UNIVERSIDADE DE SÃO PAULO INSTITUTO DE GEOCIÊNCIAS

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Intensive (P-T-fO₂) crystallization parameters of Alto Paranaíba kimberlites and diamond instability: Três Ranchos IV and Limeira I intrusions

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Parâmetros intensivos de cristalização (P-T-fO₂) para rochas kimberlíticas da Província Alcalina Alto Paranaíba e a instabilidade de diamantes: kimberlitos Três Ranchos IV e Limeira I

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To my mother, Sandra.

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"We are all time travelers, traveling together into the future. But let us make that future a place we want to visit. Be brave. Be determined. Overcome the odds. It can be done."

(Stephen Hawking)

RESUMO

Foram estabelecidas as condições de fugacidade de temperatura (T), pressão (P) e fugacidade de oxigênio (*f*O₂) para os kimberlitos Três Ranchos IV (diamantífero) e Limeira I (LM-I, estéril) do supercampo kimberlítico Coromandel-Três Ranchos (Minas Gerais e Goiás, Brasil), da província alcalina Alto Paranaíba (APAP), com o intuito de determinar uma possível correlação entre tais parâmetros intensivos de cristalização e a instabilidade de diamante daqueles magmas. As intrusões Três Ranchos IV e Limeira I foram classificados como kimberlitos macrocrísticos coerentes, com textura inequigranular evidenciada por megacristais de olivina de até 1 cm parcialmente alterados, macrocristais de flogopita (0.5-10 mm) e xenólitos crustais dispostos em uma matriz muito fina composta principalmente por perovskita, olivina, flogopita, espinélio, serpentina e carbonatos em ambas as intrusões, com adição de apatita, ilmenita e monticelita apenas em LM-I. Macrocristais de granada e xenocristais centimétricos de piroxênio e também são fases minerais presentes em Três Ranchos IV e Limeira I, respectivamente. As amostras são todas ricas em MgO, com alto teor de Mg# e são fortemente enriquecidas em elementos incompatíveis.

Concentrações de elementos maiores, menores e traços das principais fases minerais foram obtidas por análises de Microssonda Eletrônica e LA-ICP-MS, com o objetivo de aplicar diferentes geotermo-e-oxibarômetros no cálculo das condições de P-T-fO₂ e caracterizar a variação composicional dos kimberlitos TR-IV e LM-I. Núcleos de olivina de Limeira I apresentam maiores teores de NiO, CaO e menores teores de Cr₂O₃ que os dos cristais de olivina de Três Ranchos IV. O Mg# [(Mg/Mg+FeT), em prop.mol.] calculado a partir das olivinas analisadas varia de 87 a 92 mol.% para TR-IV e de 83 a 92 mol.% para LM-I. O conteúdo de elementos-traço da olivina é semelhante para ambos os kimberlitos, sendo que as concentrações de Li, Zn e Mn parecem ser maiores nas bordas dos cristais de olivina. Nas olivinas das duas intrusões, foram observados tanto um padrão de enriquecimento em Zr, Ga, Nb, Sc, V, P, Al, Ti, Cr, Ca e Mn nas porções de borda, característico do "melt trend", quanto um enriquecimento em Zn, Co, Ni e possivelmente Na nas porções de núcleo, notável no "mantle trend". Os cristais de monticelita de LM-I apresentam Mg # variando de 72 a 93.8 mol.%, com o índice Ca/(Ca + Mg) variando entre 35-58 mol%. A composição dos cristais de perovskita de LM-I e TR-IV analisados permanece próxima do ideal CaTiO₃, mas é notável uma variação dos membros finais dos núcleos (Lop₁₆ e Prv₇₈ médios) às bordas (Lop₁₃ e Prv₈₁ médios) nas amostras de TR-IV. As maiores concentrações de elementos terras raras leves (ETRL), Nb e Fe³⁺ também são observadas nas perovskitas de TR-IV. Os macrocristais de espinélios em amostras de TR-IV são ricos em Al, enquanto os cristais da matriz variam de magnesiocromita a cromita. Cristais de ilmenita são identificados somente em LM-I, sendo caracterizados pelo alto teor de MgO, com grande variação nas concentrações de Cr₂O₃. As granadas são tipo piropo (62 a 73 mol.%) e estão presentes apenas em TR-IV, com Mg# variando de 72 a 79 mol.%, classificadas como lherzolíticas (G9) e piroxeníticas (G4, G5). O diopsídio ocorre como xenocristais em LM-I e como microfenocristais em TR-IV, com Mg# variando de 85 a 91 mol.% e de 87 a 92 mol.%, respectivamente. Os xenocristais de diopsídio presentes em LM-I apresentam maior concentração de MgO e FeO e são envoltos por coroa de monticelita.

As estimativas de temperatura do kimberlito LM-I foram obtidas utilizando as composições dos xenocristais de diopsídio e as concentrações de Al presentes em cristais de olivina, resultando em um intervalo entre 718 e 985 °C. Enquanto que a pressão varia de 34 a 47 Kbar e foi calculada utilizando uma curva empírica de uma geoterma de 37 mW/m² proposta na literatura para magmas da Província Alcalina do Alto Paranaíba. Para TR-IV foram obtidas temperaturas a partir das concentrações de Al em olivina e de Ni em granada, variando de 975 a 1270 °C. O intervalo de pressão de 18 a 34 Kbar foi obtido a partir da composição dos principais elementos em granada amostrada de TR-IV. A fugacidade de oxigênio registrada em perovskitas (fase cognata de kimberlito) de TR-IV varia de NNO-7 a NNO + 4, e de NNO + 6 a NNO-4 em LM-I. A monticelita, outra fase cognata, também foi utilizada como oxibarômetro, resultando em um intervalo de NNO-4 a NNO + 2 para a intrusão LM-I, onde está presente. Também é notável uma mudança na fugacidade de oxigênio dos núcleos para a borda em perovskitas e em cristais de monticelita. As estimativas de fO_2 obtidas neste trabalho foram as primeiras calculadas para magmas da província alcalina do Alto Paranaíba. Todos os resultados de P-T- fO_2 obtidos são consistentes com dados da APAP reportados na literatura.

Os xenocristais de clinopiroxênio em LM-I foram classificados como clinopiroxênio de fácies granada de acordo com as composições obtidas neste trabalho. Essa informação, juntamente com os dados de pressão e temperatura, além da presença de Mg-ilmenita em LM-I (conhecido por ser estéril), indica que este magma kimberlítico pode ter ao menos cruzado o campo de estabilidade do diamante, e que é possível que a variação na fugacidade de oxigênio observada em ambos TR-IV e LM-I pode ter-se refletido na instabilidade destes xenocristais nestes magmas, uma vez que Limeira I apresenta condições de oxidação levemente mais altas.

Palavras-chave: Kimberlitos; província alcalina Alto Paranaíba; Parâmetros intensivos de cristalização; Fugacidade de Oxigênio.

