UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL
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HETEROGENEIDADE MANTÉLICA NA FONTE DA PROVÍNCIA MAGMÁTICA PARANÁ: NOVA EVIDÊNCIA DE 128 Ma DA PROVÍNCIA KIMBERLÍTICA ROSÁRIO DO SUL, BRASIL

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Obrigado Miro.

RESUMO

O presente trabalho representa um e estudo petrográfico detalhado, as primeiras análises de elementos maiores e traços de rocha total, dados isotópicos Sr-Nd e idade U-Pb em CaTi-perovskitas para o kimberlito Rosário-6 da Província Kimberlítica de Rosário do Sul (PKRS). Esta área está localizada na borda da Bacia do Paraná, sul do Brasil e representa o melhor afloramento de PKRS, sendo a única com amostras de rocha coesa. Mineralogia primária do kimberlito Rosário-6 compreende duas gerações de cristais de olivina: fenocristais (<2 mm) e macrocristais (>2 mm), alem de microcristais de CaTi-perovskita, apatita, ilmenita e flogopita em menor proporção, em uma matriz ígnea composta por flogopita, serpentina, Cpx, carbonato e óxidos de Fe-Ti. A rocha apresenta vários megacristais sub-arredondados de olivina (>1 cm) e lapilis centimentricos, alem de uma fase tardia de cristais poikiliticos de serpentina e carbonato. Com base na análise elementos maiores e traços classificamos estas amostras como de composição ultrabásica e ultrapotássica, relativa baixa alteração (CI até 1.5) e pequena heterogeneidade química entre elas, baixa dispersão em diagramas binários. A geoquímica é similar aos kimberlitos do Grupo I, tais como Mg# ~80, MgO ~21%, SiO_2 ~32%, CaO ~12%, K_2O ~2%, Ni = 717-800 ppm, Nd = 87.3-106.7 ppm, Ba/Nb<12, La/Nb<1.1, Ce/Pb>22 e Th/Nb<0,14. Geoquímica de elementos traço incompatíveis como LILE, HFSE e ETRL e composição isotópica Sr-Nd sugerem origem de manto sublitosférico ou mais profunda. O modelamento geoquímico sugere baixo grau de fusão de uma fonte de manto depletado e metassomatisado com cerca de 0.5% de líquidos carbonatíticos. A idade U-Pb em CaTi-perovskitas resultou em 128±8 Ma (MSWD = 3.7) para o kimberlito Rosário-6, o que está de acordo com os últimos eventos magmáticos relacionados com o auge do vulcanismo continental da Província Paraná no sul do Brasil. Este trabalho fornece novas evidências sobre o enriquecimento em elementos incompatíveis da fonte e heterogeneidades no manto presente na formação desta Província Ígnea e sobre a intrusão da PKRS em um ambiente extensional.

ABSTRACT

We report here a detailed petrographic study, the first whole-rock major and trace element geochemical analyses, Sr-Nd isotope data and U-Pb CaTi-perovskite age for the Rosário-6 kimberlite from the Rosário do Sul Kimberlitic Province (RSKP). This area is located on the edge of the Paraná Basin, Southernmost Brazil and represents the best outcrop from RSKP, being the unique with cohesive rock samples. Primary kimberlite mineralogy of Rosário-6 comprises two generation of olivine crystals: phenocrysts (<2 mm) and macrocrysts (>2 mm) in a groundmass composed by serpentine, CaTi-perovskite, clinopyroxene, phlogopite, apatite, carbonate and Fe-Ti oxides. The rock presents several sub-rounded megacrysts of olivine (>1 cm) and lapillitic components, and has a late-stage of poikilitic serpentine and carbonate crystals. Based on major and trace elements analysis we classified these samples as ultrabasic and ultrapotassic composition, with relative low alteration (CI up to 1.5) and small chemical heterogeneity without dispersion in all binary diagrams. The whole-rock geochemistry correlates well with most Group I kimberlites, such as Mg# ~80, MgO ~21 wt%, SiO_2 ~32 wt%, CaO ~12 wt%, K_2O ~2 wt%, Ni = 717-800 ppm, Nd = 87.3-106.7 ppm, Ba/Nb<12, La/Nb<1.1, Ce/Pb>22 and Th/Nb<0.14. Incompatible trace elements variations, such as LILE, HFSE and LREE, and Sr-Nd isotope composition suggest sublithospheric mantle or deeper origin. Geochemical modeling corroborates to the hypothesis of very low partial melting degree of a depleted mantle previously enriched with nearly 0.5% of carbonatitic liquids. U-Pb CaTi-perovskite age yielded a highly precision emplacement age of 128±8 Ma (MSWD=3.7) for Rosário-6 kimberlite, which is in agreement with the latter magmatic events related to Paraná continental flood basalt volcanism in the Southernmost Brazil. This work provides new evidences for the incompatible element enrichment and heterogeneities in the mantle source of this important Large Igneous Province formation and the emplacement of RSKP in an extensional environment.

SUMÁRIO

SOBRE A ESTRUTURA DESTA DISSERTAÇÃO

Esta dissertação de mestrado está estruturada em torno de artigos publicados em periódicos ou publicações equivalentes. Consequentemente, sua organização compreende as seguintes partes principais:

a) Introdução sobre o tema e descrição do objeto da pesquisa de mestrado, onde estão sumarizados os objetivos e a filosofia de pesquisa desenvolvida, o estado da arte sobre o tema de pesquisa.

b) Artigos publicados em periódicos ou submetidos a periódicos com corpo editorial permanente e revisores independentes, ou publicações equivalentes (capítulo de livro de publicação nacional ou internacional com corpo de revisores independentes), escritos pelo autor durante o desenvolvimento de seu Mestrado.

c) Anexos, compreendendo: artigo(s) nos quais o pós-graduando é co-autor, resumo(s) e artigo(s) publicado(s) em eventos, relacionado(s) ao tema central da dissertação, bem como documentação pertinente de natureza numérica (tabelas, cálculos), gráfica (figuras, diagramas, mapas, seções) e fotográfica que, por sua dimensão e/ou natureza não pode ser incluída no(s) artigo(s).

INTRODUÇÃO

O presente trabalho refere-se a uma dissertação de mestrado na área de geoquímica do Programa de Pós Graduação em Geociências, do Instituto de Geociências, da Universidade Federal do Rio Grande do Sul– PPGGeo - IGEO, UFRGS. Seguindo as normas vigentes sobre a estrutura de dissertação em formato de artigo exigida pelo PPGGeo, esta dissertação está estruturada em torno do artigo "**Mantle heterogeneity on the source of Paraná continental flood basalts: new evidence from 128 Ma Rosário do Sul Kimberlitic Province, Southern Brazil**", submetido em 14/11/2015 para publicação na revista Lithos.

Para este estudo foram utilizadas técnicas de investigação como microscopia petrográfica, microscopia eletrônica de varredura, acoplada a um sistema de energia dispersiva (MEV-EDS) e difração de Raios-X (DRX), para descrição das texturas e reconhecimento dos minerais; fluorescência de Raios-X (FRX) e espectrometria de massa acoplada a um plasma induzido (ICP-MS) para detalhar a composição química de elementos maiores e traços da rocha; espectrometria de massa térmica (TIMS), para determinar as razões dos pares de isótopos Rb-Sr e Cid e então caracterizar a fonte do magma. Para obter a idade de formação deste do kimberlito foi escolhido o método de análise isotópica U-Pb *in situ* em fenocristais de CaTi-perovskitas utilizando-se um espectrômetro de massa acoplado a um plasma induzido e a um feixe de laser (LA-ICP-MS) e o padrão GJ-01 de zircão foi utilizado, na falta de um padrão especifico para perovskita. Todas as análises foram feitas nos laboratórios do Instituto de Geociências da UFRGS com exceção da FRX e ICP-MS, que foram realizadas no "*The Earth Resources Research and Analysis - Department of Earth Sciences, Memorial University of Newfoundland (MUN)*", no Canadá, por uma integrante do grupo de pesquisa.

O estudo foi realizado com base em uma ocorrência de rocha kimberlítica que faz parte do cluster Rosário do Sul. Esta ocorrência foi denominada Rosário-6 e contem a única exposição de rocha coesa ate então. O objetivo deste trabalho é investigar a Província Kimberlítica de Rosário do Sul (PKRS) do ponto de vista petrográfico, geoquímico e isotópico de Rosário-6, caracterizando as fontes desse magma, os seus processos de diferenciação, e alguns aspectos do regime de intrusão dessa rocha. Alem disso, este trabalho pretende mostrar o potencial dessas rochas como fonte de informação sobre o manto litosférico do sul do Brasil e servir de base para outros estudos sobre a PKRS.

Mesmo com o crescente estudo sobre rochas kimberlíticas nos últimos dez anos, acentuado pelo valor compensatório do diamante, pouco se sabe sobre os seus processos de origem e formação. A partir de estudos feitos alguns avanços petrogenéticos podem ser apresentados: 1) existem diferentes fácies de kimberlitos; 2) kimberlitos são formados a partir de magmas de alta temperatura e ricos em voláteis; 3) kimberlitos podem passar por diferenciação e este processo resultar na formação de uma gama de rochas, o chamado "clã kimberlítico"; 4) os xenólitos lherzolíticos presentes nos kimberlitos contêm informações da profundidade de origem do magma parental (Mitchell, 1986). A origem desses magmas é comumente relacionada a processos de larga escala tectônica como, por exemplo: subducção de litosfera oceânica (McCandless, 1999), rifteamento de continentes (Phillips, 1988), ação de plumas mantélicas (Heaman & Kjarsgaard, 2000) e percolação de fluídos com alto teor em elementos voláteis (CO_2, H_2O, F) no manto litosférico e subastenosférico (Edgar et al., 1988). Esses processos podem atuar conjuntamente, ou de forma isolada, mas o refinamento desses modelos ainda merece mais investigações. O magmatismo kimberlítico está comumente relacionado a estruturas profundas, como falhas translitosféricas e grandes zonas de cisalhamento, como zonas favoráveis para sua ascensão.

