extend the study vertically and laterally beyond the limitations imposed by mantle xenoliths. The quantification of major- and trace-elements in mantle xenocrysts provides clues about their SCLM source rock types and major transformations (e.g., metasomatism; Griffin et al, 1999b, 2002b; O’Reilly and Griffin, 2013). The application of specific geothermobarometry techniques (e.g., Griffin et al., 1989a; Griffin et al., 1993b; Ryan et al., 1996) to the same xenocrysts allows the calculation of model paleogeotherms which can be used to construct individual SCLM sections (one dimension) and maps in several dimensions; 2D, 3D and 4D where there is sufficient temporal and geographic spread. The integration of this “chemical tomography” with other information such as ages, isotopes, petrology and geophysics, becomes a powerful tool to evaluate lithospheric domains (e.g., Begg et al., 2009), geological models and exploration targets.

This work investigates the SCLM along the so called “lineament of 125° Azimuth”, specifically on the south-western margin of the São Francisco Craton (SW-SFC). The AZ125 has been previously characterized in a few studies (e.g., Bardet, 1977; Gonzaga and Tompkins, 1991; Moraes Rocha et al., 2014, 2015), with structural, geophysical and metallogenetic insights, but there has not been an integrated focus on the origin and composition of its SCLM. Single-point studies of mantle xenoliths and xenocrysts (e.g., Costa, 2008; Fernandes et al., 2021; Carvalho et al., 2022) and geophysical models (e.g., Bologna et al., 2006; Assumpção et al., 2017) in the SW-SFC have pointed out the complexity of the SCLM below the AZ125 and its non-obvious relationship with the available resources in the region. However, an integrated picture of the lithosphere including a comprehensive understanding of the SCLM characteristics and metallogenetic potential remains to be developed. The present work is unique in its coverage (28 localities over an area of *ca* 500x150 km), number of samples (> 3000 xenocrysts from 35 igneous bodies) and its combination of modern analytical techniques with interdisciplinary approaches (geochronology, geochemistry and geophysics). Its aims are to:

- re-evaluate the history of KKAC magmatism through a multi-methodological approach;
- provide petrological fingerprints of the KKAC magmas where fresh rocks are not available;
- determine geothermal gradients and geochemical signatures of the SCLM;
- image SCLM structure and composition;
- interpret the nature and evolution of the SCLM;
- analyse the SCLM oxygen fugacity with old and new methodologies;
- integrate geochemical and geophysical datasets for a combined interpretation;
- evaluate the economic aspects linked to the SCLM;
- propose new insights on the geodynamic and metallogenetic evolution of the AZ125.

1.2. Thesis Outline

Chapter 1 – General introduction: an overview of the main concepts relevant to the research topic and contextualization of the source project which lead to this work.

Chapter 2 – Geodynamics, geology and geophysics: a summary of the general geodynamic context, followed by the description of geological and geophysical domains in the study area.

Chapter 3 – Sampling: information about sample selection and brief description of the KKAC rocks and their entrained SCLM materials.

Chapter 4 – Methods: detailed summary of analytical techniques and methodologies applied in this work.

Chapter 5 – Geochronology of kimberlites and related rocks: mineralogical and chemical characterization of KKAC geochronometers, followed by a detailed evaluation of new and previous geochronology.

Chapter 6 – Lithosphere mapping: investigation of SCLM origin and composition, including geothermobarometry data, SCLM unidimensional sections, detailed appraisal of metasomatic signatures, and data integration. A close-up on the enigmatic origin of alluvial diamonds and SCLM is also given.

Chapter 7 – Oxygen fugacity in the SCLM: results from investigations of minerals using perovskite oxybarometer and the introduction of a new potential methodology based on V/Sc variation in garnets.

Chapter 8 – The big picture: Geodynamics and metallogenesis: extension of the lithosphere mapping to 2D visualization to provide insights on the lithosphere architecture. A new geodynamic and metallogenetic perspective is suggested for the AZ125 history.

Chapter 9 – Summary and conclusions: synopsis of the main discoveries and conclusions of this work.

1.3. Basic Concepts

This section describes basic concepts focusing on specific approaches and working hypothesis which are relevant to the understanding of this thesis, without extending to a very comprehensive literature review. It starts with an introduction of the main characteristics of the subcontinental lithospheric mantle (SCLM), including the generation and development of the distinct compositional and structural features observed by lithosphere mapping studies. It provides an overview of how the SCLM linked to cratons and their margins participates in and responds to the processes affecting the lithosphere, preserving key evidence for all sorts of geological investigations. General information about the most relevant types of mineral resources linked to the SCLM is also provided.

1.3.1. Introducing the SCLM

Origin and Evolution

The SCLM is the non-convective portion of the upper mantle that is attached to the continental crust; chemically, thermally and mechanically it is distinct from the underlying asthenosphere (Griffin et al., 1999a; 2009). Its generation likely began in the Paleo-Archean (*ca* 3.5 Ga) with large melting events producing buoyant, highly depleted residues and/or cumulates which composed the first stable SCLM (Griffin et al., 2014). Re-Os data obtained for sulfides in mantle xenoliths (e.g., Griffin et al., 2014 and references therein) and results from the Global Lithosphere Architecture Mapping project (e.g., Begg et al., 2009, 2010) indicate that at least 70% of the SCLM was formed between 3.3 and 2.7 Ga. This relatively short period is linked to a massive high-degree melting episode which probably occurred at sublithospheric depths, triggered by mantle overturns (e.g., Davies, 1995; Griffin et al., 1999a; Griffin et al., 2003), or super plumes (e.g., Stein and Hofmann, 1994; Wyman and Kerrich, 2002).

The origin of the earliest SCLM is chronologically coincident with the formation of more than 60% of the continental crust (>2.5 Ga; Belousova et al., 2010; Dhuime et al., 2011; Arndt, 2013; Griffin et al., 2014) and with the beginning of a modern pattern of plate tectonics probably near the end of the Archean (e.g., Hawkesworth and Kemp, 2006; Griffin et al., 2014). Secular cooling of the Earth (see Jaupart et al., 2015), coupled with a change in the tectonic regime impacted the nature of SCLM-forming processes, leading to gradual reworking and refertilisation of the depleted Archean SCLM (O'Reilly et al., 2001, Griffin et al., 2003). In the Proterozoic, high-degree melt extraction caused by slab-induced overturns at relatively shallower depths, produced a new SCLM of transitional nature (Griffin et al., 2003). Later in the Phanerozoic, distinct mechanisms involving whole-mantle convection led to a decrease in the degree of melt extraction at even shallower depths, producing the youngest SCLM domains (Griffin et al., 2009).

The generation of post-Archean SCLM may have been mostly related to the accumulation of materials from rising plumes (e.g., in intraplate settings), while the accretion of subducted oceanic mantle was, if existing, probably secondary (Griffin et al., 2009); at present, oceanic material is not accreting to the SCLM of young portions of the continents (Griffin et al., 1999a). This evolutionary history shows the variation in the composition and structure of the SCLM through time and emphasizes that the mechanisms that formed Archean SCLM appear to be distinct from those forming younger SCLM (Griffin et al., 2003, 2007).