ABSTRACT

Temperature (T), Pressure (P) and Oxygen fugacity (*f*O₂) conditions were established for the Três Ranchos IV (diamond-bearing) and Limeira I (sterile) kimberlites of the Coromandel-Três Ranchos kimberlite field (Minas Gerais and Goiás, Brazil), Alto Paranaíba Alkaline Province (APAP), in order to draw a possible correlation between these intensive crystallization parameters and diamond instability. Both Três Ranchos IV and Limeira I are classified as coherent macrocrystic kimberlites, with an inequigranular texture formed by partially-to-fully altered olivine, phlogopite megacrysts up to 1 cm wide, macrocrysts (0.5-10 mm-sized), and crustal xenoliths set in a very fine groundmass composed mainly by perovskite, olivine, phlogopite, spinel, serpentine and carbonates identified in both intrusions. Apatite, ilmenite and monticellite are also present, but only in LM-I. Garnet macrocrysts and centimetric pyroxene xenocrysts phases are also present in Três Ranchos IV and Limeira I, respectively. The samples, strongly enriched in incompatible elements, are all MgO-rich, with high Mg# content.

In order to apply different geotherm-and-oxybarometers in the calculation of $P-T-fO_2$ conditions and to characterize the compositional variation of TR-IV and LM-I kimberlites, major, minor and trace-element concentrations of the main mineral phases were obtained by electron microprobe and LA-ICP-MS. Olivine cores of Limeira I present higher NiO, CaO and lower Cr₂O₃ contents than those from Três Ranchos IV. Mg# [(Mg/Mg+FeT), mol.%) ranges from 87 to 92 mol.% in TR-IV and from 83 to 92 mol.% in LM-I. The trace-element contents of olivine are similar in both kimberlites, the concentrations of Li, Zn and Mn appearing to be higher at olivine rims. In olivines from both intrusions, a pattern of enrichment in Zr, Ga, Nb, Sc, V, P, Al, Ti, Cr, Ca, and Mn in rims regions, is observed in the "melt trend" whereas enrichment in Zn, Co, Ni and possibly Na in cores regions, is found in the "mantle trend." In monticellite specimens from Limeira I, Mg# ranges from 72 to 93.8, while Ca/(Ca+Mg) ratios range from 35 to 58 mol.%. The perovskite composition in both LM-I and TR-IV remains close to the ideal CaTiO₃, perovskite, but a variation from core endmembers (average Lop₁₆ and Prv₇₈) towards the rims (average Lop₁₃ and Prv₈₁) can be noticed in TR-IV samples. The highest concentrations of light rare earth elements (LREE), Nb, and Fe³⁺ are also observed in perovskites from the TR-IV kimberlite. Macrocrystic spinels of TR-IV kimberlite are Al-rich, whereas the groundmass crystals range from magnesiochromite to chromite. Ilmenites from LM-I are characterized by high MgO values at a given TiO₂, with a large variation in Cr₂O₃. Pyrope garnets (62 to 73 mol.%) are present only in TR-IV, with Mg# ranging from 72 to 79 mol.%, being classified as lherzolitic (G9) and pyroxenitic (G4, G5). Diopside occurs as xenocrysts in LM-I and as microphenocrysts in TR-IV, with Mg# ranging from 85 to 91 and from 87 to 92, respectively. Xenocrystic diopsides from LM-I present higher MgO and FeO concentrations with monticellite grains along crystal rims and fractures.

Temperature estimates for the LM-I kimberlite, obtained from the composition of diopside xenocrysts and Al-in olivine concentrations, ranging from 718 to 985 °C. Pressure ranges from 34 to 47 Kbar, as calculated using an empirical curve from a 37-mW/m² geotherm proposed in the literature for Alto Paranaíba magmas. For TR-IV, temperature values ranging from 975 to 1270°C were obtained from Al-in olivine and Ni-in garnet concentrations. Pressures in the range from 18 to 34 Kbar were obtained from major element composition of garnet samples from TR-IV kimberlite. The fO_2 of the TR-IV constrained by perovskite (kimberlite cognate phase) oxygen barometry ranges from NNO-7 to NNO+4, while for LM-I values range from NNO+6 to NNO-4. For the LM-I intrusion, monticellite, another cognate phase used as an oxybarometer, yielded a value range of NNO-4 to NNO+2. A change in the oxygen fugacity from cores towards rim recorded in the perovskites and the monticellite crystals is also noticed. The oxygen fugacity estimates of this work are the first ever calculated for magmas of the Alto Paranaíba Alkaline Province. All P-T- fO_2 values obtained are consistent with literature data on the APAP.

Clinopyroxene xenocrysts from LM-I were classified as garnet-facies clinopyroxene, according to the compositions obtained in this work. Such results, along with pressure, and temperature data from and the presence of Mg-ilmenite in LM-I (known to be sterile), indicate that the kimberlite magma might have at least crossed the diamond stability field. The variation in oxygen fugacity observed in both kimberlites possibly reflects the instability of diamonds in these magmas since LM-I presents slightly higher oxidation conditions.

Keywords: Kimberlites; Alto Paranaíba Province; Intensive parameters of crystallization, Oxygen Fugacity.

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CHAPTER 1 - INTRODUCTION

1.1 Theme Presentation

Kimberlites are ultramafic rocks formed from low-grade partial melting of deep (>150 km) mantle portions under high volatile pressure (Mitchell, 1986). Kimberlites are of remarkable scientific and economic relevance for providing a better understanding about the genesis and evolution of primitive magmas, and for being able to carry diamonds as they are emplaced into the upper crust (Mitchell, 1995).

Kimberlites record the highest known oxygen fugacity values of terrestrial magmas, a phenomenon related to the presence of deep oxidized sources and to the interaction of ferrous iron and carbon-fluid equilibrium during ascent (Canil & Bellis, 2007). The fO_2 of this type of magma mainly reflects the conditions of their source regions (Carmichael, 1991). Thus, kimberlites provide environmental information from depths greater than 200 km, as evidenced by the xenocrysts they bear. Moreover, in some cases the oxygen fugacity of kimberlite magmas can partially control the quality and the presence of diamonds in these rocks (Canil and Fedortchouk, 2001; Fedortchouk et al., 2005).

It is also known that other intensive variables (e.g., P-T) may have an important role in the presence of diamonds in kimberlites. During the ascent of kimberlite magmas, several processes such as decompression (Carmichael and Ghiorso, 1986), cooling, degassing, assimilation of crustal and mantle minerals (Sparks, 2013), crystallization (Carmichael and Nicholls, 1967) and interaction with crustal fluids (Ogilvie-Harris et al., 2009) can cause significant variations in pressure, temperature, volatile content, and oxygen fugacity (Ballhaus and Frost, 1994). Such processes can lead these magmas to experiment changes in mineral assemblages, mineral and melt compositions and physical properties (Ogilvie-Harris et al., 2009).