Wagner (1914) classificou os kimberlitos em dois tipos: basáltico e micáceo. Essas terminologias foram baseadas principalmente em investigações microscópicas das rochas e, embora a petrografia de ambos os tipos tivesse diferenças substanciais, o único fator em comum que poderia associá-las era a presença de diamante e xenocristais mantélicos. A classificação dos kimberlitos em "Grupo I" e "Grupo II" surgiu baseando-se em dados isotópicos (Smith, 1983). O Grupo I é formado de kimberlitos derivados do manto astenosférico e constituídos principalmente de Olivina, serpentina e calcita, e uma razão $^{87}Sr/^{86}Sr$ baixa e $^{143}Nd/^{144}Nd$ alta. Enquanto os do Grupo II são rochas mais ricas em flogopita derivadas do manto litosférico com razões $^{87}Sr/^{86}Sr$ e $^{143}Nd/^{144}Nd$ mais altas e mais baixas respectivamente. Smith (1983 and 1985) apresenta diversos diagramas discriminatórios entre kimberlitos grupo I e II usando oxido de sílica, elementos traço e razoes de elementos traço e.g. SiO_2 vs. Pb, Th/Nb, Nb/La, Ce/Sr. A partir de estudos como em Fraser et al. (1985), Fraser (1987), Dawson (1987) e outros, ficou evidente que os Grupos I e II são mineralógica e quimicamente distintos e que o Grupo II tem uma maior semelhança com lamproítos que os kimberlitos do Grupo I. Seguindo essa linha de raciocínio Mitchell (1991, 1995) sugeriu que essas rochas derivam de magmas parentais distintos e que o grupo II deveria ser tratado como um outro tipo de rocha que não kimberlitos.

Kimberlitos estão espalhados pelo mundo, concentrando-se preferencialmente em regiões cratônicas, como na África do Sul (Kaapvaal craton), Oeste Africano (Man Shield), Índia (Dharwar craton), Canadá (Superior craton) e Austrália (Kimberly Block). No Brasil os kimberlitos são mais conhecidos na região central, distribuindo-se preferencialmente ao longo de dois lineamentos: o Azimute 125 e o Lineamento Transbrasiliano NE-SW. O primeiro é o principal lineamento em número de ocorrências kimberlíticas (ex. Província Ígnea Alto Parnaíba, Juína, Bambuí, Coromandel), enquanto que o segundo é conhecido pela sua extensão e por cruzar diversas faixas móveis e bacias (ex. Faixa Brasília, Faixa Araguaia, Faixa Paraguai, Bacia do Paraná, Bacia do Parnaíba). Este último originado durante o orógeno Brasiliano Neoproterozóico, quando os Crátons São Francisco e Amazônico se chocaram. Os kimberlitos, tais como Fazenda Largo e Redondão, teriam aproveitado esta estrutura (Tompkins, 1994).

No Rio Grande do Sul ocorrem raros corpos kimberlíticos e os que ocorrem foram pouco estudados, principalmente por não terem importância econômica e consequentemente tiveram baixa divulgação. Estes corpos ocorrem de maneira esparsa e ao longo da porção sudoeste e sudeste do estado. Na região sudoeste, as ocorrências de rochas kimberlíticas foram agrupadas na Província Kimberlítica de Rosário do Sul (PKRS; Edler et al., 1998). Nessa província são conhecidos 4 *clusters*: Rosário do Sul, São Gabriel, São Xavier e Capivaras, ocorrendo na forma de pipes, diques e soleiras. Por ser um litotipo que sofre intemperismo muito rapidamente, grande parte das ocorrências são encontradas através de um solo resultante característico ou por concentrado de minerais pesados diagnósticos. Na região sudeste existe o Diatrema Canguçu, a 200 km SE da PKRS, nessa região as rochas kimberlíticas intrudem as do Complexo Granítico-Gnáissico Pinheiro Machado, estas últimas com idades entre 758 a 575 Ma (Caldasso & Sander, 1994). Os corpos de kimberlitos desta região ocorrem distribuídos ao longo de estruturas com orientação NW-SE (Edler et al., 1998). Quando os corpos são plotados no mapa geológico da folha 1:250.000 de São Gabriel, constata-se que diversas ocorrências de kimberlitos se encontram concordantes à interseção do lineamento de Ibaré com falhas de direção NE. Estes dados corroboram os estudos realizados por Ribeiro (1980), que caracteriza a ocorrência de intrusões ultramáficas alcalinas junto às interseções de fraturas N25º-50°E e N25º-50°W, originadas no Pré-Cambriano e reativadas durante o Mesozóico. Caldasso & Sander (1994) descrevem a ocorrência de um corpo kimberlítico denominado de "Alfeu 1", entre cruzamentos de zonas de cisalhamento dúcteis N40°E, originadas no Pré-Cambriano, com falhas N35°-50°W. Isto enfatiza a importância da reativação de paleoestruturas como zonas favoráveis para a intrusão de rochas potássicas ultramáficas de afinidade alcalina, assim como em Phillipp et al. (2006). Os kimberlitos da PKRS ocorrem com inúmeros fragmentos de xenólitos, com formas arredondadas e alongadas, além de fenocristais e xenocristais de minerais máficos em uma matriz de tamanho de grão muito fino (Pires et al., 2010; Maciel et al., 2010). Segundo esses autores, os xenólitos são compostos por espinélio, perovskita, flogopita, granada e melilita. Os fenocristais máficos são essencialmente de olivina e a matriz é composta por serpentina, flogopita, carbonato, espinélio, perovskita, apatita e zircão.

O cluster Rosário do Sul foi revisitado e dentre mais de vinte ocorrências foi encontrado apenas um afloramento de rocha com amostras coesas denominado Rosário-6. No contexto tectônico, este cluster está localizado na borda sudoeste da Bacia do Paraná e encaixado em arenitos eólicos da Formação Pirambóia do grupo Passa Dois do Permo-Triássico. Rosário-6 apresenta em torno de 7m² de rocha aflorante, maciça e com forma aparentemente tabular próximo a uma drenagem que alimenta o Rio Ibicuí da Armada. A textura é inequigranular e conta com a presença de megacristais centimetricos em meio a uma matriz muito fina, mas esta proporção varia no afloramento. O grau de alteração é baixo, a textura foi bem preservada possibilitando um bom estudo petrológico. Existem poucos estudos sobre a PKRS e o corpo Rosário-6 ainda não havia sido estudado com detalhe, apenas em relatórios internos da CPRM com petrografia básica apenas.

Os dados de campo indicam que as rochas intrusivas do cluster Rosário do Sul pertencem ao clã kimberlítico, estão distribuídas preferencialmente em torno de um desvio no curso do rio Ibicuí da Armada. Estes estão tectonicamente posicionados na borda da Bacia do Paraná no arco de Rio Grande e alinhados com a zona de cisalhamento de Ibaré NW-SE no limite entre os Terrenos Taquarembó e São Gabriel com um azimute próximo de 125. Os corpos são encontrados como *pipes, plugs* e corpos tabulares. Rosário-6 pertence à fácies hipabissal no modelo clássico de Kimberlitos. A textura é claramente inequigranular com fenocristais, macrocristais e megacristais de olivina, alem disso, em menor proporção CaTi-perovskita, apatita e ilmenita. A matriz é muito fina e basicamente composta por serpentina, flogopita, Cpx, óxidos de Fe e Ti, além de apatita, calcita. A presença de grandes quantidades de lapilis centimetricos é uma característica importante. Assim como a petrografia a geoquímica de Rosário-6 é similar aos kimberlitos do Grupo I, com valores de SiO_2 e K_2O relativamente baixos, valores de TiO_2, Nb e razão Ce/Pb mais altos, alem de razões baixas de Th/Nb e La/Yb. Entretanto apresenta valores anômalos, semelhantes às das rochas do Grupo II como altos teores de Rb, Ba e Sr. Estas anomalias sugerem uma influencia de líquidos carbonatíticos na fonte de Rosário-6, provenientes de antigas placas subductadas que metassomatizaram a fonte dos kimberlitos. A idade de cristalização, determinada por U-Pb em CaTi-perovskita, resultou em uma idade de 128±8 Ma. Esta idade coincide com a época dos pulsos finais do vulcanismo basáltico da Bacia do Paraná que teve seu auge em ~132 Ma. As razões isotópicas iniciais $^{86}Sr/^{87}Sr$ e $^{143}Nd/^{144}Nd$ (baixa e alta, respectivamente) são claramente compatíveis com as assinaturas de kimberlitos Grupo I e outras litologias de origem astenosférica. Os dados geoquímicos e isotópicos sugerem uma fonte de manto depletado metassomatizado com líquidos provavelmente carbonatíticos. Para isso foi modelado uma fonte de composição mista entre um lherzolito (99.5%) e um carbonatito (0.5%), e que sob fusões de baixo grau (<2%) seriam capazes de gerar as rochas de Rosário-6.