Composition

Most of the SCLM compositional evidence derives from mantle xenoliths and xenocrysts sampled by kimberlites and related deep-seated magmatic rocks, alkali basalts *s.l.*, and from exposed massifs in orogenic belts. From all materials available, garnet xenocrysts, and to minor extent chromite xenocrysts, are the most widespread (laterally and vertically) and cost-effective probes of the SCLM, as they are frequently recovered during diamond exploration campaigns. Compositional studies, especially those based on xenocrystic garnets (e.g., Griffin et al., 1999b, 2002b) have confirmed that SCLM is dominated by ultramafic rocks (olivine-rich), with minor pyroxenites (frozen basaltic melts) and eclogites (clinopyroxene + garnet). The peridotite mantle wall-rocks vary from dunites (olivine) to harzburgites (olivine + orthopyroxene), wehrlites (olivine + clinopyroxene) and lherzolites (olivine + orthopyroxene + clinopyroxene), with more or less aluminous phases (garnet, spinel or plagioclase) depending on the pressure and temperature conditions involved (Griffin et al., 2009; O'Reilly and Griffin, 2013). The Cr content of garnets provides evidence about the degree of depletion of host SCLM rocks, while its correlation with Ca deliver clues about the source rock types (Griffin et al., 1999b; 2002b). High concentrations of elements such as Zr, Y and Ti, in SCLM garnets indicate refertilisation processes (Griffin et al., 2002b) related to metasomatism.

Mantle metasomatism is the compositional change resulting from the interaction between mantle wall-rocks and fluids, and can be divided in three types: *modal* metasomatism (Harte, 1983), when new minerals are added (e.g., phlogopite peridotites, MARID - Mica (phlogopite), Amphibole (K-richterite), Rutile, Ilmenite and Diopside rocks and pyroxenites; *cryptic*, when pre-existing minerals are compositionally modified, but no new phases are added; and *stealth*, when new mineral phases added are indistinguishable from possible major mantle phases (e.g., garnet and/or clinopyroxene). Metasomatic processes involve different types of fluids such as silicate and carbonatite melts, C-O-H (water, CH_4 and CO_2) fluids and dense brines, which move through the mantle via grain-boundary infiltration or crack propagation (O'Reilly and Griffin, 2013). A specific metasomatic process caused by the infiltration of asthenospheric melts contemporaneously with the intrusion of kimberlites and related rocks, is evidenced by the occurrence of high-T garnets in the SCLM (O'Reilly and Griffin, 2013). Similar garnets are found in sheared peridotite xenoliths, which are fragments of strongly metasomatised lithospheric mantle (Smith et al., 1991; Smith and Boyd, 1992; Griffin et al., 1996), indicative of thermal perturbation near the base of the SCLM ("kinked" geotherms, see Chapter 4 of this work).

Griffin et al. (1999b, 2002b) used major- and trace-element analyses of a large dataset of Cr-pyrope garnets to separate specific classes through multivariate statistics. Populations derived from the Cluster Analysis by Recursive Partitioning (CARP) technique were grouped into five major categories:

(1) depleted harzburgites: identified by subcalcic garnets from host rocks that experienced strong melt depletion, strongly depleted in Y and HREE;

(2) depleted lherzolites: identified by garnets that potentially equilibrated with clinopyroxene, depleted in Y, HREE and HFSE, with minor Zr enrichment;

(3) depleted/metasomatised peridotites (±phlogopite): identified by garnets from harzburgites depleted in major elements, Ti and Ga, but enriched in Y and Zr, and garnets from the lherzolites depleted in Y and HREE, but enriched in Zr and LREE. Host rocks were depleted and subsequently refertilised; "Phlogopite-metasomatism" signatures are related to carbonatitic melts.

(4) fertile lherzolites: identified by garnets representing significant refertilisation of depleted rocks, with abundant HREE and moderate HFSE contents; such garnets can also be derived from relatively undepleted parts of the asthenosphere.

(5) melt-metasomatised peridotites: mostly identified by garnets from high-T sheared lherzolite xenoliths, enriched in Zr, Ti, Y and Ga; "Melt-metasomatism" signatures are related to silicate melts.

Considering the secular evolution of the SCLM (e.g., Beyer et al., 2006), which can occur on a short time scale (see Griffin et al., 2003), groups of garnet xenoliths and xenocrysts from regions with different ages and tectonic settings exhibit a very close correlation between SCLM composition and tectonothermal age, or the age of the last major thermal perturbation in the overlying crust (Griffin et al., 1998a, 2003). Adapting Janse's (1994) classification of the tectonothermal age of crustal regions, the authors recognized three distinct SCLM suites: Archons (>2.5 Ga), Proton (2.5-1.0 Ga) and Tecton (< 1.0 Ga).

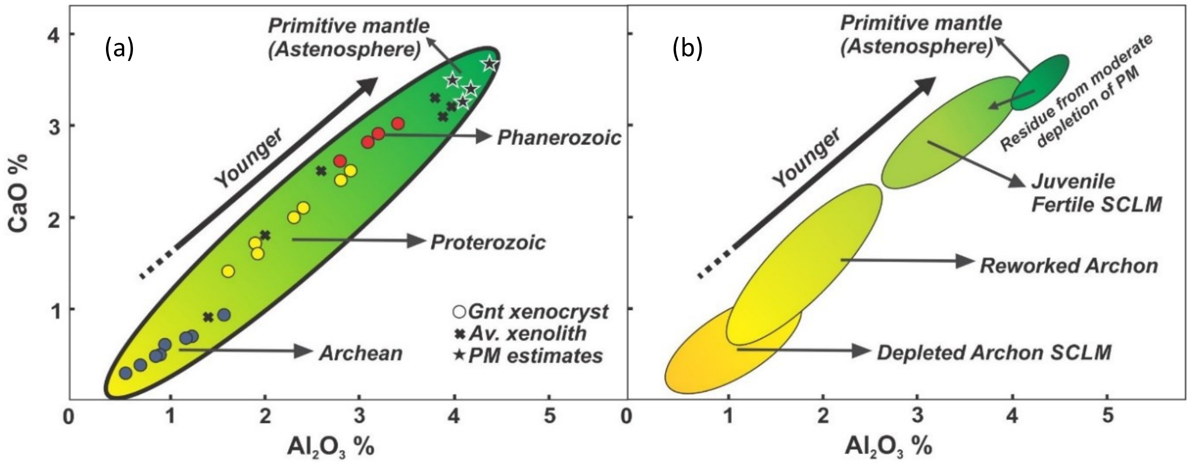

Figure 1. Secular evolution of the SCLM composition (CaO *vs.* Al_2O_3) over time: (a) based on garnet xenocrysts and mantle xenoliths classified according to their tectonothermal ages (see text for details; modified from O'Reilly and Griffin, 2006); and (b) calculated from garnet concentrates, average of xenolith suites and peridotite massifs, and garnet lherzolites from Tecton localities which are only slightly depleted compared to the primitive mantle (data from Griffin et al., 1999b; modified from Griffin et al., 2003). Gnt, garnet; Av., average.; PM, primitive mantle.

The degree of depletion in SCLM rocks consistently decreases from Archon to Proton to Tecton regions, while the degree of refertilisation related to metasomatism increases (Figure 1; Griffin et al., 1999a). This is emphasized by the fact that relatively the high abundance of harzburgitic garnets (e.g, Boyd and Gurney, 1986; Schulze, 1995), especially low-Ca, high-Cr types, is a unique feature of Archon regions (Griffin et al., 1998a; Griffin and O'Reilly, 2007). Archon SCLM is strongly depleted and the peridotites, commonly strongly stratified (e.g., Lac de Gras, cf. Griffin et al., 1999a), have higher Si/Mg (higher orthopyroxene/olivine) than highly depleted rocks in oceanic and arc-related settings, with anomalously low Fe contents (relative to Mg#, at low Al contents) and lower Cr#, Ca/Al and Fe/Al at any Mg# (Figure 1; Boyd, 1989; Griffin and O'Reilly, 2007); anomalously low Ni, Zn and Co contents are also characteristic (Griffin et al., 1999b).

Relative to Archons, garnets from calcic harzburgites are less abundant in Proton SCLM which is rich in fertile lherzolites, rarely refertilised, with the concentration of Al in peridotites decreasing at constant Fe and Cr contents (Griffin et al., 2003). Tecton SCLM is completely lacking in depleted garnets and dominated by fertile lherzolites compositionally similar to Primitive Mantle, which are very rare in Archon and Proton suites (Griffin and O'Reilly, 2007).