This research aims to calculate intensive crystallization parameters (pressure, temperature, and fO_2) in Cretaceous kimberlites of the Alto Paranaíba Alkaline Province (APAP) in eastern Brazil separated as either diamond-bearing or sterile occurrences. The APAP is one of the largest potassic-ultrapotassic provinces in the world (>15.000 km³; Gibson et al., 1995; Brod et al., 2000; Araujo et al., 2001; Comin-Chiaramonti and Gomes, 2005), consisting of a diversity of ultrapotassic rock types such as kimberlites, lamproites and large volumes of kamafugite fields, and several plutonic alkaline complexes with associated carbonatites (Brod et al., 2000). The rocks of the province have also been largely studied due to their economic

potential for industrial minerals and elements (e.g. diamonds from the Canastra 1 kimberlite, phosphorus, niobium, titanium and rare earth elements – REE) found as either residual phases or supergene enrichment over Catalão I e II, Salitre and Tapira carbonatite intrusions (Biondi, 2005; Cabral Neto et al., 2017; Comin-Chiaramonti et al., 2005; Guarino et al., 2013).

The ultrabasic potassic rocks generated by the Cretaceous alkaline magmatism that took place in the central and southeastern portions of the Brazilian platform are important in the understanding of the composition and evolution of the lithospheric and sublithospheric mantle in the region, from the study of xenoliths and xenocrysts samples from these magmas (e.g., Araujo et al., 2001; Bizzi et al., 1994; Brod et al., 2000; Carlson et al., 1996; Gonzaga and Tompkins, 1991; Junqueira-Brod et al., 2004, 2002; Leonardos and Meyer, 1991; Meyer et al., 1994; Meyer and Svisero, 1980). Many intrusions exhibit mineralogical and petrographic features of kimberlite or kamafugite but, due to new schemes and the reviewed classification and identification of different crystal populations (Araujo et al., 2001), a reevaluation of these rocks is necessary. Even considering the above-mentioned references, different levels of information correspond to well-known occurrences, especially in the Alto Paranaíba Alkaline Province, where mantle xenoliths and xenocrysts are abundant.

The Alto Paranaíba region is the second largest source of diamonds in Minas Gerais (Karfunkel et al., 2014; Svisero et al., 2017 and references therein). Among its hundreds of known kimberlite intrusions, 18 are estimated to be diamond-bearing occurrences. Examples are Alpha-9, Delta-18, Douradinho-11, Japecanga-6, Limpeza-5, Limpeza-19, Omega-1, Omega-9, Santa Clara-1, Três Ranchos-4, Três Ranchos-101, Três Ranchos-102, Três Ranchos-104 e Vargem-3 (Cabral Neto et al., 2017). Among the reasons that could explain the presence of diamonds only in a few bodies are: i) the depths at which magmas form; ii) variations in oxygen fugacity conditions, which would lead to greater unstabilization of the diamonds carried by these magmas; and (iii) local mantle heterogeneities that would allow sampling of certain minerals (such as diamond) possibly absent in other portions.

As detail study targets, we selected the Três Ranchos IV (TR-IV) intrusion, which is known to be a microdiamond-bearing intrusion, and the sterile Limeira I (LM-I) intrusion. In addition, contrasting the data acquired in this study with those from the literature, we can estimate the variation of the intensive parameters of crystallization for the whole Province. This research aims at understanding the behavior of such parameters in kimberlitic magmas and the reactions of these magmas with mantle xenocrysts (crystal-liquid reactions). Also, we discuss some possible implications associated with the diamond potential of these intrusions. In these

magmas, diamonds are considered xenocrysts that can be preserved in metastable conditions by the rapid ascent and crystallization of kimberlitic liquids (Mitchell, 1986). However, as demonstrated in experimental works, change of certain intensive parameters can lead to greater destabilization and reaction between xenocrysts and the magma (Canil and Bellis, 2007). This is a pioneering study of APAP rocks and the first approach to quantify especially the oxygen fugacity from cognate phases and to discuss the implications of the variation of this intensive parameter.

1.2 Overview of Kimberlites

Kimberlites are ultrabasic hybrid igneous rocks of potassic and ultra-potassic affinity (Mitchell, 1986). These lithotypes are extremely enriched in incompatible elements, occurring mainly in the interior of cratonic regions as undeformed dikes, sills, and pipes (Sparks et al. 2013). However, some aspects of kimberlite petrogenesis, such as the nature of the source, depth of melting, and their relationships with subcontinental-lithospheric mantle (SCLM) remain partially unsolved. This is mostly due to the presence of mantle/crustal xenocrysts and xenoliths that modify the primary composition of kimberlitic magmas, and also because of extensive post-emplacement alteration. (Berg and Allsopp, 1972; Mitchell, 1986; Paton et al., 2007; Kamenetsky et al., 2014). Knowledge of kimberlitic rocks has changed over the past decades. Several authors have attempted to define emplacement models based on petrological, mineralogical, textural and compositional studies (Arndt et al., 2010; Bussweiler et al., 2015; Cas et al., 2008a; Cas et al., 2008b; Clement and Reid, 1989; Jelsma et al., 2009; Kavanagh and Sparks, 2009; Mitchell, 1995; Russell et al., 2012; Scott Smith et al., 2013; Smith, 2017; Sparks et al., 2006; Wilson and Head, 2007). This topic presents a full overview of kimberlite evolution. Classifications, magma generation, and emplacement models are reviewed, and the evolution of their understanding by different authors is discussed.

The term "Kimberlite" was adopted as a reference to porphyritic mica-bearing peridotites first found in Kimberley, South Africa (Mitchell, 1986). Nonetheless, kimberlites from other regions have been more recently studied in an effort to improve the understanding of their genesis on a global scale. Detailed studies of the worldwide distribution of kimberlites demonstrated that they occur in cratonic regions within Archean basements (Dawson, 1989; Janse and Sheahan, 1995), but are also present in off-craton regions in all continents, in different emplacement settings. Diamondiferous members only occur in cratons, mobile belts or shields, underlain by thick subcontinental lithosphere mantle - SCLM (Jelsma et al., 2009). A

compilation of worldwide occurrences of diamond-bearing kimberlites is presented in Figure 1.

Mineralogically, geochemically, isotopically and petrographically, kimberlites can be divided into two main groups, Group I and Group II (Mitchell, 1995; Le Maitre, 2002; Becker and Le Roex, 2006). The first classification of kimberlites recognized two distinct petrographic facies in occurrences in South Africa: the basaltic (Group I) and the micaceous (Group II) types (Wagner, 1914). This classification was first revised by Mitchell (1970), who excluded the term "basaltic kimberlite" on the basis that kimberlites neither contain feldspar nor bear any genetic or mineralogical resemblance with basalts. The current reclassification of kimberlites was proposed by Smith (1983) contrasting two specific patterns of initial Sr, Pr and Nd isotopic compositions, named Group I e Group II Kimberlite.