Os próximos trabalhos nessas rochas deverão incluir a análise química de minerais, além de estudos de petrologia experimental, para desvendar a origem e a evolução desses magmas, além de tentar reproduzir as condições de formação deste kimberlito.

ARTIGO CIENTÍFICO

Mantle heterogeneity on the source of Paraná continental flood basalts: new evidence from 128 Ma Rosário do Sul Kimberlitic Province, Southern Brazil

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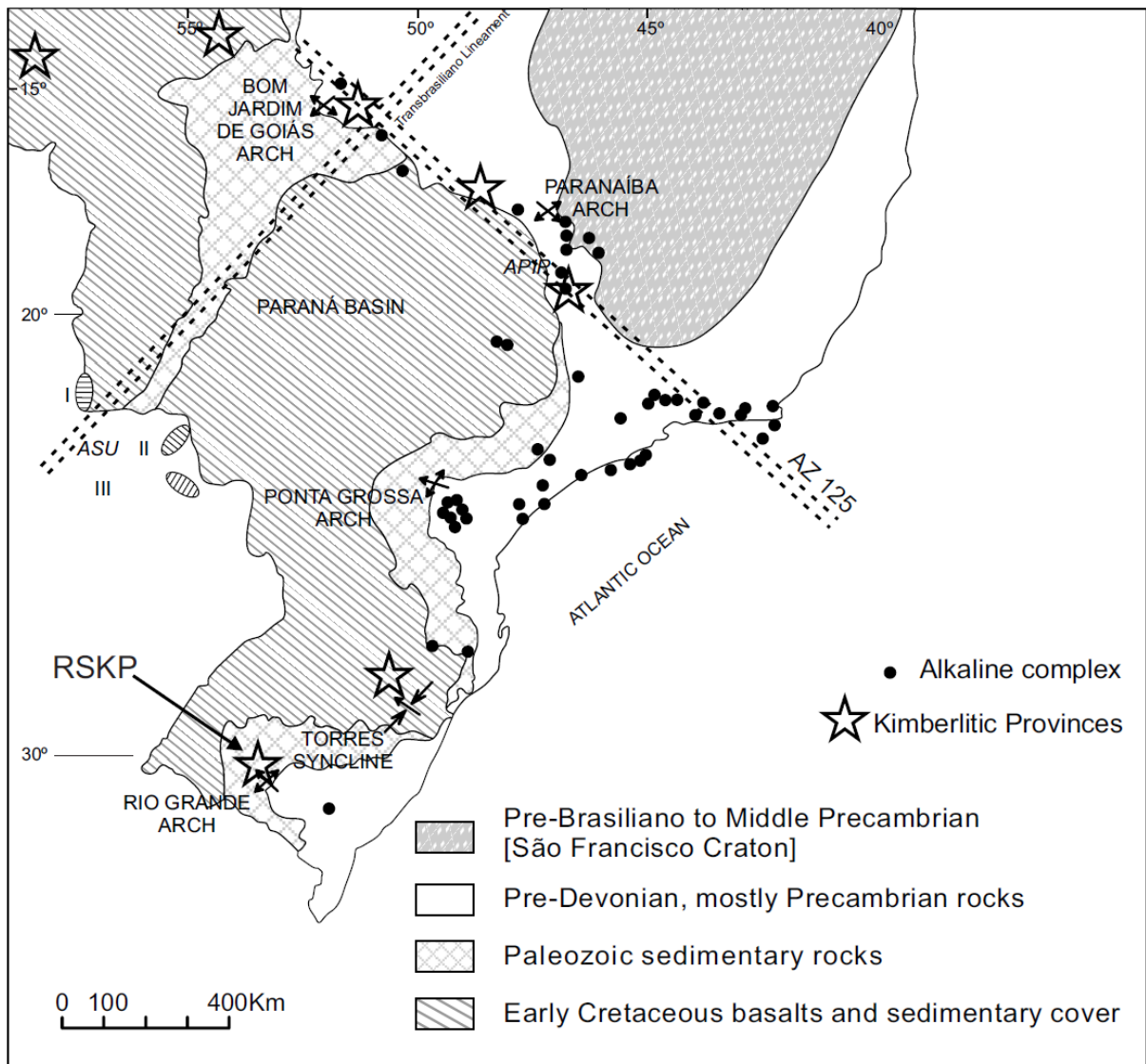
Abstract

We report here a detailed petrographic study, the first whole-rock major and trace element geochemical analyses, Sr-Nd isotope data and U-Pb CaTi-perovskite age for the Rosário-6 kimberlite from the Rosário do Sul Kimberlitic Province (RSKP). This area is located on the edge of the Paraná Basin, Southernmost Brazil and represents the best outcrop from RSKP, being the unique with cohesive rock samples. Primary kimberlite mineralogy of Rosário-6 comprises two generation of olivine crystals: phenocrysts (<2 mm) and macrocrysts (>2 mm) in a groundmass composed by serpentine, CaTi-perovskite, clinopyroxene, phlogopite, apatite, carbonate and Fe-Ti oxides. The rock presents several sub-rounded megacrysts of olivine (>1 cm) and lapillitic components, and has a late-stage of poikilitic serpentine and carbonate crystals. Based on major and trace elements analysis we classified these samples as ultrabasic and ultrapotassic composition, with relative low alteration (CI up to 1.5) and small chemical heterogeneity without dispersion in all binary diagrams. The whole-rock geochemistry correlates well with most Group I kimberlites, such as Mg# ~80, MgO ~21 wt%, SiO_2 ~32 wt%, CaO ~12 wt%, K_2O ~2 wt%, Ni = 717-800 ppm, Nd = 87.3-106.7 ppm, Ba/Nb<12, La/Nb<1.1, Ce/Pb>22 and Th/Nb<0.14. Incompatible trace elements variations, such as LILE, HFSE and LREE, and Sr-Nd isotope composition suggest sublithospheric mantle or deeper origin. Geochemical modeling corroborates to the hypothesis of very low partial melting degree of a depleted mantle previously enriched with nearly 0.5% of carbonatitic liquids. U-Pb CaTi-perovskite age yielded a highly precision emplacement age of 128±8 Ma (MSWD=3.7) for Rosário-6 kimberlite, which is in agreement with the latter magmatic events related to Paraná continental flood basalt volcanism in the Southernmost Brazil. This work provides new evidences for the incompatible element enrichment and heterogeneities in the mantle source of this important Large Igneous Province formation and the emplacement of RSKP in an extensional environment.

1. Introduction

Kimberlites are broadly known for being the host of diamonds. They are originated in the Earth's deep upper mantle, which make them an interesting and important source to better understand mantle evolution in such deep regions. The genesis of kimberlites and related rocks has been widely investigated all over the years (e.g. Clement, 1982; Rock, 1991; Mitchell, 1995). In summary, it has been ascribed to active-mantle plume processes (Heaman et al., 2004; Rao et al., 2011), continental extension events (Jelsma et al., 2004; Tappe et al., 2008), and/or to subduction processes (Currie and Beaumont, 2011). Considering their deep upper mantle genesis, kimberlites may bring samples from the mantle levels deeper than ≥ 140 km, and consequently transport mantle materials, e.g. diamonds, to the Earth surface. Kimberlites, together with their entrained peridotitic (dunite, harzburgite, lherzolite) and eclogitic (garnet, clinopyroxene) materials, provide a unique opportunity for investigating deep mantle processes (Pasteris, 1984). As reviewed by Rao et al. (2011 and references therein), kimberlites are defined as a "clan" of volatile-rich (dominantly CO_2) potassic ultramafic rocks that generally occur as volcanic pipes, small plugs, dykes and sills. These rocks are characterized by occurrence of distinctive inequigranular texture resulting from the presence of two generations of olivine, as well as other minerals (megacryst/macrocryst) including magnesian ilmenite, pyrope, diopside (subcalcic), phlogopite, enstatite and Ti-poor chromite. Kimberlites have ultramafic, potassic and volatile-rich features, with enrichment in both compatible and incompatible trace elements, which suggests a mantle source with a complex evolutionary history (Becker and Le Roex, 2006).

In Brazil, the occurrences of kimberlite rocks are small but the kimberlitic provinces are dispersed from each other (Fig. 1). Phanerozoic alkaline rocks, including kimberlites, are more common in the Central region of Brazil, distributed preferentially in the azimuthal trend known as "AZ 125", as well as in the NE-SW oriented Transbrasiliano Lineament (Gonzaga and Tompkins, 1991). The potassic and kimberlite magmatism activities during Mesozoic period in Brazil and Africa were associated to the opening of the South Atlantic along more than 2.000 km extension (e.g. Bardet, 1977; Bizzi et al., 1993; Gibson et al., 2006). Svisero and Chieregati (1991) present several kimberlite intrusions based on tracking of heavy minerals in the Alto Parnaiba Igneous Province (APIP) region, Central to Southeast and in South of Brazil. In these regions there are a large number of chimneys with diameters between 100 and 800 m large, generally covered by an altered soil. In the Southernmost Brazil, alkaline rocks are mainly concentrated in the central-eastern area of the Sul-riograndense Shield and intrude both the Phanerozoic covers around the Paraná Continental Flood Basalt (PCFB), and the Precambrian basement (Phillipp et al., 2006). These alkaline rocks are mainly phonolites and subordinate kimberlites/lamproites (Svisero and Chieregati, 1991; Tedesco and Robaina, 1991; Caldasso and Sander, 1994).