Structure

It is widely accepted that the SCLM is thermally conductive and generally more depleted than the underlying mantle; hence more buoyant and tectonically stable. However, the typical variation in degrees of depletion/fertilisation in distinct tectonothermal domains (Archon, Proton and Tecton) and the heterogeneous composition of the SCLM reflect changes in the physical properties of the lithosphere (e.g., Djomani et al., 2001; O'Reilly and Griffin, 2006; Afonso et al., 2008). This was evidenced by constructing empirical thermal profiles with depth (paleogeotherms) using mantle xenoliths and xenocrysts (e.g., Ryan et al., 1996; Sand et al., 2009; Goncharov et al., 2012). In most areas, xenolith-based geotherms tend to follow modelled geotherms characteristic of conductive heat flow.

The paleogeotherms attested that the thermal state of the SCLM and the thickness of the lithosphere registered by volcanic rocks at the time of their eruption is strongly correlated with their tectonothermal ages (Chapman and Pollack, 1977; O'Reilly and Griffin, 1996). They generally increase from Archon (35-45 mW/m^2) to Proton (45–50 mW/m^2) to Tecton regions (50-55 mW/m^2; Figure 2a). In areas sampled by alkali-basaltic volcanism, such as South-East Australia and Eastern China they record even higher (strongly upward-convex) geotherms indicative of advective heat transport (O'Reilly and Griffin, 1985; O'Reilly et al.,1997, 2001). Archon regions where the highly depleted Archean SCLM is expected to have the lowest density (Figure 2), have the thickest lithosphere (>160 km), colder geotherms (30–45 mW/m^2), and the highest buoyancy and stability (see O'Reilly and Griffin, 1996 and references therein), especially in well-preserved parts where the SCLM has remained extremely dehydrated and more viscous (Lenardic and Moresi, 1999; Griffin et al., 2003). Contrarily, Tecton regions with extremely fertile SCLM are expected to have denser, less buoyant lithosphere (Figure 2b), and higher geothermal gradients ($\geq$ 50 mW/m^2) with higher chances of delamination (SCLM removal). Proton regions are likely to have lithosphere with physical properties intermediate between these extremes (see Griffin et al., 2003 for details).

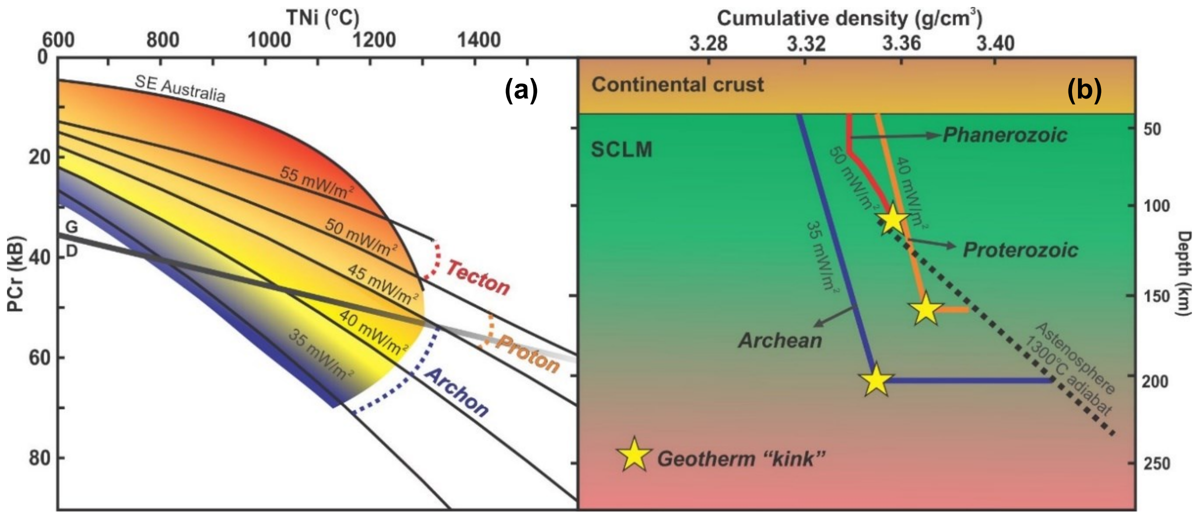

Figure 2. SCLM structure for regions with different tectonothermal ages, where density is inversely correlated to cooling: (a) typical empirical xenolith-based geotherms expected for Archon, Proton and Tecton localities; SE Australia geotherm from O'Reilly and Griffin (1985) is commonly found in regions with young intraplate magmatism reflecting advective heat transport (modified from O'Reilly and Griffin, 2006); (b) SCLM density profiles by age, within the geothermal range showed in (a); stars represents the geotherm "kink" (see Chapter 4 for details) expected at the "lithosphere-asthenosphere boundary" or as preferred in this work, the base of the depleted lithosphere (BDL; modified from Djomani et al., 2001).

Oxygen fugacity

The oxidation state, measured in terms of oxygen fugacity (ƒO_2) log units, is one of the most important parameters of the SCLM because, together with temperature, it controls most of the physical and chemical activity of oxygen between mantle reservoirs, and between mantle and crust (Frost, 1991). The ƒO_2 influences key aspects of the SCLM such as melting, composition, speciation of volatiles (e.g., C, H, O) and multivalent elements (e.g., Fe, V, Cr), stability of C-bearing phases (diamond, graphite and carbonates), mineral/melt partitioning, degassing and metal fertility, as demonstrated by several studies (e.g., Mungall, 2002; McCammon and Kopylova, 2004; Frost and McCammon, 2008; Goncharov et al., 2012; Berry et a., 2013; Richards, 2015; Brounce et al., 2015; Yaxley et al., 2012, 2017; Woodland and Seitz, 2018; Griffin et al., 2018; Aulbach et al., 2019; Tassara et al., 2020; Moretti and Neuville, 2021 and references therein). Most of the information about the redox evolution of the SCLM, ƒO_2 mechanisms and distribution comes from experiments (e.g., Ballhaus et al., 1991; Holycross and Cottrell, 2022), quantification via proxies/oxybarometers in mantle-derived rocks such as mid-ocean ridge basalts and peridotites (e.g., V/Sc, Li and Lee, 2004; Lee et al., 2005; garnet and spinel oxybarometers, Miller et al., 2016) and modelling of element-partitioning behaviour (e.g., Canil, 1997; Mallmann and O'Neill, 2009; Nicklas et al., 2018, 2019). Estimates of fO_2 recorded by minerals (e.g., perovskite; Bellis and Canil, 2007) frequently found in volatile-rich magmas such as kimberlites are also used.

The present redox state of the SCLM has evolved from a complex combination of mechanisms and processes which are still being debated. According to Stagno and Aulbach (2021) the variation in oxidation patterns in the Earth's interior was due to: (a) early accretion of variably oxidized blocks and meteoritic impact; (b) the formation of magma ocean(s), core segregation, and mantle crystallization; (c) establishment of mantle convection; and (d) recycling by subduction. Many studies argue that the redox state of the upper mantle has remained almost constant at the FMQ (fayalite-magnetite-quartz) oxygen buffer since 3.5 Ga (e.g., Canil, 1997, 2002; Delano, 2001; Li and Lee 2004; Hibbert et al., 2012). However, opposing results such as those from cratonic peridotites, eclogites, Archean picrites and basalts (e.g., Jacob and Foley, 1999; Woodland and Peltonen, 1999, Smart et al., 2009; Aulbach and Viljoen, 2015; Aulbach et al., 2017a) are consistent with a more reduced Archean upper mantle which may have been progressively oxidized through time (Foley, 2011, 2021). More recently, Nicklas et al. (2019) proposed that a secular oxidation of the mantle from 3.48 to 1.87 Ga, due to homogenization of primordial mantle redox heterogeneities, was followed by nearly constant oxygen fugacity to the present (Nicklas et al., 2018).