Group I kimberlites comprise ultrabasic, volatile-rich (CO₂) and potassic rocks whose frequent macrocrysts (0.5-10 mm) and megacrysts (around 1-20 cm) set in a fine-grained matrix constitute a distinctive inequigranular texture (Mitchell, 1995; Le Maitre, 2002; Becker and Le Roex, 2006). In contrast, Group II kimberlites show closer affinity to lamproites and are rarer than Group I ones. They consist in ultrapotassic, peralkaline, and volatile-rich (H₂O) rocks with phlogopite macro- and microphenocrysts, with groundmass micas that vary in composition from "tetraferriphlogopite" to phlogopite (Le Maitre, 2002). Nevertheless, due to the lack of further studies, the definition of Group II kimberlites is not well established yet. Rocks of this clan were also named "orangeites" by Mitchell (1995, 1986) as they might not be classified as kimberlites due to their unique character and occurrence in the Orange Free State, South Africa.

Group II kimberlites are thought to derive from the metasomatized lithospheric mantle, which is unique to each continent, while Group I ones, originated from the asthenospheric mantle, show similar isotopic signature in each occurrence (Mitchell, 2006). Likewise, another difference between the two groups is the composition of the xenoliths and xenocrysts that they include. Group I kimberlites usually contain a broad range of mantle xenoliths (peridotites, metasomatized and shared peridotites), eclogites, MARID (Mica-Amphibole-Rutile-Ilmenite-Diopside) rocks, wherlites and a suite of megacryst minerals. Group II kimberlites incorporate sheared peridotites and metasomatized xenoliths, with rare or absent megacrysts (Field et al., 2008).

In general, the classification used for deposits is not consistent with the volcanology and genetic terminology. Most of it is not descriptive and is difficult to understand, yet kimberlites are volcanic deposits (Cas et al., 2008c). Nowadays, efforts have been made toward a new





approach to kimberlite classification (Cas et al., 2008b, 2008c). These terminologies will be described in the "Pipe formation and models" section.

1.2.1 Mineralogy

The broad mineralogical variation of kimberlites is caused by differentiation processes whereby minerals form from three distinct sources: (i) crustal/mantle xenocrysts and xenoliths (e.g. olivine, garnet, spinel, Cr-diopside, phlogopite, and diamond), that may be carried along with the arising magma; (ii) discrete nodule or megacryst suite; and (iii) phases crystallized from the kimberlite (Mitchell, 1986, Le Maitre, 2002). Although the term *xenocrysts* may offer an excellent understanding of mantle processes, most authors do not recommend it to be used in the definition of a kimberlite. The main mineral phases in kimberlitic rocks are olivine, phlogopite, monticellite, calcite, serpentine, ilmenite, diopside, spinels, perovskite, phlogopite, and apatite.

Olivine, volumetrically the most important constituent of kimberlites, is ubiquitous, deriving mainly from disaggregated mantle-derived peridotite or dunite (Clement, 1982; Mitchell, 1986; Arndt et al., 2010). Authors such as Mitchell (1970, 1986, 1995), and Clement et al. (1983) agree that olivine can occur as xenocrysts and 'primary' or phenocrysts. As the larger olivine crystals might have evolved from either xenocrysts (i.e. mantle-derived) or phenocrysts (i.e. melt-derived), Clement et al. (1984) proposed the use of the non-genetic term "macrocrysts" for the larger crystal suite (Kjarsgaard et al., 2010; Bussweiler et al., 2015). 'Macrocrysts' is used to describe large, sub-angular to rounded, single crystals or crystal aggregates with habit, undulose extinction and recrystallized grains that suggest a different origin to the kimberlite magma (Arndt et al., 2010). Another descriptive term is 'phenocrystic' olivine, which refers to smaller grains identified as sub to the euhedral strain-free crystals with planar faces (Arndt et al., 2010). Crystallized olivine corresponds to around 5 vol.% of kimberlites and originates from heterogeneous crystallization (Brett et al., 2009). It occurs mainly as rims on xenocrystic derived olivine. Fine-grained euhedral olivine crystals occur as a minor, up to 0.5% component, being related to homogeneous crystallization (Brett et al., 2009).

In general, both Group I and Group II kimberlites exhibit large rounded-to-anhedral crystals (e.g., olivine, phlogopite) set in a fine-grained matrix composed of several phase minerals (Table 1). The macrocryst and megacryst (some of which possibly xenocrysts) assemblage of Group I kimberlites is composed by anhedral crystals of olivine, diopside,

Table 1 - Summary of Group I and Group II mineralogical characteristics after Howarth et al. (2011).

	Group I	Group II
Olivine		
Macrocryst	Abundant	Common in unevolved kimberlite Rare in evolved kimberlite
Phenocryst	Common-sub/euhedral	Common – minor – sub/euhedral
Mica		
Macrocrysts	Minor phlogopite	Common phlogopite
<i>Microphenocrysts</i>	Rare phlogopite	Common phlogopite
Groundmass	Common phlogopite-kinoshitalite laths	Common phlogopite-tetraferriphlogopite (poikilitic plates)
Spinels	Abundant, large	Minor to rare.
	Typically, Mg-chromite zoned to Mg-ulvöspinel	Mg-chromite rarely zoned to Ti- magnetite
Monticellite	Common, may be pseudomorphed by carbonate or serpentine	Common in unevolved kimberlites, typically pseudomorphed by carbonate or serpentine
Diopside	Primary diopside absent may occur in contaminated groundmass	Microphenocrysts. Common to rare
Perovskite	Common, rounded-euhedral	Rare, subhedral to poikilitic
Apatite	Common to rare, euhedral prisms or acicular radiating aggregates	Common euhedral prisms and poikilitic plates
Melilite	Common - always pseudomorphed	Common — always pseudomorphed
Carbonates	Simple assemblages, common calcite, minor dolomite	Common calcite, common Sr–Mn–Fe dolomites, minor witherite, ancylite, and strontianite
Serpentine	Abundant secondary and primary in segregations	Common secondary
Sanidine	Absent	Groundmass in evolved kimberlite
K-richterite	Absent	Groundmass in evolved kimberlite
Aegirine	Absent	Groundmass in evolved kimberlite
Leucite	Absent	Groundmass in evolved kimberlite
K–Ba hollandite	Very rare	Common
Mn ilmenite	Rare	Common
Zr-silicates	Very rare	Common
Barite	Rare	Common
Megacrysts	Characteristic	Rare to absent

magnesian ilmenite, phlogopite, pyrope, Ti-poor chromite and enstatite, that is normally believed to have disaggregated from mantle-derived eclogite, lherzolite, harzburgite or metasomatized peridotite xenoliths (Table 1). Most diamonds are also found in this suite, but less commonly. Olivine macrocrysts are present in all but fractionated kimberlites (Mitchell, 1995; Le Maitre, 2002). Phases like magnesian ilmenite, diopside, olivine, Ti-pyrope, relatively poor Cr-enstatite (<2% Cr₂O₃) are classified as megacrysts. The fine-grained matrix contains primary euhedral-to-subhedral olivine, together with one or more of following phases: monticellite, phlogopite, perovskite, spinel, carbonate, apatite, and serpentine. Late-stage poikilitic micas of the barian phlogopite kinoshitalite series are is also common in this clan of kimberlites. Serpentine and calcite are the most abundant alteration minerals, replacing earlier-formed olivine, monticellite, apatite and phlogopite (Mitchell, 1995; Le Maitre, 2002).