Figure 1. Simplified map of Kimberlitic Provinces, alkaline and alkaline-carbonatite complexes of Brazil modified after Morbidelli et al. (2000) and Svisero and Chieregati (1991). I, II and III correspond to Paraguayan alkaline occurrences (Alto Paraguay, Amambay and Central provinces, respectively).

The emplacement of the PCFB, which was accompanied by the intrusion of carbonatites and alkaline complexes in Brazil, was distributed in Santa Catarina, Paraná, Goiás, Mato Grosso and Minas Gerais states (Bell 2001; Le Roex and Lanyon 1998; Morbidelli et al., 2000; Pirajno 1994). Gibson et al. (2006) suggest the emplacement of some of these carbonatites and associated alkaline complexes in two phases: at 145 Ma and 127.5 Ma. These ages are correlated to the Paraná-Etendeka Large Igneous Province (LIP) at 134.6±0.6 Ma proposed by Janasi et al. (2011), Rocha-Júnior et al. (2012) and Thiede and Vasconcelos (2010). The occurrence of kimberlites in South Brazil, in Rio Grande do Sul state, was denominated by Edler et al. (1998) as Rosário do Sul Kimberlitic Province (RSKP).

This work presents the first age and the best study of a kimberlite rock from Rio Grande do Sul state which we consider to be the last melt associated with the Paraná-Etendeka LIP formation in southern Brazil. Based on the mineral assemblage and whole-rock geochemistry this kimberlite is more akin to South African Group I than other Brazilian kimberlites. U-Pb age data demonstrate that the kimberlite and some alkaline magmatism at South America were contemporaneous and occurred at the end of PCFB volcanism. The prime goal of this paper is to lay the groundwork for further detailed petrological studies on the RSKP that will certainly give more information about the mantle characteristics and its evolution beneath South American lithosphere.

2. Geological setting and field characteristics

The RSKP contain four clusters of kimberlitic/lamproitic rocks: São Gabriel, Capivaras, São Xavier and Rosário do Sul. The later were recently revisited, and we identified more than 20 occurrences, among pipes and plugs, all highly weathered. One little outcrop, however, stands out for its excellent rock preservation: Rosário-6, from the Rosário do Sul cluster and all petrographic and geochemical studies described in this work are based on Rosário-6 samples. RSKP fresh rocks are rarely found due to the high weathering and the large area of sedimentary cover. The rock terminology suggested by Cas et al. (2008, 2009) classifies the Rosário-6 rocks as a serpentinized subvolcanic aphanitic kimberlite with varying proportions of macro and megacrysts of olivine. The RSKP is located on southwestern edge of the Paraná Basin (Fig. 2). This study describes the occurrences of the Rosário do Sul cluster, principally based on samples from Rosário-6, the only known outcrop with cohesive rock from the RSKP.

The RSKP is mostly intruded in Phanerozoic sedimentary rocks of the Paraná Basin and occur distributed throughout NW-SE oriented structures, generally in the intersections of the Ibaré lineament and younger NE faults (Edler et al., 1998). These data corroborate with the studies of Ribeiro (1980), who characterized the occurrence of alkaline ultramafic intrusions along the intersections of N25-50E and N25-50W regional structures originated in the Precambrian and reactivated during the Mesozoic. Caldasso and Sander (1994) also described the occurrence of a small kimberlite pipe in the Canguçu Diatreme called "Alfeu Kimberlite", in the intersection of N40E Precambrian ductile shear zones and N35-50W faults. These studies demonstrate how important the early structures reactivations are for the intrusion of these potassic ultramafic rocks with alkaline affinity (Philipp et al., 2006). Structures such as the Ibaré shear zone, a transpressive and sinistral system (Heilbron et al., 2004), between Taquarembó and São Gabriel terrains, have directions consistent with those described by Edler et al. (1998) and Ribeiro (1980). This discontinuity between terrains may have been used as decompression region for the kimberlites ascension. The Rosário do Sul cluster has one occurrence with ~7 m^2 exposure of cohesive mafic rock extended by discontinuous E-W direction, intruded into Perm-Triassic sandstones of Paraná Basin, clearly disturbed and fractured due to this mafic intrusion called Rosário-6 kimberlite. The outcrop is thin (1-3 m thick), cohesive rock, massive and inequigranular with several crystal sizes ranging from megacrysts (≥1 cm) to phenocrysts (<2 mm) in a very fine groundmass. The distribution of these megacrysts in the outcrop is heterogeneous, with some parts with different proportions. Some of the hosted sandstones which are in contact with the kimberlite were undergone to a temperature reaction that gave them a metamorphic aspect reducing its porosity and increasing its rigidity. Near to this outcrop exist a sandstone with peculiar green color and columnar-like fractures originated due thermal interaction between the intrusive rock/fluids and its sedimentary host rock.

Figure 2. Geological map of Rio Grande do Sul State, South Brazil, and the tectonic domains. In detail is the cluster Rosário do Sul, around the Ibicuí da Armada river bends.

3. Samples and analytical methods

Several samples from Rosário-6 were collected for this study. However, after a careful examination, five samples were selected for geochemistry, based mainly on their textural representativeness, absence of megacrysts, lowest degree of weathering and lack of veins of any nature. Macro and micro petrographic analysis were performed in order to describe the mineral assemblage and textures. Mineral characterization was possible with whole rock X-ray diffraction (XRD) coupled with scanning electron microscopy (SEM/EDS) analysis. The techniques were performed in the laboratories of the Geosciences Institute (IGeo) at the Universidade Federal do Rio Grande do Sul (UFRGS; Brazil) and Westfälische Wilhelms Universität, Münster, respectively. Whole-rock major and trace elements analysis were conducted through X-ray Fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS), respectively; both methods were carried out in The Earth Resources Research and Analysis (TERRA) - Department of Earth Sciences of Memorial University of Newfoundland, Canada. Sr-Nd isotopic analysis using thermal inductive mass spectrometer (TIMS) for isotopic characterization; and U-Pb geochronology on CaTi-perovskites using Laser ablation coupled to an ICP-MS (LA-ICP-MS), in order to determine the crystallization age of these rocks, were performed in the Isotopic Geology Laboratory (LGI-UFRGS).

The XRD analyses were examined in powder form using a Siemens D-500 Diffractometer. Data were collected with CuKα radiation, an angular rate of 2° to 80° (2θ), a step of 0.05° and a counting time of 2s per step for all samples. Back-scattered electron images and EDS analysis were provided by a
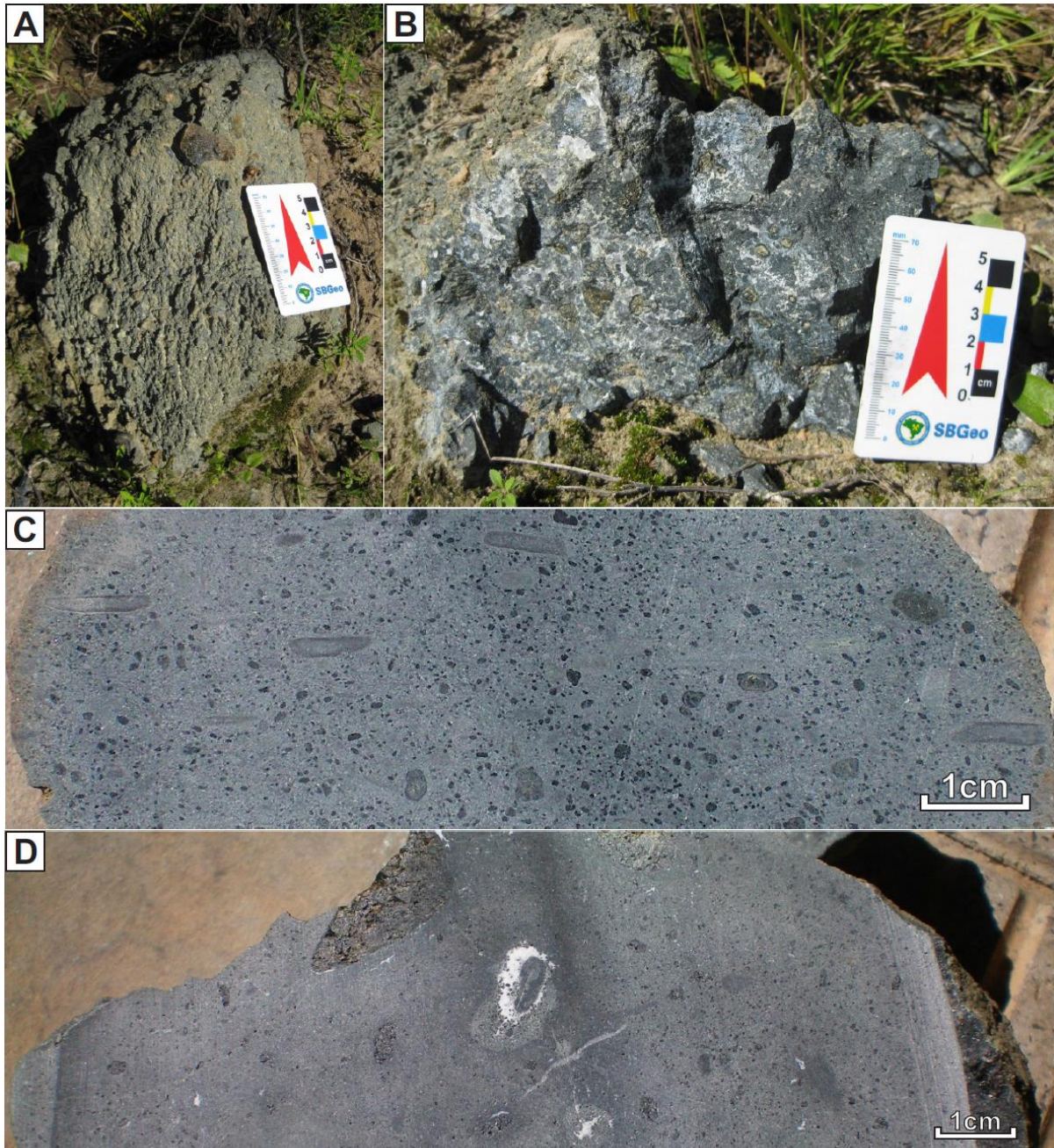
scanning electron microscope (SEM) JEOL-JSM 5800 with energy dispersive system — EDS, with an acceleration voltage from 0.3 to 30 kV; an image point resolution of 3.5 nm; a magnification range of 18× to 300.000× and a five-axis goniometric motorized stage. XRF major elements data were obtained using glass beads, which were prepared by mixing 1.5mg of rock powder with 6.0mg of lithium metaborate and 1.5mg of lithium tetraborate. The mixture was placed into a platinum crucible and a few drops of lithium bromide were added as a wetting agent. The crucibles were then placed in the Leco Fluxer and heated at ~850°C for 8.5 minutes and fused at ~1050°C for 11.5 minutes. The glasses were analyzed using X-ray fluorescence (Bruker S8 Tiger sequential wavelength-dispersive XRF).