Under modern conditions, indications are that the fO_2 distribution in the SCLM is heterogeneous and oxidation state might decrease with depth (Wood et al., 1990; Woodland and Koch, 2003; Goncharov et al., 2012; Dymshits et al., 2020). The range of fO_2 estimated for spinel peridotites, which represent SCLM at shallower levels (<60 Km), is $\Delta FMQ\pm2$ (i.e. within two log units of the fO_2 defined by the reaction Fayalite →Magnetite + Quartz), but significant variations may occur across different tectonic settings. For example, subduction might oxidize the mantle by transport of oxidized surface materials to depth (Frost and McCammon, 2008; see Cottrell et al., 2021 for more details). At deeper SCLM levels, in principle the fO_2 of garnet peridotites tends to decrease with depth due to the temperature and pressure effects on garnet/pyroxene Fe_2O_3 partition coefficients and Fe^{3+}/Fe^{2+} equilibria, respectively (e.g., Gudmundsson and Wood, 1995; Canil and O'Neill, 1996; Woodland and Koch, 2003; Frost and McCammon, 2008; Yaxley et al., 2012; Stachel and Luth, 2015). However, perturbations such as the infiltration of metasomatic agents into the system can modify this trend (e.g., Goncharov et al., 2012), resulting in a non-obvious correlation with the degree of depletion/fertility (Woodland et al., 2006; Ionov and Wood, 1992). Griffin et al. (2018) argued that the oxidation of highly reduced C-O-H-N fluids ascending from deep upper mantle, in some mantle regions, via interaction with thick SCLM eventually forms diamonds and agents (CO_2 and H_2O) for metasomatism and melting processes, while at shallower levels the solid phase will be either graphite or amorphous C. Although in general ascending melts tend to be more oxidized, this is dependent on how much they interact with the mantle wall-rocks and how far up they go. Thus, the travel length and time determines if the melts are either oxidizing or reducing.

1.3.2. Cratons and their margins

Cratons are defined as rheologically and compositionally distinctive domains of the continental lithosphere, which have been stable since the Precambrian (e.g., Alkmim, 2004). Cratonic cores may have survived several tectonic events without pervasive deformation, because of their thick (>200 km), cold (35-40 mW/m^2), melt-depleted, rheologically rigid and buoyant lithospheric keels (e.g., Michaut and Jaupar, 2009). These isostatically positive mantle roots produce relatively flat topographies, close to the sea level, in the Archean/Paleoproterozoic crust (e.g., Foley, 2008). The low-density and high-viscosity nuclei (e.g., O'Neill et al., 2008) produce distinctive geophysical signatures such as high seismic velocity zones and high resistivity (e.g., Pavlenkova et al., 1996). However, numerous studies indicate that cratonic lithosphere can be altered, eroded, fragmented and reassembled during supercontinent cycles (e.g., Menzies et al., 1993; Xu et al., 2000; Foley, 2008; Hu et al., 2018; Celli et al., 2020; Sun and Dasgupta et al., 2020; Liu et al., 2021; Gernon et al., 2022). During collage periods, the amalgamation of converging cratonic blocks usually incorporates passive margins, micro-continents, intra-oceanic arcs and other continental fragments to form marginal orogenic belts. The accretionary processes, which commonly include subduction, shape cratonic geometries and result in high surface topography and consequently, thicker continental crust (~45 km; e.g., Durrheim and Mooney, 1991).

Lithological assemblages found in these orogenic zones reflect the overprint imposed by collisional processes, involving metamorphism and intense deformation. Orogenic events also trigger subsidence in the cratonic interior and favour the accumulation of sediments in intracratonic basins. Continental breakup, driven by rifting processes, can lead to disruption of cratons and their mantle-keels. Independently of the mechanisms that lead to separation (e.g., mantle plumes) and modification of the cratonic roots (e.g., metasomatism), there is a common association of these events with magmatism. Large Igneous Provinces and mafic dyke swarms are commonly interpreted as the surface expression of mantle plumes impingement (e.g., Beccaluva et al., 2020; Pessano et al., 2021 and references therein) and that this activity may trigger cratonic fragmentation (Hill, 1991) and erosion (e.g., Foley, 2008). Some most recent views (Gernon et al., 2022) suggest that rift-driven mantle instabilities migrate through the base of the lithosphere causing removal of the deep parts of mantle keels and emplacement of kimberlites and related magmas. Lithosphere thinning (e.g., North China craton, Zhu et al., 2011; North Atlantic craton, Tappe et al., 2006; Wyoming craton, Carlson et al., 2004), may increase heat flow and cause isostatic uplift. Transformation processes in the cratonic mantle influence its buoyancy and stability, and furthermore control their ability to provide resources like diamonds and ore-forming elements (e.g., Au, Cu, PGE).

Although lithospheres are not forever (see O’Reilly et al., 1998; 2001), the protracted history of cratons and their extensively reworked margins contains the most valuable evidence about Earth’s evolution. Only cratons are long-lived enough to provide Early Earth records such as primitive crust and mantle relicts (e.g., Griffin et al., 2014; Paquette et al., 2015). Also, they can deliver insights about mantle redox variations (e.g., Foley, 2011), primitive tectonic regimes (e.g., Pease et al., 2008; Perchuk et al., 2020) and early life (e.g., Mojzsis et al., 1996; Nutman et al., 2016). Finally, cratons are also the key to unravelling conditions that have favoured the formation of valuable mineral deposits through time.

1.3.3. SCLM metallogenesis

The SCLM is a “*durable, buoyant and rigid reservoir for ore-forming elements…*” (Griffin et al., 2013), and the genesis and accumulation of several important resources like diamonds, platinum-group elements (PGE), Ni-Cu-(PGE) and (Cu-)Au (Figure 3) are related to the origin and evolution of its physical-chemical characteristics (e.g., Malkovets et al., 2007; Richardson and Shirey, 2008; Groves et al., 2010; Begg et al., 2010; Fiorentini et al., 2010; Naldrett et al., 2010; Mair et al., 2011; Saunders et al., 2011; Tassara et al., 2017). Moreover, the SCLM has been advocated as metal-booster, in which redox-state changes during the ascent of magmas can lead to an increase on the extraction of metals (e.g., Au; Tassara et al., 2020).

Diamonds

Diamonds, as an economic resource, are primarily related to kimberlites which inevitably are linked to cratonic lithosphere. Even though kimberlites, and to a minor extent lamproites, are undoubtedly the main source of gem-like diamonds (Figure 3a; e.g., Boyd and Gurney, 1986), a larger variety of lithotypes may also be diamondiferous, at nano-, micro- or macro-scale, across several tectonic settings.