The primary mineralogical difference between Group I and Group II kimberlites is the amount of phlogopite, which is more abundant in Group II ones. This phase occurs as macrocrysts, microphenocrysts, and groundmass, composing around 50% of the assemblage (Mitchell, 1995). The chemical composition of the phlogopites is also distinctive between both types. Group II phlogopite is lower in Al₂O₃ (4-11 mass%) and higher in FeO (10-15 mass%) than Group I phlogopite (Mitchell, 1995).

1.2.2 Geochemistry

Kimberlites are MgO (20-38%) and CaO (5-14%) rich, Al₂O₃ (<3%) and Na₂O (<0.3%) poor ultrabasic rocks (SiO₂ <35%) with high LOI and mg# and potassic to ultrapotassic in character. Their K₂O ratio can reach about 7% in Group II kimberlites due to the increase in the amount of phlogopite (Clement, 1982; Mitchell, 1986, 1995). In general, Group I kimberlites also contain higher TiO₂, CaO, and CO₂, and lower SiO₂ and K₂O contents than Group II ones (Figure 2). Kimberlites also show lower Al₂O3 and Na₂O amounts than other basic and alkaline rocks (Becker and Le Roex, 2006).

Because of their hybrid nature, the geochemistry of kimberlites is complex. Their primary character is often modified by secondary post-emplacement alteration and by the presence of upper mantle and/or crustal xenoliths (Mitchell, 1986; Le Roex et al., 2003). Thus, whole rock geochemistry results do not represent the rock's primary composition, but that of a mixture with xenoliths (olivine) and alteration phases (serpentine, carbonate). Clement, (1982) proposed a contamination index (C.I) to estimate these combined effects in kimberlites. C.I. is the contamination index expressed by (Equation 1).

$$C.I = [(SiO_2 + Al_2O_3 + Na_2O) / (MgO + 2K_2O)]$$
(1)

It is known that crustal contamination raises SiO₂, Al₂O₃ and Na₂O contents relative to MgO, and that emplacement alteration extracts MgO from the rock to form clay deposits and hydrous phases with SiO₂ and Al₂O₃ (Mitchell, 1986). Likewise, higher contamination ratios lead to a much larger SiO₂ + Al₂O₃ + Na₂O than MgO + K₂O, resulting in higher C.I. When C.I. is close to 1, the sample is completely devoid of crustal contamination or alteration (Clement, 1982). Kjarsgaard et al. (2009) also suggested a C.I. = 1.5 as a contamination/alteration brink: samples with C.I.>1.5 will have enough crustal fragments and will have undergone substantial alteration, which compromises the bulk rock geochemical signature (Kjarsgaard et al., 2009).

Both Group I and Group II kimberlites are characterized by extreme incompatible element and light rare element (LREE) enrichment, moderate to heavy rare earth element (HREE) values, which indicates very low degree of partial melting of source, and simple linear (normalized) REE distribution and depletion (Mitchell, 1986; Le Roex et al., 2003; Davies et al., 2004; Harris et al., 2004; Chalapathi Rao et al., 2005; Becker and Le Roex, 2006; Coe et al., 2008; Felgate, 2014). Group II kimberlites are enriched in Pb, Rb, Ba, and LREE and show Cr and Nb depletion compared with Group I ones. As for Group I kimberlite, they are characterized by lower Ba/Nb (<12), Th/Nb (<1.1) and higher Ce/Pb (>22) ratios than the former (Felgate, 2014). The ratios of some trace elements in Group I (e.g. Ce/Pb, Nb/U, La/Nb, Ba/Nb, Th/Nb) indicates affinity to ocean island basalts (OIB). The ratios of some trace elements of Group I kimberlites (e.g. Ce/Pb, Nb/U, La/Nb, Ba/Nb, Th/Nb) indicates affinity to ocean island basalts (OIB). The ratios of some trace elements of Group I kimberlites (e.g. Ce/Pb, Nb/U, La/Nb, Ba/Nb, Th/Nb) indicates affinity to ocean island basalts (OIB). The ratios of some trace elements of Group I kimberlites (e.g. Ce/Pb, Nb/U, La/Nb, Ba/Nb, Th/Nb) indicates affinity to ocean island basalts (OIB). The ratios of some trace elements of Group I kimberlites (e.g. Ce/Pb, Nb/U, La/Nb, Ba/Nb, Th/Nb) indicates affinity to ocean island basalts (OIB). The ratios of some trace elements of Group I kimberlites (e.g. Ce/Pb, Nb/U, La/Nb, Ba/Nb, Th/Nb) indicates affinity to ocean island basalts (OIB). The ratios of some trace trace island basalts (OIB). Based on these ratios, Smith (1983) proposed that these rocks and OIB's share the same asthenospheric source in their genesis. Group I kimberlites also show refractory Mg numbers and Ni content akin to SCLM ones, which makes it difficult to attribute them to a simple convecting asthenospheric source (Becker and Le Roex, 2006).

The distinction between both groups of kimberlites in terms of isotope geochemistry is very difficult (Smith, 1983). Sr and Nd isotopic signature of Group I Kimberlites are sometimes slightly depleted, but very similar to the bulk earth, being the most indicative for isotopic studies in both groups (Sarkar, 2011). Group I kimberlites are less radiogenic in Sr (~0.703) and more radiogenic in Nd (~0.51260) as compared to the current Bulk Earth composition, showing OIB affinity. Group II kimberlites, on the other hand, are highly radiogenic in Sr (~0.707-0.712) and

Nd (~0.5124-0.5120) compared to the Bulk Earth composition, being associated with SCLM sources (Smith, 1983; Becker and Le Roex, 2006; Felgate, 2014).

Hf isotope geochemistry is an alternative method for differentiating between Group I and Group II kimberlites. Group I ϵ Hf_i¹ values vary from 5 to -10. In ϵ Hf_i¹ vs ϵ Nd_i¹ diagrams, Group I kimberlites plot well below the mantle array.² In Group II kimberlites, ϵ Hf_i¹ values range from -5 to -25, falling along the mantle array as their ϵ Nd_i values are more negative (-6 to -12) compared with those of Group I kimberlites. Negative Hf isotope signatures are evidence for sublithospheric kimberlitic source. Along with its megacrysts, the isotopic characteristics of Group I kimberlites require a source with low time-integrated Lu/Hf relative to Sm/Nd, which suggests an ancient source component (>1Ga) represented by deeply subducted oceanic basalts that became incorporated into the convecting mantle source region (Nowell et al., 2004).