For trace and rare earth elements analysis, 0.1g of sample powder were digested with the high pressure digestion technique developed by Diegor et al. (2001). The element concentrations were determined with an ICP–MS (PerkinElmer ELAN DRCII). The data acquisition was performed in a multichannel mode. Total counting time per mass, at one point per peak, was 10s; dwell time per mass was 0.05s. Three external standards were used with different elements with different concentrations each one, and one inner standard (Sc, In, and Re, U) with different concentrations each one. Indium was also used for drift correction. External standards, inner standard (standard addition) and surrogate calibration for Nb, Ta and Mo (Zr and Hf using), were the strategies to deal with the interrelated matrix, drift, and interference problems (Jenner et al., 1990). Data reduction was done offline using a spreadsheet from the laboratory. More details about the data acquisition are available in Jenner et al. (1990). Around 0.5 to 0.8 g of each sample was crushed in an agate mortar and leached with HCl 0.1 N in order to eliminate the crustal alteration. For isotopic analyses, 0.1g of leached residue was spiked with mixed ^{87}Rb–^{84}Sr and ^{149}Sm–^{150}Nd tracers and then digested with HF, HNO_3, HCl until complete dissolution. Then, the solution was completely dried and the residue was homogenized in 3ml of HCl 2.5N. Column procedures used cationic AG-50W-X8 (200– 400 mesh) resin in order to separate Rb, Sr and REE; and anionic LN-B50-A (100–200 Am) resin in order to separate Sm and Nd. Each sample was dried to a solid residue and then loaded with 0.25N H_3PO_4 (Rb, Sr, Sm and Nd), on appropriate filaments (single Ta for Rb, Sr, Sm, and triple Ta–Re–Ta for Nd). The samples were run in a multi-collector VG Sector 54 thermal ionization mass spectrometer in static mode. Sr and Nd ratios were normalized to ^{86}Sr/^{88}Sr=0.1194 and ^{146}Nd/^{144}Nd=0.7219, respectively. Measurements for the NIST standard NBS-987 gave ^{87}Sr/^{86}Sr=0.710260±0.000014, JNDI standard gave ^{143}Nd/^{144}Nd=0.512108±0.000010. Blanks were <60 pg for Sr, <500 pg for Rb, <150 pg for Sm and <500 pg for Nd. U-Pb in situ LA-ICP-MS analyses in CaTi-perovskite were performed in a Neptune Finnigan equipment. GJ-01 zircon standard was used, due to the absence of perovskite standards as described in Bühn et al. (2009). The laser was set up to produce a 30µ diameter spots with ~0.5 mJ/pulse output energy. The data reduction was performed using ISOPLOT 3.0 (Ludwig, 2003).
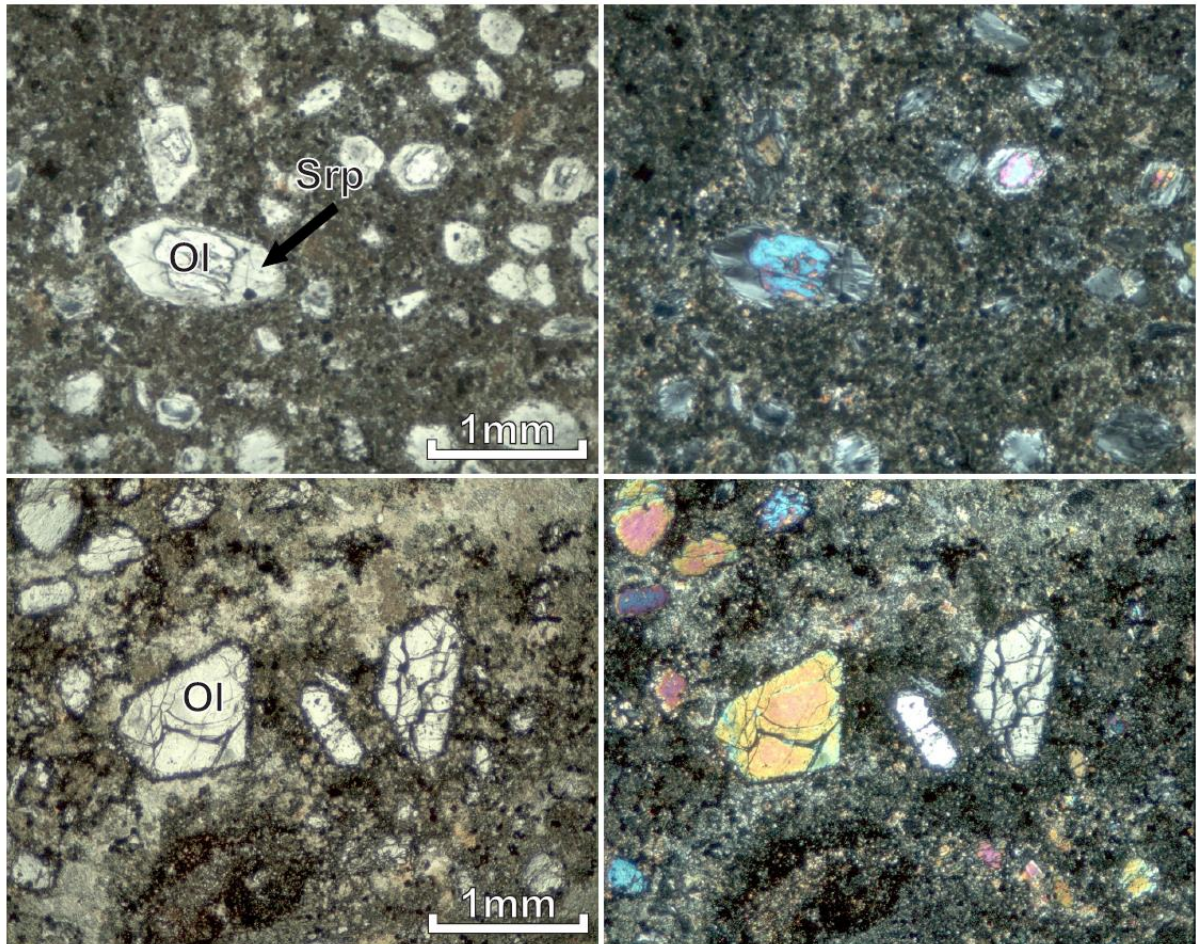
4. Petrography

Macroscopically, Rosário-6 kimberlite samples are cohesive, massive, and present a dark gray to green color. The samples used in this study are all fairly inequigranular with crystals immersed in an aphanitic groundmass. Megacrysts (>1cm) of olivine are commonly found in the samples (Fig. 3A to D). According to the classification of kimberlites intrusions proposed by Kjarsgaard (2007) and Cas et al. (2008), Rosário-6 is a hipabyssal body associated to root zone or a feeder magma dike. Thin-section analysis exhibits and identifies the "macrocrystic" nature of the rock, with >10% vol. of macrocrysts (>2 mm). These macrocrysts may have been derived from disaggregated mantle xenoliths (Clement et al., 1984; Le Roex et al., 2003).