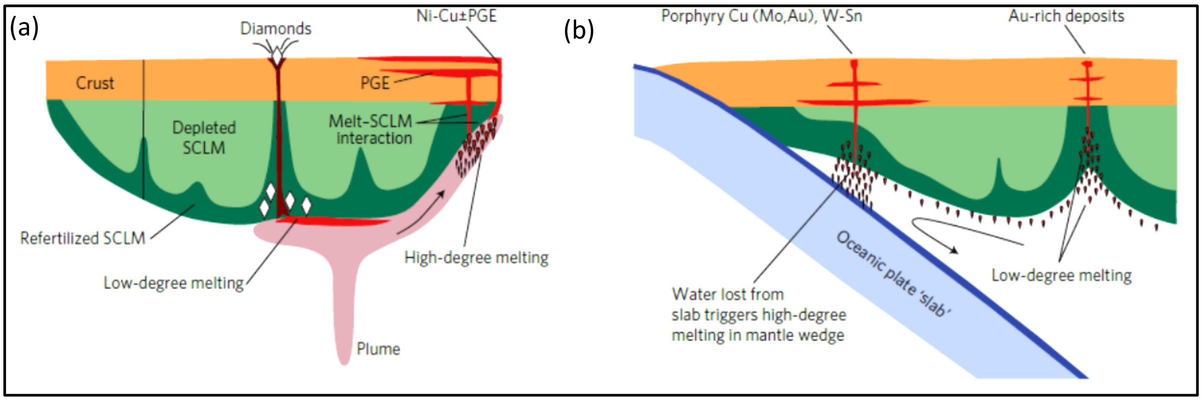

Figure 3. Cartoon from Griffin et al. (2013) showing the interaction between the SCLM metallogenic reservoir and magmas: (a) plume-driven events that might form kimberlites which transport diamonds also cause melting of thinner SCLM regions and interaction SCLM/crust for the formation of Ni-Cu and PGE deposits; (b) different types of convergent-margin settings where Au-poor deposits form from asthenospheric or crustal melts and/or low-degree melting of asthenosphere can produce Au-rich SCLM metasomatism. Au-enrichment can be driven by subsequent melting forming Cu-Au, epithermal or intrusive-related orogenic Au; possibly Carlin-type and orogenic Au as well.

Dobrzhinetskaya et al. (2022) provides a detailed compilation of most reported occurrences of diamonds in eclogites and other rocks from ultra-high pressure metamorphic terrains, ophiolites and lavas from modern volcanic eruptions (e.g., Tolbachik, Russia; Karpov et al., 2014). More unusual contexts include volcanoclastic komatiites (e.g., Capdevila et al., 1999) and modern oceanic mantle (e.g., Wirth and Rocholl, 2003). In the SCLM, the most important diamond source rocks are peridotites, followed by eclogites, that in a global scale are much less important but may dominate production from some examples (Stachel and Harris, 2009). For the purpose of this work, this overview on diamond genesis and key physical-chemical aspects is limited to that observed in peridotitic xenoliths/xenocrysts in the continental lithosphere, and in the deeper mantle (e.g., transition zone).

A. Peridotitic sources: It is important to recognize that diamonds are xenocrysts which reside in the mantle for a long period of time (see geochronological review by Smit et al., 2022), thus it is challenging to correlate their growth conditions with source and carrier rocks (e.g., kimberlites). However, inclusions of trapped melts/fluids and minerals (e.g., garnet, chromite, clinopyroxene) and mantle xenoliths have provided many insights. Cartigny et al., (2014) have argued that diamonds are formed only when carbon is thermodynamically stable, which is estimated at temperatures >950°C and depths below 150 km (~45 kbar), mostly within the “diamond window” of 150-250 km; considering typical continental heat flows (38-42 mW/m^2). Geothermobarometry data on mineral inclusions indicate that the formation of lithospheric diamonds occurs over the temperature range of about 1160-1200°C - regardless of source rock types - and pressures between 4.5 and 6.5 GPa (~140-200 km; Stachel and Harris, 2008; Stachel and Luth, 2015; Nimis, 2022). Besides temperature and pressure, oxygen fugacity and metasomatism also play a major role on diamond genesis and destruction (Figure 4; e.g., Stachel et al., 2004; Cartiginy et al., 2014; Smit and Shirey, 2020; Weiss et al., 2021). The cratonic SCLM is a relatively oxidized (ultra)depleted layer with variable degrees of metasomatism, above a Fe-rich carapace of relatively fertile peridotites where kimberlites and related rocks might be formed (Tappe et al., 2017; Woodhead et al., 2017; see Griffin et al., 2018 for details). When highly reduced asthenosphere-derived metasomatic fluids (e.g., CH_4-rich) reach the base of the SCLM, they are progressively oxidized and reactions such as and $CH_4 + O_2 \rightarrow C + 2H_2O$ and $SiO_2 + 3CH_4 \rightarrow SiC + C + 3H_2 + CO_2$ will first provide favourable conditions for diamond growth (Figure 4, stage I; Griffin et al., 2018).

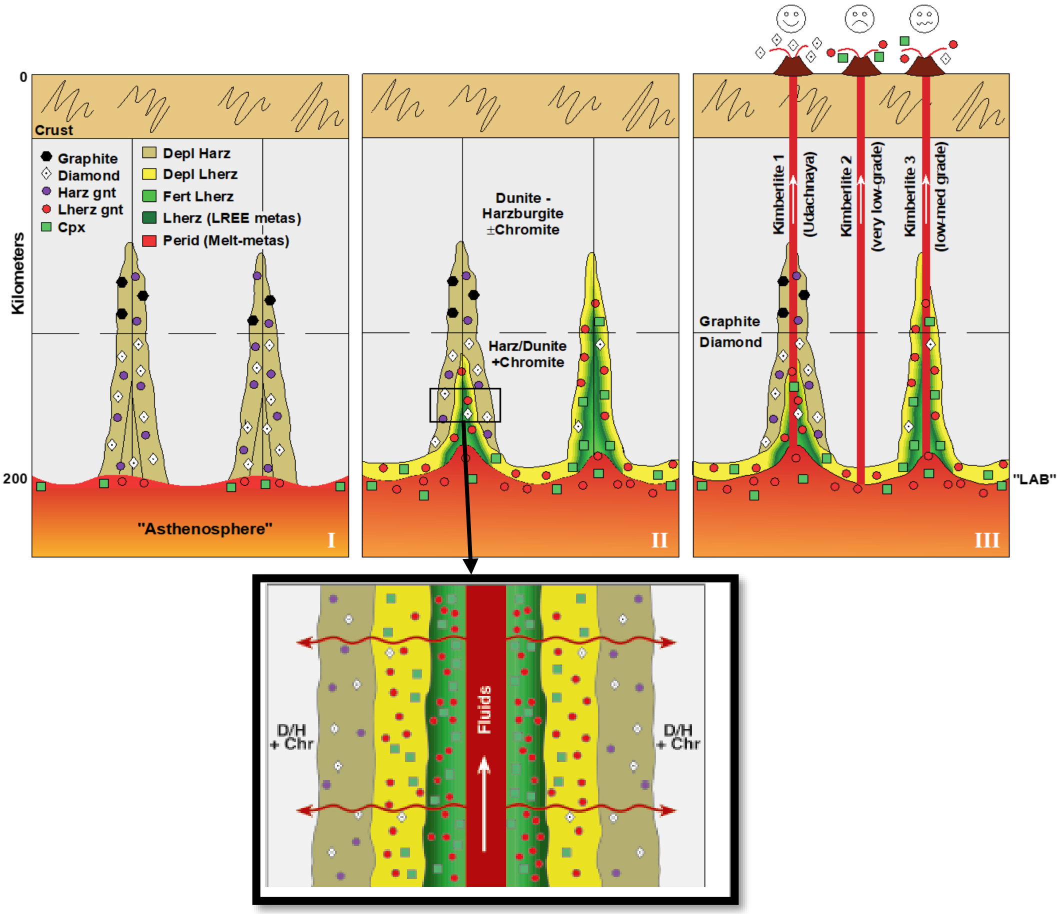

Figure 4. Cartoon from Malkovets et al. (2007) representing the progression of SCLM metasomatism and the directly correlation with diamonds formation/destruction: (I) the relatively oxidized harzburgites/dunites form the Archean SCLM are metasomatized by asthenospheric Si-bearing CH_4-rich fluids, which initially favour the crystallization of diamond/graphite; (II) as the metasomatism process continues with the infiltration of more melts/fluid (zoomed detail), diamond/graphite stops precipitating while harzburgites are refertilised by melt-related metasomatism (stronger in the right conduit); relict harzburgitic diamonds remain in the lherzolites; (III) later, kimberlites and related rocks erupt, sampling distinct parts of the depleted/metasomatised lithosphere. High-grade pipes are those which sampled preserved portions of SCLM from stage (I), while barren pipes sampled unmetasomatised SCLM; low-grade pipes sample highly metasomatized SCLM with relict diamonds. D, dunite; H or Harz, harzburgite; Lherz, lherzolite; Fert, (re)-fertilised; Perid, peridotite; Cpx, clinopyroxene; Gnt, garnet; Chr, chromite; LREE, light rare-earth elements; metas, metasomatised.