On-craton and off-craton tectonic settings exert ambiguous control over the geochemistry of kimberlites. Group II kimberlites are characterized by small systematic differences in major and trace element and Nd-Sr isotope ratios between on-craton and off-craton settings, which suggests that both sources share similar evolutionary trends. Off-craton Group I kimberlites, on the other hand, show lower SiO₂ and MgO, but higher FeO, TiO₂, CaO, and CO₂ values than on-craton occurrences, possibly implying a derivation from more fertile mantle sources (Becker and Le Roex, 2006). Also, authors of experimental studies have proposed that partial melting at lower pressure decreases SiO₂ and MgO while increasing FeO, Al₂O₃, CaO and CO₂ contents (Herzberg, 1992; Dalton and Presnall, 1998; Gudfinnsson and Presnall, 2005; Becker and Le Roex, 2006). Such changes in major element composition are supported by the absence of diamonds in off-craton Group I kimberlites (Clifford, 1966; Becker and Le Roex, 2006), even when both types derive from within the garnet stability field, given similar fractionated HREE patterns.

1.2.3 Magma generation

The mantle conditions under which kimberlites are generated can be determined from experimental studies, geochemistry, xenolith, and xenocryst content, and also from the characterization of mineral inclusions. There are, however, some limitations. Kimberlitic magmas are most likely to undergo compositional changes as they arise, erupt or intrude the upper crust, being also commonly altered in near-surface (Sparks, 2013). Nevertheless, despite these ambiguities, a few concepts are well-established. Given their silica depletion and high incompatible trace elements contents, kimberlites may derive from very low-grade mantle

melts. These rocks form at depths that are great enough (~150 Km) for diamond stability conditions to be present, at temperatures higher than the volatile-enriched mantle solidus i.e., 1.350 to 1.450°C at the base of the lithosphere (Priestley et al., 2006; Sparks, 2013).

High pressures and temperatures in simplified mantle systems restrict kimberlite petrogenesis (Gudfinnsson and Presnall, 2005; Dasgupta and Hirschmann, 2006; Sparks, 2013). At high pressures, carbonated mantle (CMAS-CO₂, Carbonatitic Melts Along with Solidus) initially forms carbonatites as very low-degree melts at the solidus curve (Figure 2). Temperature increases while the accumulation of magma remains very low. From 200°C to 300°C above the solidus curve, magmas of kimberlitic affinity are generated, with the presence of a significant amount of silica (Sparks, 2013). However, kimberlitic magmas require generation temperatures of 1,500°C or higher in simplified experimental systems (Figure 2). Other components added to the experimental systems, such as Fe, alkalis, and water, can reduce the solidus to at least 100°C below the temperatures at which kimberlitic melts are generated. Such conditions are more consistent with temperatures estimated for the base of continental lithosphere (Sparks, 2013). An unresolved issue is that transitional kimberlitic melts with silica contents between those of carbonatites and basalts originate in narrow temperature ranges during the progressive partial melting of similar CMAS mantles. Other components, such as water, K and P may be responsible for the temperature ranges in which kimberlitic melts appear to form (Sparks, 2013).

Russell et al. (2012) suggested that kimberlites are generated by orthopyroxene assimilation during the ascent of the carbonate melts that represent their primary sources (Figure 3). Exsolution of CO₂ "depletes" the magma as it becomes enriched in silica and magnesium. This model explains the common absence of orthopyroxene xenocrysts in kimberlites. Olivine xenocrysts are typically found in kimberlites, being usually interpreted as originated from disaggregation of depleted mantle xenocrysts (harzburgites). Orthopyroxene crystals exhibiting dissolution textures related to reaction with carbonatitic kimberlites may occur (White et al., 2012; Sparks, 2013). Alternative reasons for the absence of orthopyroxene in kimberlites are that olivine xenocrysts originate from rupture of dunite rather than harzburgitic xenoliths and that orthopyroxene is unstable in water-rich kimberlitic melts (Mitchell, 2008; Arndt et al., 2010a; Sparks, 2013).

Carbonatite melts are common products of partial melting in carbonate-rich sources at pressures higher than 2.5 GPa (Russell et al., 2012). A few experimental studies have shown



Figure 2 - Schematic model of CO2 solubilities in silicic to carbonatitic melts (Brooker et al., 2011; Russell et al., 2012): (a) CO₂ solubility limits for silica-saturated and silica-undersaturated melts and hypothetical solubilities of carbonatite and kimberlite melts; (b) Pressure and composition dependence of CO₂ solubility across the carbonate-silicate transition. The effect of pressure (numbers on lines, MPa) on CO₂ solubility is limited compared with the effect of composition (SiO₂ and Al₂O₃). (c) Schematic model (Russell et al. 2012) of assimilation-induced fluid exsolution of carbonatite and proto-kimberlite melts. Orthopyroxene (Opx) assimilation drives non-silicate melts (left-hand side) to more silicic compositions (right-hand side), after Sparks (2013).



Figure 3 - Mechanism model of kimberlite ascent, showing: (a) Diverse ascent paths through cratonic mantle lithosphere (CML) shown as dashed arrows. Also shown is the line below which diamond is stable relative to graphite; (b) Melts produced by melting of carbonated peridotite transit mantle lithosphere as dykes by crack-tip propagation, liberating dense (sinking) xenoliths to the CO_2 -rich silica undersaturated melt, causing effervescence of buoyant (rising) CO_2 -fluid; (c) Xenoliths disaggregate and release individual mineral grains (for example, ol) to carbonatitic melt; opx grains are assimilated, preferentially promoting volatile exsolution. Deep-seated volatile production supports continued, crack-propagation-limited magma ascent; (d) Chemical evolution of melt during ascent. After Russel et al. (2012).

that the carbonated peridotite solidus melts at 2.5 GPa, and that it will be enriched in CO₂ but poor in SiO₂ as carbonate is stable in mantle assemblages. Such melts, that have been experimentally produced, contain over 40% dissolved CO₂ and are able to accommodate a large amount of H₂O (Russell et al., 2012). Likewise, Russell et al. (2012), suggested that the onset of kimberlites is marked by the asthenospheric production of such melts, (Figure 2a, b; (Canil and Bellis, 2008). Figure 3 presents a mechanistic ascent model that considers a carbonate-richmelt and the diversity of kimberlite compositions as the mechanical mixing of mantle olivine (70–80%) (Patterson et al., 2009; Russell et al., 2012). Modeling of the ascending melt chemical evolution is presented in Figure 3, it was interpreted that the amount of orthopyroxene assimilated is linearly related to the distance traveled in the mantle lithosphere, with assimilation and decarbonization essentially instantaneous (Russell et al., 2012). The interpretation of this ascension model is that there is a linear correlation between the amount of orthopyroxene assimilated and the upward displacement of the magma in the mantle lithosphere.