Figure 3. Characteristic macrotextures of Rosário-6 Kimberlite: A) outer cape of the kimberlite outcrop; B) high concentration of xenocrysts sample; C) inequigranular texture with some imbricated lapilli's; D) macrocrystic sample slice with the presence of olivine megacryst (on top) in the very fine groundmass and carbonatic alteration (middle).
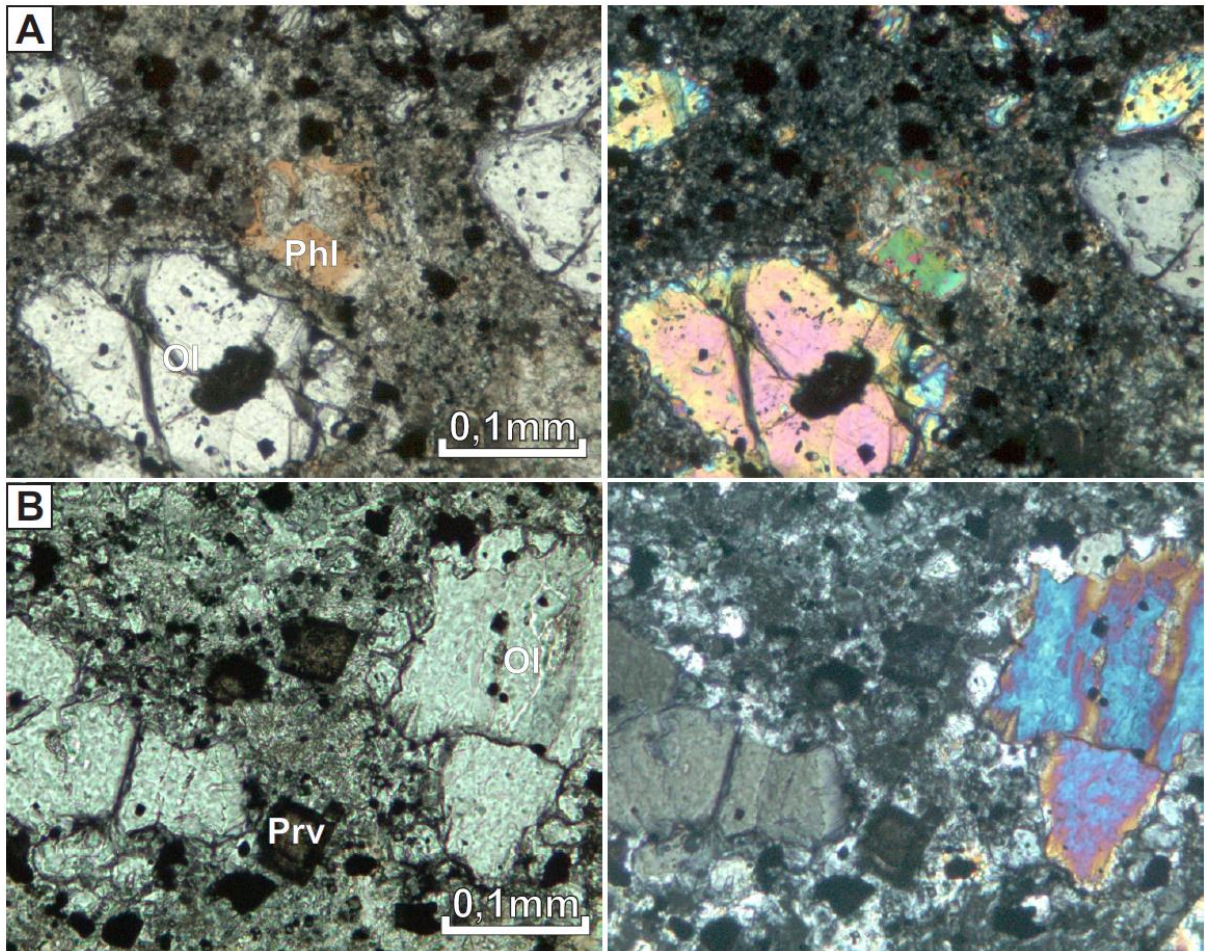
The rock presents phenocrysts of olivine, CaTi-perovskite, ilmenite and minor apatite in a very fine groundmass. Olivine is the most abundant phenocryst phase in the groundmass (Fig. 4A) ranging in size from 0.5 to 2 mm, and with two visible types of crystal habit: euhedral and subhedral, the latter with sub-rounded and corroded edges. Fractures, oxide inclusions and kink bands are common feature among the olivine macro and megacrysts. The phenocrysts of olivine are generally partially or completely replaced by serpentine in most samples. Phlogopite phenocrysts are almost absent, when founded they are completely or partially altered (Fig. 5A).
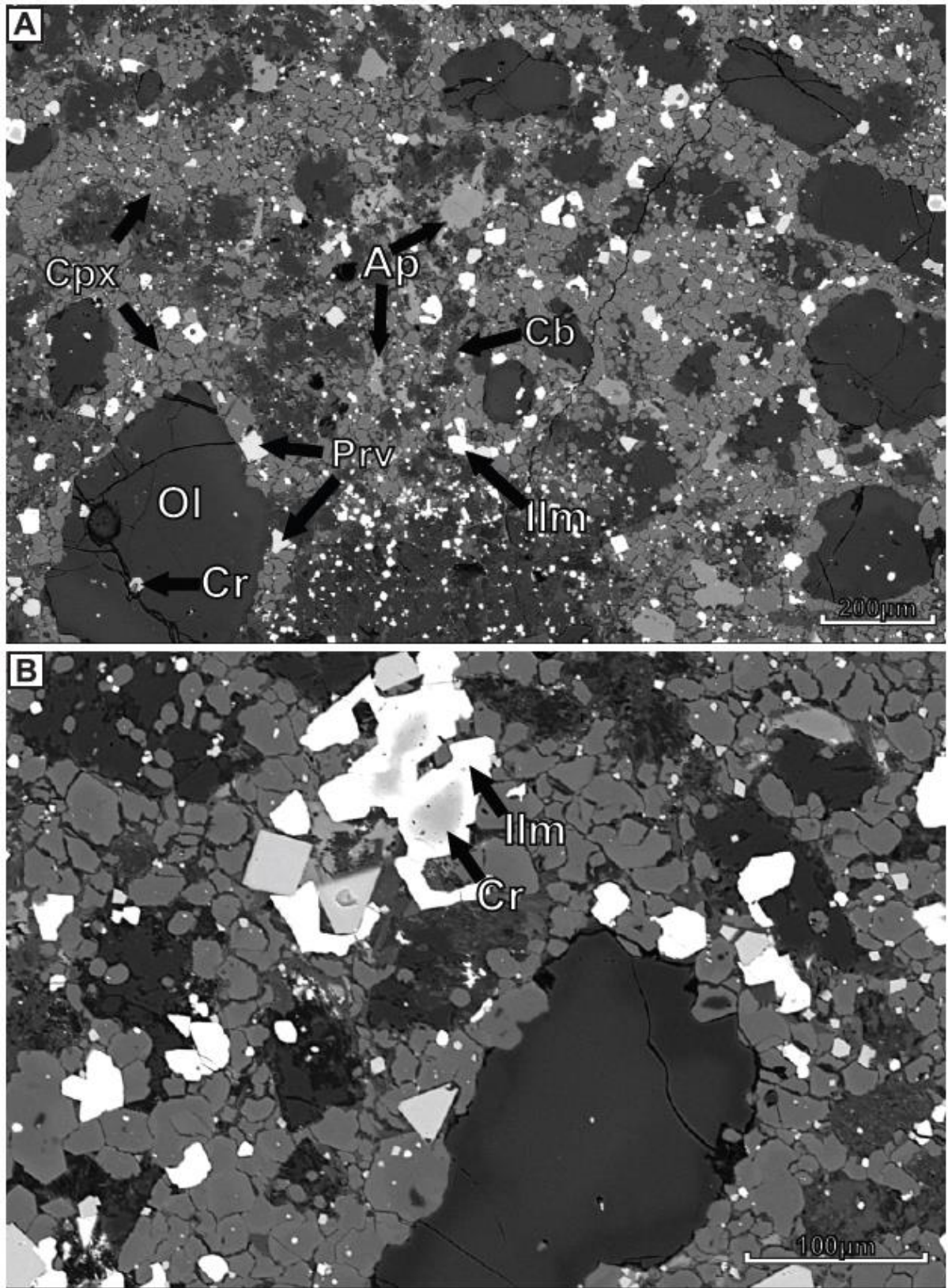

Figure 4. Petrographic features of Rosário-6 Kimberlite. A) partially serpentinized olivine phenocrysts; B) euhedric and subhedric olivine phenocrysts in a segregationary groundmass. Left: Plane polarized light; Right: Cross-polarized light. Ol = olivine, Srp = Serpentine.