Further increase in melts/fluids fO_2 by metasomatism, causes resorption/dissolution of diamonds and depending on the degree of this process, they remain as relics in fertile rocks or completely disappear (Figure 4, stages II and III; McCammon et al., 2001; O'Reilly and Griffin, 2013; Stachel and Luth, 2015); e.g., diamonds are not forever! (see Smit and Shirey, 2020). Alternative models argue in favour of the reduction of carbonates as paired mechanism for diamond growth, besides the oxidation of CH_4 fluids (Stachel and Harris, 2009).

Deeper sources: Much higher temperature and pressure ranges are linked to the formation of diamonds at depths below the lithosphere (300-800 km or more; see review by Smith and Nestola, 2021). This have been supported by the identification of unusual inclusions in diamonds such as $CaSiO_3$-perovskite, bridgmanite, ringwoodite, stishovite and methane (e.g., Moore and Gurney, 1985; Stachel and Harris, 2008; Harte, 2010; Smith et al., 2016; Kaminsky et al., 2012, 2013), C-H-O-N isotopes (e.g., Zedgenizov et al., 2014) and plasto-elasto-geobarometry methods (Anzolini et al., 2019). Besides the common multi-mineral phases entrapped, super-deep diamonds show higher degrees of plastic deformation (e,g., Cayzer et al., 2008) and resorption than lithospheric diamonds (e.g., Moore, 2014), and also lower contents of nitrogen impurities (e.g., Moore, 2009; Smith and Kopylova, 2014).

Subduction is a preferred mechanism for the reintroduction of carbon from the crust (e.g. graphite) into the mantle, and to the formation of super-deep diamonds (e.g., Tappert et al., 2005; Bulanova et al., 2010; Walter et al., 2008, 2011; Pearson et al., 2014; Cartigny et al., 2014; Burnham et al., 2015; Seitz et al., 2018; Smith et al., 2018; Doucet et al., 2021), which might include the generation of carbon-bearing fluids/melts via low-degree carbonatitic melting, dehydration of subducted slabs and metallic melt inclusions of Fe-Ni-C-S from subducted serpentinites or iron disproportionation reactions (Smith and Nestola, 2021). Palot et al. (2017) have indicated that both reduced and oxidized C-rich fluids from recycled crustal sources would favour the growth of sublithospheric diamonds. Once formed, these diamonds are transported to mantle depths where they can be eventually carried by kimberlites and related rocks.

Types: Diamond are classified mainly on nitrogen impurities, but also colour, clarity, size, inclusion types, infrared spectroscopy (IR) and ultra-violet (UV) absorption are significant indicators (Breeding and Shigley, 2009 and references therein). Type I is the most abundant group (>98%) referring to diamonds that originated in the lithospheric mantle as described above. Both subtypes Ia and Ib contain high levels of N impurities (~5-3000 ppm; Kaiser and Bond, 1959; Tappert and Tappert, 2011), but in type Ia N variably occupies A and B centers of the crystal structure (IaB, IaAB, IaA), while type Ib has simple N substitution (Tappert and Tappert, 2011). Type II are mostly the much rarer sublithospheric diamonds with significantly low (< 5ppm; Tappert and Tappert, 2011) amounts of N; rare lithospheric diamonds can be classified as type II (e.g., Gurney et al., 2010). Subtypes IIa and IIb differ through colour and presence of impurities, being diamonds type IIa incolor and pure, and diamonds type IIb blue with 1-10 ppm of B (Smith et al., 2018).

A recently-proposed special category is the CLIPPIR (Cullinan-like, Large, Inclusion-Poor, Pure, Irregular and Resorbed diamonds (Smith et al., 2016, 2017, 2018), which can include a few type IIa. Their significance rests on the extraordinary environment of formation under highly reducing metal-saturated conditions in the deep mantle (360–750 km), supported by the presence of Fe-Ni-C-S metallic melt and a fluid layer of methane ± hydrogen (Smith et al., 2016); strain due to deep Earth conditions is observed in their internal structure. Additionally, they have particularly high economic value as gemstones due to the large size and high quality of the gems (e.g., Cullinan diamonds).

Secondary sources, from where?: For several years diamond primary sources have been explored with approached relying on the features described above, especially the presence of heavy-mineral indicators (HMI) such as harzburgitic garnets, commonly called G10 garnets (e.g., Schulze, 2003). However, in many localities such as the Alto Paranaíba diamondiferous field in Brazil, within the study area on the present work, the main source of diamonds is secondary (e.g., riverbeds) and the use of HMI or other methods has not yet provided clues about highly diamondiferous primary souces. The biggest challenges are not only recovering the original host-rock localities, but also definying a tectonic/genetic model for such a mixed reservoir which can include all types of diamonds. Those of subslithospheric origin especially disobey classification and formation criteria that traditional SCLM studies might provide.

Magmatic ore deposits

It is still a matter of debate whether or not the SCLM actively participates as a metal reservoir, which can potentially source magmatic ore deposits such as those exemplified in Figure 3b. Griffin et al., (2013) provide details of specific examples where traditional models account for other origins (e.g., crustal) rather than SCLM for the metals. Evidence about the major role of the SCLM in important deposits such as those of Ni, Cu and PGE elements (e.g., Bushveld) comes, for example, from the presence of metal alloys and sulphur in enriched xenoliths (e.g., Lorand and Luguet, 2016) and Re-Os results of sulphides in coexisting diamonds (Richardson and Shirey, 2008). Moreover, data from some gold deposits such as Iron-oxide copper-gold (IOCG) deposits (e.g., Groves et al., 2010) suggest that a combination of a mantle-sourced metal-rich region with trans-lithospheric zone(s) of weakness and a tectonic/thermal trigger could be a SCLM-based model (Griffin et al., 2013). More recently, other authors (Tassara et al., 2017) found native gold in mantle xenoliths from the SCLM beneath the Patagonia, Argentina, linking mantle refertilisation (plume-driven) with the formation of large auriferous provinces in the region. Another work in the same region (Tassara et al., 2020) demonstrated that redox gradients which oxidize melts during their ascent through the SCLM change such parameters as sulphur speciation and solubility that can boost the metal fertility of the system and thus the probability of forming large Au deposits. This emphasises the metallogenic significance of the SLCM not only for diamonds, but also for other world-class magma-related deposits, broadening the relevance of the present work.

1.4. Background

1.4.1. Diamonds: historical records and exploration projects

Records from the 19th century indicated the first occurrences of diamonds in Brazil close to ~1720 (e.g., Barbosa, 1991), in the washings of gold mines in the Diamantina district, eastern Minas Gerais. A report estimated a production reaching >10 million carats (cts) by 1850, with diamonds so abundant in the region that children could easily collect them in their backyards; Svisero (1995) indicated that the diamond production was near to 1,000,000 cts/year which was ~2% of the global production at that time. This favourable scenario placed Brazil as the global leader in diamond production for more than 150 years (see Svisero et al., 2017 for detailed historical record). In the Coromandel region, within the Alto Paranaíba Igneous Province (APIP) in western Minas Gerais, some of the most profitable deposits were recognized, with the notable discovery of several very large gem-quality diamonds (>50 cts; Figure 5; e.g., Svisero, 1995; Svisero et al., 2017) including the famous Presidente Vargas (726.6 cts), the largest from Brazil and one of the largest in the world, Darcy Vargas (460 ct) and Coromandel VI (400.7 ct).