Recent advances in the study of kimberlite (Kavanagh and Sparks, 2009; Lensky et al., 2006; Russell et al., 2012; Sparks et al., 2009, 2007; Wilson and Head, 2007) have focused on the variety of the magma properties and the influence of volatile exsolution on magma ascent. Kimberlites are clustered in space and time (Field et al., 2008), which configures a set of clusters controlled by major structural features (e.g., southern African kimberlites have Jurassic and Cretaceous ages). Such features are unleashed by tectonic triggering mechanisms (Sparks, 2013). Two different approaches explain the spatial/temporal kimberlite clustering: a) kimberlites are generated in pulses as a response to mantle dynamics, the ascent of a deep mantle plume; and/or b) they are generated continuously, and special conditions such as craton deformation provide the trigger for the ascent. Torsvik et al. (2010) proposed that kimberlites are primarily related to old continental craton areas that overlie stable mantle plume sources at the core-mantle boundary (Sparks, 2013).

1.2.4 Pipe formation and models

Kimberlite intrusions are shaped and structurally controlled by the competency of the country rock. Because of their morphological appearance, they are generally referred to as *pipes* (Mitchell, 1986). The different zones that form a kimberlite pipe vary considerably in texture and mineralogy. Clement (1982) and Clement and Reid (1989) provided the basis for a first textural classification of kimberlites. They proposed that a typical kimberlitic pipe is composed

of three distinct zones: crater, diatreme (or pipe), and root. Textural and compositional characteristics specific to each zone separate a given intrusion into crater-facies, diatreme-facies, and hypabyssal-facies kimberlite, respectively. A simple, non-genetic terminology was suggested by Kjarsgaard (2007): volcanoclastic (VK, fragmental rock) kimberlites and hypabyssal (HK, non-fragmental rock) kimberlites (Figure 4). Volcanoclastic kimberlitic rocks, in turn, can be subdivided into pyroclastic kimberlites (PK), resedimented volcanoclastic kimberlites (RVK), and massive volcanoclastic kimberlites (MVK) (Figure 5).

Coherent kimberlites can be either extrusive or intrusive, and their differentiation requires knowledge of their context. Extrusive examples include kimberlite lavas, which are far less abundant than their intrusive counterparts. Intrusive coherent kimberlites are usually restricted to root zones and diatreme facies, being represented by uniform homogeneous rocks, non-fragmental textures. They encompass hypabyssal (Clement and Reid, 1989) and magmatic kimberlites (Sparks et al., 2006). These rocks result of direct crystallization from kimberlitic magmas prior to degassing and fluidization (Clement and Reid, 1989), being well qualified to determine primary kimberlite compositions. Compelling evidence indicates that many examples intrusive coherent kimberlites are pyroclastic in origin and may have formed via welding processes (Brown et al., 2008b, 2008a; Crawford et al., 2009; Buse et al., 2011; Hayman and Cas, 2011; van Straaten et al., 2011).

Volcanoclastic kimberlites subdivide into pyroclastic kimberlites (PK), resedimented volcanoclastic kimberlites (RVK) and epiclastic kimberlites (EVK). These forms are restricted to crater facies and upper diatreme facies of pipes (Cas et al., 2008b; Felgate, 2014; Sparks et al., 2006). Pyroclastic kimberlites originate from explosive volcanic eruptions and are deposited by primary pyroclastic processes, displaying no indication of resedimentation. Generally deposited as tuff rings, they are very unconsolidated and limited in terms of preservation potential (Sparks et al., 2006). Resedimented volcanoclastic kimberlites contain eroded/abraded pyroclastic materials mixed with an-kimberlitic materials eroded from their country rocks. Such kimberlites are located in the peripheral portions of pipes within the crater facies. Epiclastic volcanic kimberlites are the final kimberlite type and the rarest. This type is commonly ascribed to kimberlitic materials (either volcanic or coherent) affected by surface processes, typically formed at the top of pipes within crater facies (Cas et al., 2008a; Felgate, 2014; Sparks et al., 2006).

The formation of a kimberlite pipe is destructive and results in a cavity that connects the upper crust and the Earth's surface. Such conducts usually consist of downward-tapering

Kimberlite Terminology



Kimberlite Pipe Zone, Infill and Facies Terminology

Pipe Zone		Pipe Infill Textural Interpretation		Kimberlite Facies	
Crater Zone	+	Volcaniclastic Kimberlite	=	Crater Facies	
	+	Pyroclastic Kimberlite	=	Crater Facies	
	+	Resedimented	=	Crater Facles	
		Volcaniclastic Kimberlite			
Diatreme Zone	+	Volcaniclastic Kimberlite	=	?? Facies	
	+	Tuffisitic Kimberlite	=	Diatreme Facies	
Root Zone	+	Hypabyssal Kimberlite	=	Hypabyssal Facies	

Figure 4 - Comparison of the three conventional kimberlite pipe models and the preexisting terminology associated with the in-filling deposits (modified from Field and Scott Smith, 1999): (a) Narrow, tapering, steep-sided southern African kimberlite model (Class 1). (b) Open bowl-shaped Canadian Prairies kimberlite body (Class 2). (c) Dual tapering to flaring Lac de Gras type kimberlite pipe model (Class 3). After Cas et al. (2008a).



Figure 5 - Components and textural aspects of coherent and fragmental volcanic and high-level intrusive rocks after Cas et al. (2008b).

structures that reach hundreds to thousands square meters in cross sections (Field et al. 2008). Sparks et al. (2006) proposed that kimberlites have an early waxing stage of eruption and that as the erupting magma is initially overpressured at Earth's surface, the cratering explodes. As the kimberlite pipe widens and deepens, the supply rate of explosively erupting magma remains high enough to any rock fragments that reach it from wall rock collapse to be removed by the high-speed magma flows (Sparks, 2013). Therefore, the space that corresponds to the pipe is mostly created before rock fragments are removed from it. Nevertheless, pipe enlargement and infilling may be contemporaneous during the eruptive magma activity (Sparks, 2013).

1.2.5 Volatile contents

Kimberlite magmas are usually assumed to be volatile-rich (Sparks, 2013), and some evidence may help constrain their actual volatile composition. Methods used to define the primary volatile composition of other magmas (e.g., directly from gas emissions from active volcanoes, melt inclusions, mineral assemblages) cannot be applied to kimberlites (Sparks, 2013). Direct evidence for CO₂ comes from the occurrence of igneous carbonate in some kimberlite intrusions and rare lavas, and from phlogopite indicating the presence of water (literature reviewed in Sparks et al. 2006). Kimberlites commonly contain high water and CO₂ contents, but these cannot be taken as primary magmatic volatile contents as they may be of secondary origin (Sparks, 2013). Experimental studies of possible kimberlite compositions at a variety of water, CO₂, and mixed water-CO₂ mixtures at moderate pressures give poor results in terms of reproducing primary mineral assemblages in order to help constrain volatile contents (Sparks et al., 2009; Brooker et al., 2011; Sparks, 2013).