The CaTi-perovskite phenocrysts are very small, well dispersed and normally euhedric (Fig. 5B). The groundmass is basically composed by microlites of serpentine, clinopyroxene, phlogopite, olivine, apatite, Fe-Ti oxides and some carbonate. Despite weathering, some samples have fresh phenocrysts and segregation texture preserved as well (Fig. 4B). The Figure 6A and B show refined images from electronic microscopy of the groundmass of Rosário-6 kimberlite. The groundmass seems heterogeneous, with segregationary texture and/or an advanced reabsorption around phenocrysts and also destabilization processes of dissolution and recrystallization.
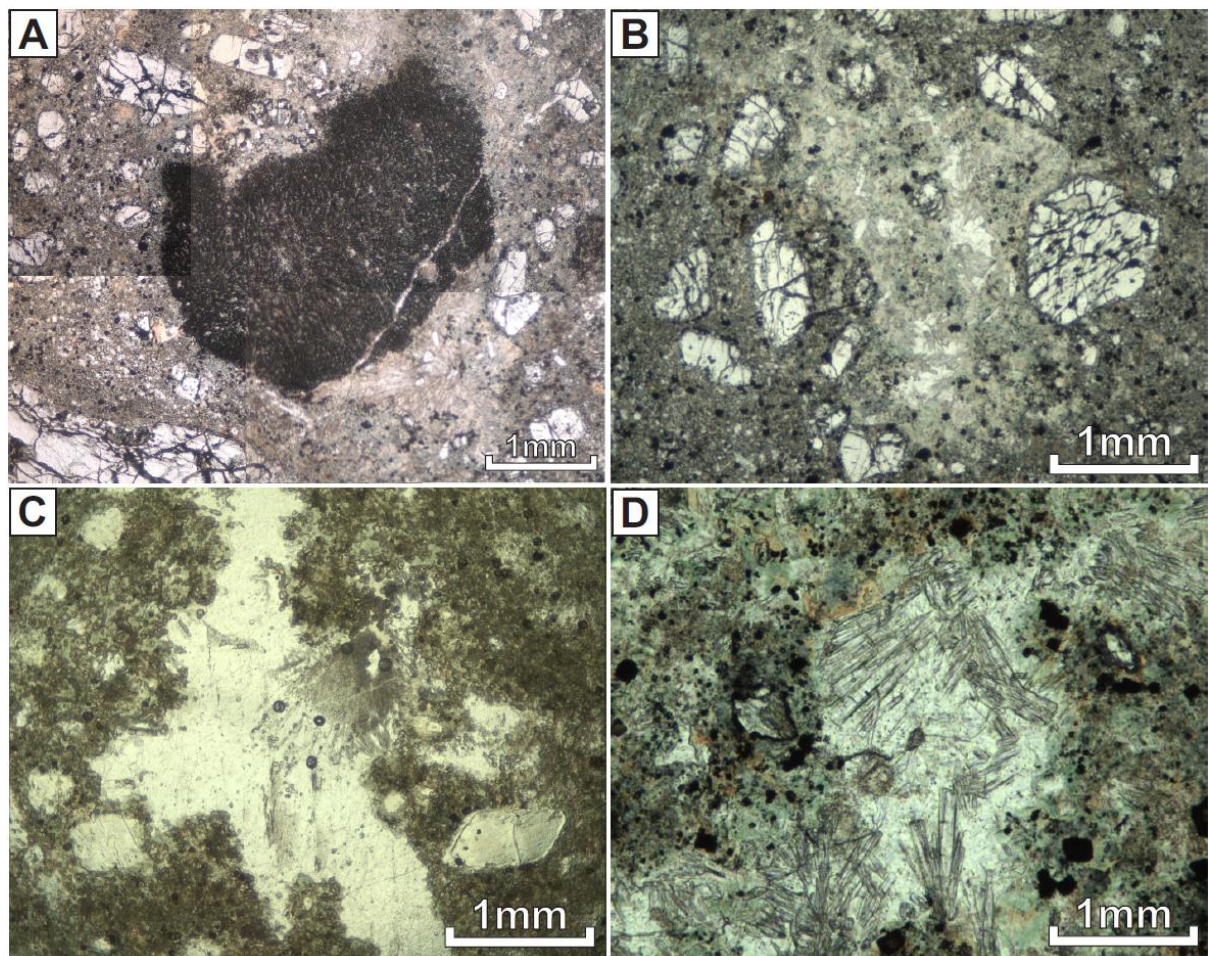
Figure 5: Photomicrographs of Rosário-6 phenocrysts. A) highly altered phenocryst of phlogopite; B) phenocryst of CaTi-perovskite. Left: Plane polarized light; Right: Cross-polarized light. Phl = phlogopite, Prv = perovskite, Ol = olivine.

Figure 6. SEM-BSE Image of Rosário-6 groundmass. A) mineral assemblage and texture overview; B) dissolution and recrystallization of ilmenite phenocryst with Cr-rich core. Cb = Carbonate, Ap = apatite, Cpx = clinopyroxene, Ol = olivine, Cr = cromite, Ilm = ilmenite, Prv = perovskite.
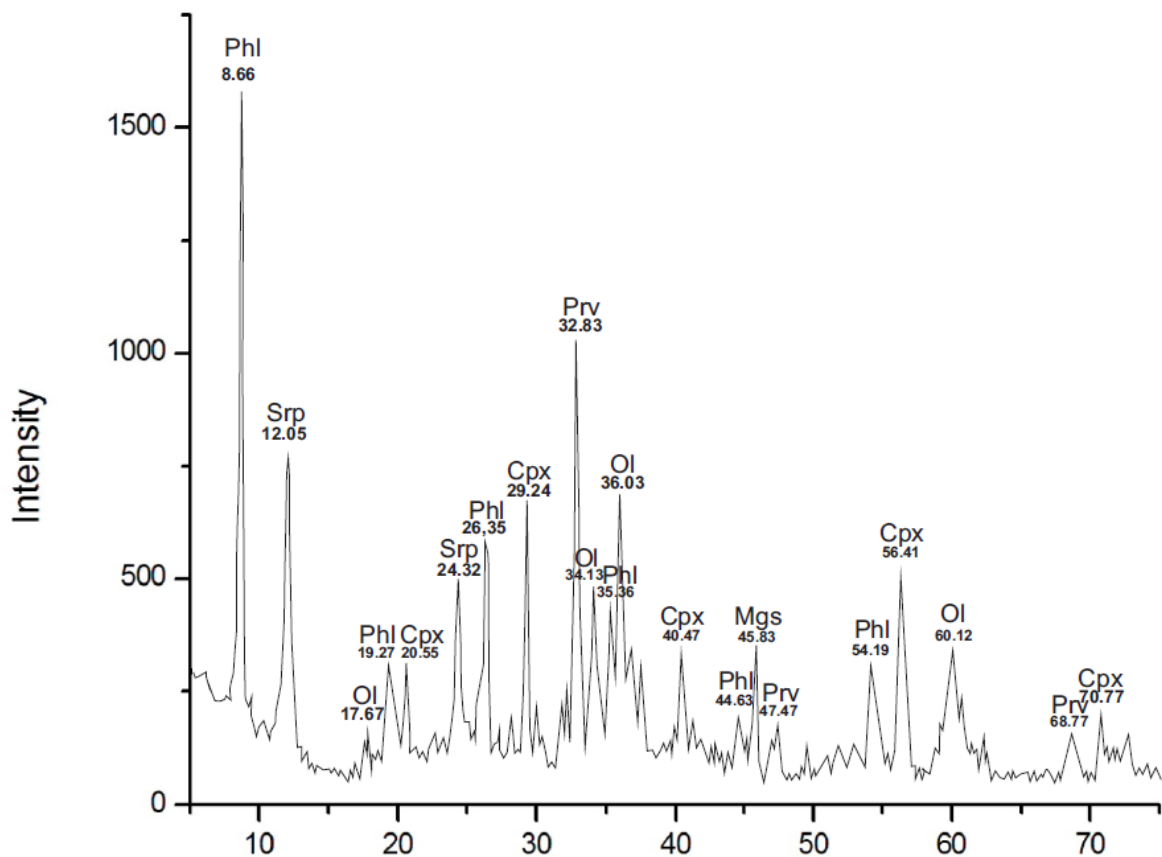
We identified some components, which are described as magmatic destabilization textures, as a product of reactions involving a former phenocryst (e.g. garnet, phlogopite, ilmenite) or part of it that had its structure partially or completely "broken". This occurs due changes on magmatic conditions during its ascension. Figures 7A to D shows examples of these components and textures. They are normally identified here as having an undefined grain boundary and/or a poikilitic-like texture, at times confusing and mixing with the groundmass. Carbonate frequently form pools or trails in the matrix and segregation textures (Skinner and Clement, 1979). An example of these textures are in figure 7C and D consisting of acicular crystals in the midst of a carbonate surrounded by microcrysts of phlogopite, apatite, CaTi-perovskite, spinel, ilmenite and microlites. Crustal xenoliths or xenocrysts were not found in Rosário-6 kimberlite samples. The petrographic features presented here are more similar to Group I kimberlites, with abundant olivine phenocrysts and xenocrysts, perovskite, groundmass phlogopite and no phenocrysts characteristic of Group II kimberlite.
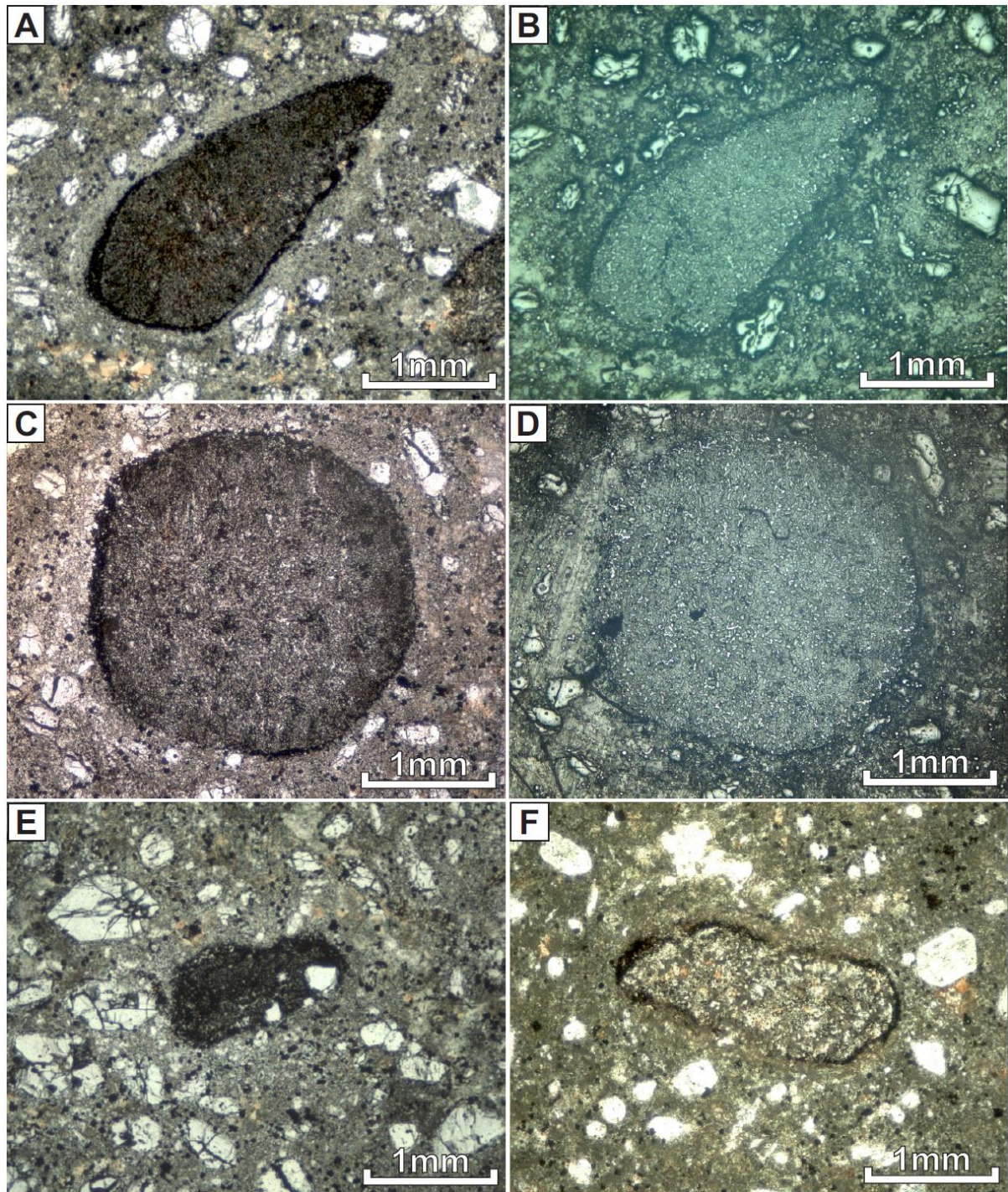