However, all of these findings were in secondary (alluvial) sources and the first potentially economic kimberlite in the APIP was discovered only years later, through the efforts of the company SOPEMI; the pioneer Vargem-1 diatreme described by Svisero et al. (1977, 1986, 1995). Later, several other kimberlite prospects were identified along a corridor (Svisero et al., 1982) that was characterized by Gonzaga and Tompkins (1991) as the lineament of 125° Azimuth (see Chapter 2).

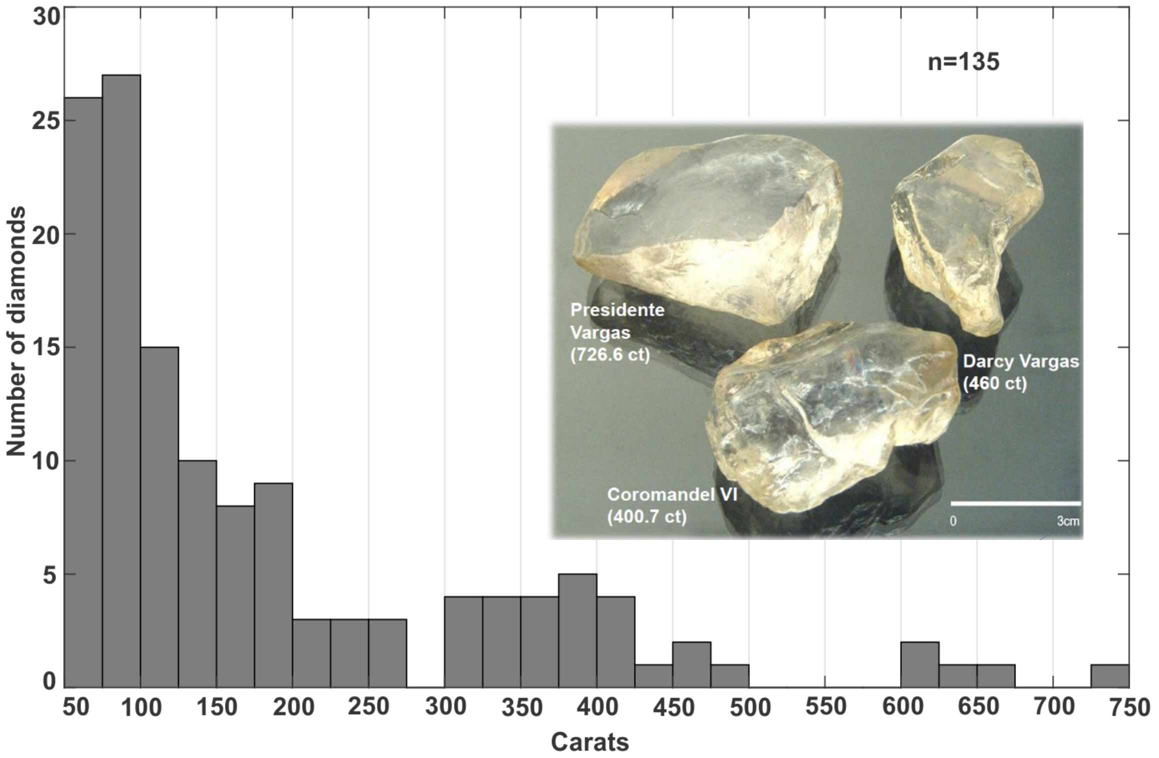

Figure 5. Frequency distribution of historically reported diamonds of >50 cts weight in the secondary sources of the APIP region and surroundings; weights are binned in 25-cts intervals.

The SOPEMI works were taken over by the De Beers Group, which carried out an extensive exploration program in the following years, revealing hundreds of other kimberlites in the APIP and other provinces. Other pipes were reported by Rio Tinto, Brazilian Diamonds, Vaaldiam and Prospec, Five Star Diamonds and other companies, including the Geological Survey of Brazil (GSB-CPRM) with the Brazilian Diamond Project (2011-2014). This significantly increased the number of known occurrences all over the country, but up to the present most gem-quality diamonds mined in Brazil are from secondary sources such as riverbeds and conglomerates. Nonetheless, a few diamondiferous kimberlites have been identified so far in Brazil, but only one kimberlitic field (Brauna kimberlites; Donatti-Filho et al., 2013a, b) is currently operating as a mine with average recovery grades ~24 carats per hundred tons (cpht; Lipari Mineração Ltda). Other diamondiferous kimberlites in the APIP and in other kimberlite fields in the same region (e.g. Canastra Highlands) are generally low to very low grade compared to worldwide deposits, and seem unlikely to have produced the large amounts found in secondary sources, nor the size of the gems. Morphological analyses showing an absence of mechanical transportation features in the diamonds suggest nearby primary sources (e.g., Kaminsky et al., 2001). According to Benitez (2009) most of the alluvial diamonds are above 2.1 cts and have octahedral and rhombododecahedral shapes; predominantly colourless to yellowish colours. There are many theories about the possible primary sources of these gemstones (e.g., Gonzaga et al 1994; Chaves et al., 2008a; Pereira et al., 2007, 2021), and some such as Gonzaga and Tompkins (1991) argued that diamonds found in Lower Cretaceous sediments are not correlated with kimberlite bodies in the APIP, while others proposed alkaline-carbonatitic complexes as main sources (Karfunkel et al., 2015). To date, this still a matter of intense debate.

1.4.2. Brazilian diamond project

The economic relevance of diamond deposits, the enigmatic nature of diamond occurrences in Brazil, and the petrological/geochemical/geophysical challenges to exploration, such as deep weathering, lead the GSB-CPRM to create the Brazilian Diamond Project which is the basis for the development of the present work. Systematic field work sampling alluvium materials and hard rock of kimberlites and related rocks previously identified was done over 4 years to create a library and a database (https://www.geoportal.cprm.gov.br/diamante/) of HMIs (Cr-pyrope, chromite, olivine), rock samples and diamonds (Figure 6); both donations from diamond companies and new samples are included. Apart from the bureaucratic aims of establishing the extent of Brazil’s natural resources, the project was expected to improve diamond-related geological knowledge and evaluate the new economic opportunities for the country.

The Project reached all regions from Brazil, over 20 mega-localities encompassing >400 geological maps. It was executed in three stages from data compilation and interpretation to the generation of new data (including geochemistry), to data integration. Currently, the database contains information on 1365 pipes including new discoveries of the Project (e.g., the Santa Fé pipes in the northeast of Brazil). In total, 1069 rock samples, 2160 heavy-mineral concentrates, 875 diamonds and >50 drill cores were recovered, and integrated with a very large dataset compiled from previous work, to generate several technical reports about diamond potential. These comprise the main features of the project that gave birth to the present work.