1.3 Research Aims

The main question of this study regards the influence that intensive parameters such as pressure, temperature, and oxygen fugacity (T, P, and O2) might have on the greater instability of carried (or possibly carried) diamond xenocrysts when sterile and diamond-bearing kimberlite magmas from Alto Paranaiba Alkaline Province are compared with one other. A few specific goals established to support this discussion are: (1) the petrographical characterization of Três Ranchos IV (diamond-bearing) and Limeira I (sterile) kimberlites by focusing on mineral instability textures suggestive of intensive parameters changes during crystallization; (2) the characterization of major, minor and trace elements of TR-IV and LM-I kimberlites (bulk compositions) and their minerals in terms of compositional variation; (3) the

determination of temperature, pressure (through xenocrysts assemblage) and oxygen fugacity (through cognate assemblage) conditions of the kimberlite magmas based on the chemical composition of the main mineral phases of both intrusions; (4) calculation of the same intensive parameters for other intrusions of the province from available chemical data; (5) comparison of textures and reactions with new and available data in order to interpret the petrogenesis of the kimberlite magmas, by comparing them in terms of diamond preservation.

1.4 Study Area Location and Access

Três Ranchos IV and Limeira I intrusions are located in Goiás (GO) and Minas Gerais (MG) states in southeastern Brazil, respectively. TR-IV kimberlite occurs at the former Alagoinha farm, 8 km from Três Ranchos City (GO). From São Paulo (SP) Três Ranchos is mainly accessed through Bandeirantes (SP-348), BR-050 or Gustavo Capanema (GO-030) highways and secondary roads that lead to the intrusion (UTM: W 201787/ S 7972758). LM-I intrusion is located 28 km north of Monte Carmelo City MG. From São Paulo, Monte Carmelo is reached through Bandeirantes (SP-348), BR-050 and MG-190 highways and secondary roads that led to the kimberlite (UTM: W 239626/ S 7946091).

CHAPTER 7 - SUMMARY AND CONCLUSIONS

In the Alto Paranaíba Alkaline Province, especially regarding relations between P-T- fO_2 conditions, the main mineral phases chemistry and bulk rock geochemistry allowed for the differentiation of two kimberlite intrusions, one sterile and the other a diamond-bearing one (Limeira I and Três Ranchos IV, respectively). Several geothermobarometers were used in the calculation of these intensive parameters of crystallization, resulting in temperatures ranging from 718 to 985°C for Limeira I and from 975 to 1270°C for Três Ranchos IV. Pressure ranges in intervals of 34 to 47 Kbar and 18 to 34 Kbar for the kimberlites, respectively. In Três Ranchos IV, fO_2 constrained by the perovskite oxygen barometry ranges from NNO-7 to NN+4, while in Limeira I it ranges from NNO+6 to NNO-4. The results are compatible with those available of APAP in literature.

The Três Ranchos IV and Limeira I are coherent macrocrystic kimberlites, with an inequigranular texture formed by partially-to-fully altered olivine, phlogopite megacrysts up to 1 cm wide, macrocrysts (0.5-10 mm-sized), and crustal xenoliths set in a very fine groundmass composed mainly of perovskite, olivine, phlogopite, spinel, serpentine and carbonates, and also apatite, ilmenite and monticellite in LM-I. Garnet macrocrysts and centimetric pyroxene xenocrysts are also bearing phases in Três Ranchos IV and Limeira I, respectively.

Both Limeira I and Três Ranchos IV kimberlites are ultrabasic rocks that are MgO-rich, high Mg#, CaO-rich, Al₂O₃-poor, Na₂O-poor and potassic to ultrapotassic in composition (K_2O = 0.9–1.6 mass% and 0.7-1.2 mass% respectively). The high LOI is largely due to the abundant presence of volatile-bearing phases such as carbonates, serpentine, and phlogopite. All major element values are supported by literature data. The relatively low K₂O is a typical characteristic of uncontaminated kimberlites worldwide. The kimberlites are strongly enriched in incompatible elements.

The olivine Mg# values, which range from 87 to 92 mol.% in Três Ranchos IV and from 83 to 92 mol.% in Limeira I, are consistent with the olivine compositions from APAP kimberlites (82-92 mol.%). Olivine cores of Limeira I present higher NiO, CaO and lower Cr₂O₃ contents than those of Três Ranchos IV. Most cores fall within the "mantle trend". Although rim compositions are representative from "melt trends", this trend is only identified in a few olivines of TR-IV and LM-I, that show extensive serpentinization around crystals, with rims that may not be preserved. The "melt trend" shows enrichment in Zr, Ga, Nb, Sc, V, P, Al, Ti, Cr, Ca, and Mn, whereas enrichment in Zn, Co, Ni and possibly Na in the "mantle trend" is

observed in both kimberlites. In Limeira I, monticellite Mg# ranges from 72 to 93.8 mol.%, while Ca/(Ca+Mg) ratios range between 0.35-0.58 mol.%.

Perovskite compositions in both Limeira I and Três Ranchos IV remain close to ideal CaTiO₃, yet a variation in endmember compositions from cores is noticeable (TR-IV: average Lop₁₆ and Prv₇₈; LM-I: average Lop₅ and Prv₉₁) towards the rims (TR-IV: average Lop₁₃ and Prv₈₁; LM-I: average Lop₄ and Prv₉₂). In TR-IV and LM-I, perovskite compositions are characterized by relatively high concentrations of Sr, Nb, Zr, and REE and a strong positive correlation between Nb and Ta; Nb and Zr; Mn and Fe. The primitive mantle-normalized REE patterns of the perovskite from both kimberlites have smooth, highly fractionated trends, with extreme LREE enrichment and no Eu anomalies.

The macrocrystic spinels of the Três Ranchos IV kimberlite are Al-rich, whereas groundmass crystals range from magnesiochromite to chromite. The ilmenite from Limeira I is characterized by its high MgO content at a given TiO₂, with a large variation in Cr₂O₃. Garnet is present only in Três Ranchos IV, identified as pyrope (62 to 73 mol.%) with Mg# ranging from 72 to 79 mol.%. The crystals correspond to lherzolitic (G9) and pyroxenitic (G4, G5) garnets according to the Cr₂O₃ and CaO contents. Clinopyroxene occurs as xenocrysts in Limeira I and as microphenocrysts in Três Ranchos IV, and are identified as diopside with Mg# ranging from 85 to 91 and from 87 to 92, respectively. The xenocrystic clinopyroxene from Limeira I presents higher MgO and FeO concentrations.

The Limeira I clinopyroxene xenocrysts analyzed in this work are identified as garnetfacies ones (Mg-rich chromium diopsides with moderate Al and low tschermacks contents), which can be interpreted as mantle xenocrysts derived from disaggregated garnet-facies lherzolite xenoliths.

This indicates that the magma that originated the intrusion, which is known to be sterile, must at least have crossed the diamond stability field. It is possible that the variation in oxygen fugacity observed in Limeira I and Três Ranchos IV kimberlites may have reflected in the instability of diamonds in these magmas since LM-I presents slightly higher oxidation conditions, thus not being diamondiferous. However, diamond oxidation during groundmass crystallization may have been too slow due to the lower T and the short time for kimberlite emplacement to have notable effects on diamond preservation.

CHAPTER 8 - REFERENCES

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