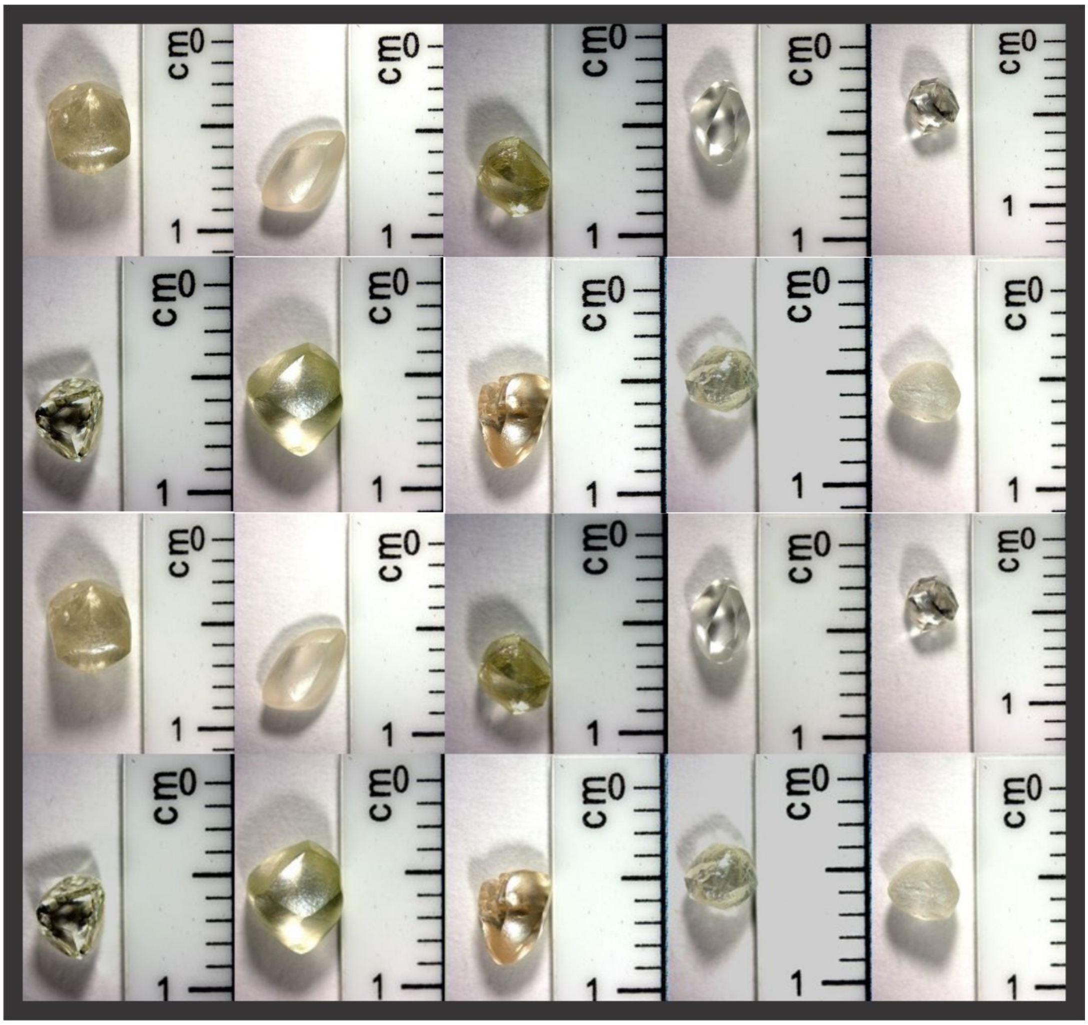

Figure 6. Alluvium diamonds from the SW-SFC. Samples donated to the Brazilian Diamond Project by diamond exploration companies.

CHAPTER IX. SUMMARY AND CONCLUSIONS

- For heavily weathered KKAC rocks, the combined use of microstructural, chemical and multiple techniques (major- and trace-element patterns, coexisting and cogenetic melts, oxygen fugacity, textures and heavy-mineral associations) is a promising approach to identifying parental magmas of resistate minerals.

- The cross-evaluation of multiple geochronometers, isotopic systems and methods, combined with textural and chemical evidence, has enabled more robust age interpretations as it allows identification of older xenocrysts in younger magmas, which represent only maximum intrusion ages.

- The filtering of new and published age data from the SW-SFC, using these principles, indicates that most KKAC rocks intruded in the period of 76-88 Ma (median = 81 Ma). “Cryptic” kimberlite magmatism, in which early magmas stalled and froze within the lithosphere, may have begun as early as 110 Ma. There is no significant difference in the intrusion ages of kimberlites, kamafugites and other KKAC magmas across the study area.

- The Cretaceous lithosphere in the SW-SFC had typical cratonic model geotherms (37.5-42.5 mW/m^2) and variable thickness (110-175 km) with short-range compositional variability over a large scale. The mean depth for the Base of the Depleted Lithosphere (BDL) is *ca* 140 km, ranging up to 175 km.

- The evolution of the SCLM below the AZ125, at least in the SW-SFC, started with originally cratonic Archean mantle, which was progressively modified by extension, subduction-related tectonism, intense metasomatism and refertilisation processes, reflecting multiple episodes of infiltration by both silicate and carbonatitic melts. The results provide a rare picture of craton-margin lithospheric erosion during continental collision and later magmatism related to continental dispersal.

- Relatively depleted mantle sections are found both on- and off-craton, confirming geophysical models showing cratonic lithosphere extending beneath the SBO, which has been overthrust by at least 150 km. The chemical tomography provides robust basis for geophysical data interpretation.

- The intense magmatism observed in the SCLM below the SW-SFC was controlled by a series of melt/fluid channels linked to lithosphere-scale discontinuities, especially in the Alto Paranaíba Igneous Province (APIP).

- The newly characterized Tecton-lherzolite (TL) trend identified from trace-element data indicates the physical mixing of inclusion of asthenospheric and lithospheric materials in extensional and/or compressional regimes.

- The values of oxygen fugacity calculated for perovskites of all textural classes lie within the broad range of cratonic mantle and kimberlites worldwide and of KKAC rocks in the SW-SFC. The fO_2 values of ΔFMQ -2 or lower from classes B and D perovskites probably represent the fO_2 of parental melts derived the from the deep lithosphere.

- Further information on fO_2 in the SCLM of the study region required the development and calibration of a new oxybarometer based on V/Sc in pyrope garnets (V/Sc^{gnt}). V/Sc^{gnt} is largely controlled by the partitioning of V/Sc between clinopyroxene and garnet, which varies with the changing of valence states of V as fO_2 decreases.

- In cratonic SCLM most depleted garnets define a sharp upper limit of V/Sc^{gnt} at each temperature, rising with depth toward the local BDL. The Craton Reference Line (CRL) may represent the primordial distribution of fO_2 in the Archean SCLM. Reworked SCLM (Protons and Proton/Archons) tends to show more scattered patterns and many grains lying above the CRL, while Tecton localities show very coherent low V/Sc^{gnt} that is independent of temperature.

- The V/Sc analysis of garnet populations shows that the SCLM below the study area is significantly more reduced at most depths than typical cratonic mantle, with more than half the analyses lying above the CRL. This probably reflects the introduction of reduced mantle-derived fluids into a thinner SCLM, with correspondingly less oxidation capacity. This difference in the overall fO_2 distribution of the SCLM may be a factor in producing the range of compositional differences among the KKAC magmas in the study region.

- Trends in V/Sc^{gnt} vs T also characterise different metasomatic processes. Phlogopite-related metasomatism, often linked to carbonatitic fluids, is more oxidizing than the asthenosphere-derived melt-related metasomatism; the removal of V during metasomatism also lowers the V/Sc^{gnt}.

- The timing and placement of the SW-SFC KKAC magmas are consistent with a geodynamics model (Gernon et al., 2022) in which kimberlitic magmatism is driven by interaction between the SCLM and convective instabilities generated during the rifting associated with the initiation of continental breakup. The magmatism thus can be interpreted as a far-field effect related to the opening of the South Atlantic Ocean (*ca* 127 Ma) in the last stages of Gondwana's breakup.

- These findings suggest that the alluvial diamonds of the region reflect secondary concentration of rare diamonds, survivors of the metasomatic processes, carried up in the very abundant low-grade KKAC pipes. The presence of large sublithospheric diamonds in the alluvial deposits can be related to the physical mixing of asthenospheric and lithospheric mantle proposed above. This analysis indicates that this region may host low-grade/high-value kimberlites, such as those in Northern Lesotho, requiring new exploratory frontiers to be opened. This also reveals novel pathways to other mineral resources linked to the SCLM, such as gold and other magmatic ores.

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