Figure 7: Late-crystalline or advanced reabsorption components and segregationary textures. A) a former macrocryst replaced by microcrysts of oxides and apatite; B) image of the diffuse boundary and assimilation of a former macrocryst replaced by microcrysts of serpentine and apatite; C) total replacement by carbonate; D) late stage assimilation with acicular crystals of apatite in a poikilitic carbonate and a halo of phlogopite, spinel, CaTi-perovskite and serpentine. All images in plane polarized light.

The groundmass of a selected sample (CAR-4) was submitted to XRD analysis, resulting in a diffractogram containing strong diffraction peaks for phlogopite, serpentine (chrysotile) and perovskite (Fig. 8). Pelletal lapilli components with elliptical and spherical shapes filled with an aphanitic material and a reaction halo are widespread in Rosário-6 samples and may form starting from autholiths of previous crystalline components or even liquid/gas pockets (Fig. 9). These lapilli's are millimetric to centimetric size and can be found even folded or aligned, always with a reaction boundary and alteration halo. Gernon et al. (2012) proposed that pelletal lapilli are formed when fluid melts intrude into earlier volcanoclastic infill close to the diatreme root zone. Intensive degassing produces a gas jet in which locally scavenged particles are simultaneously fluidized and coated by a spray of low-viscosity melt. The presence of these lapilli components may indicate a transition from magmatic to pyroclastic behavior, thus offering fundamental insights into eruption dynamics and constraints on vent conditions.

Figure 8. Representative X-Ray diffraction pattern for Rosário-6 sample (CAR-4). Numbers indicate the characteristic "d" values for each mineral. Phl = phlogopite, Srp = serpentine, Ol = olivine, Cpx = clinopyroxene, Prv = perovskite, Mgs = magnesite.

Figure 9. Lapillitic components: A) elliptic lapilli with aphanitic boundary and halo of alteration in plane polarized light; B) same as figure A in reflected light; C) spherical lapilli with corroded and very fine boundary in plane polarized light; D) same as C in reflected light; E) lapilli with olivine crystals interaction; F) groundmass and lapilli or macrocryst highly altered.

5. Geochemistry

The major and trace element compositions of Rosário-6 kimberlites are reported in Table 1, and selected variation diagrams are shown in Figures 10 and 11. For comparison, the samples of Group I, Group II and transitional Kimberlites from South Africa and some Brazilian Kimberlites e.g. Alto Parnaiba Igneous Province (APIP), Brauna and Fazenda Largo are also plotted.

5.1. Crustal Contamination

Petrographic examination of the Rosário-6 kimberlites samples revealed absence of crustal xenoliths. Clement (1982) developed a Contamination Index (CI) for kimberlites which is expressed as a ratio of some oxides: $(SiO_2+Al_2O_3+Na_2O)/(2K_2O+MgO)$, and has been widely used in assessing kimberlite and lamproite whole-rock major oxide chemistry contamination (e.g. Mitchell, 1986; Taylor et al., 1994). The CI is influenced by crustal contamination and weathering, but also by olivine accumulation. Clement (1982) found that uncontaminated kimberlites have CI ranging from 1 to 1.5, and Mitchell (1986) highlight that kimberlites with Al_2O_3 <5 wt% are contamination-free. Another attempt to assess the degree of contamination and weathering, as well as to constrain the primary volatile contents of the Rosário-6 kimberlite samples, is the binary diagrams showing the geochemical dispersion of mobile and immobile elements. In most cases of Rosário-6 samples, however, fractionation is difficult to see because elements do not define clear trends and have small dispersion e.g. MgO vs. Ni, K_2O vs. TiO_2, Th vs. Nb. All Rosário-6 kimberlite samples have CI values of 1.5 and Al_2O_3 >5 wt%, and despite the high content of Al_2O_3, they are considered to have suffered little alteration.
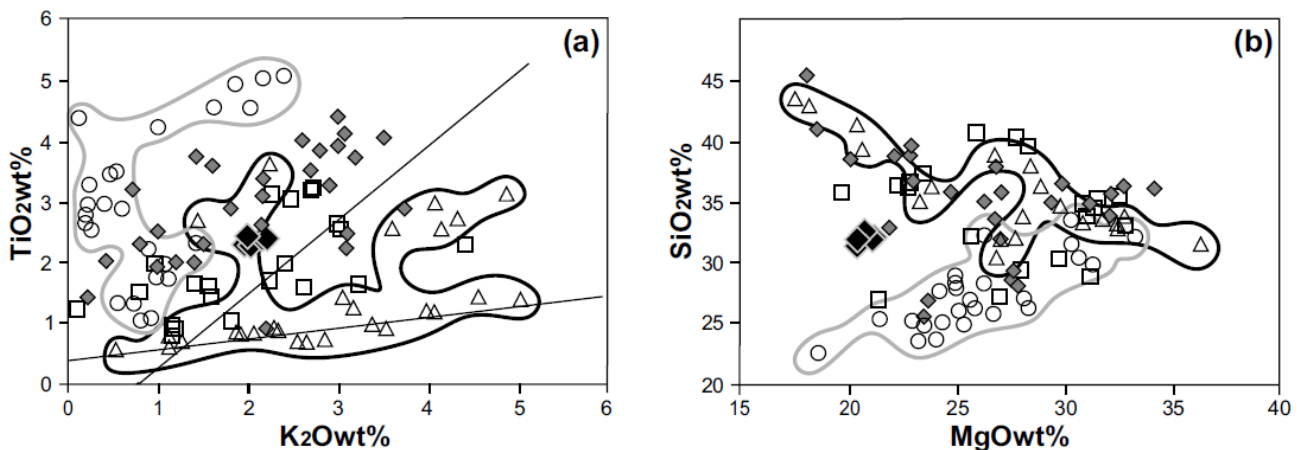
5.2. Major element geochemistry

The predominant characteristics for Rosário-6 kimberlite are the low SiO_2 (31-32 wt%), moderate MgO (20-21 wt%), and high Al_2O_3 (~7 wt%) contents. These kimberlites samples also show relative high Fe_2O_3 (~11 wt%), very low Na_2O (less than 0.1 wt%, except for one sample) and high K_2O and TiO_2 contents, both around 2 wt%. The losses on ignition values (LOI) are around 8 and 10%, which is typical for this volatiles-rich lithotype (Mitchell 1986; 1995). The absence of correlation between LOI and MgO (not shown) suggest that these volatiles are from the magma itself and are not related to secondary alteration (deuteric). The rock is ultrabasic and ultrapotassic, with Mg# around 80 (MgO/(MgO+FeO)x100, calculated assuming Fe_2O_3/FeO = 0.15 and molar oxide compositions), which is relatively high, suggesting that these rocks are close to its primary composition. Figure 10a shows a plot of TiO_2 vs. K_2O containing fields of Group I and Group II kimberlites (Smith et al., 1985), in which the Rosário-6 samples fall between Group I and II, but closer to Group I field, which emphasizes the important presence of Ti phases in the solidus condition. Kimberlites of Group I generally show good dispersion and lower contents of MgO and SiO_2 than Group II (Fig. 10b). Rosário-6 samples generally plot between Group I and II in the diagrams, like a "transitional" group, but the petrographic features coupled with chemical characteristics suggest more similarity to Group I than Group II kimberlite.

Table 1. Whole-rock geochemical data for Rosário-6 kimberlite.

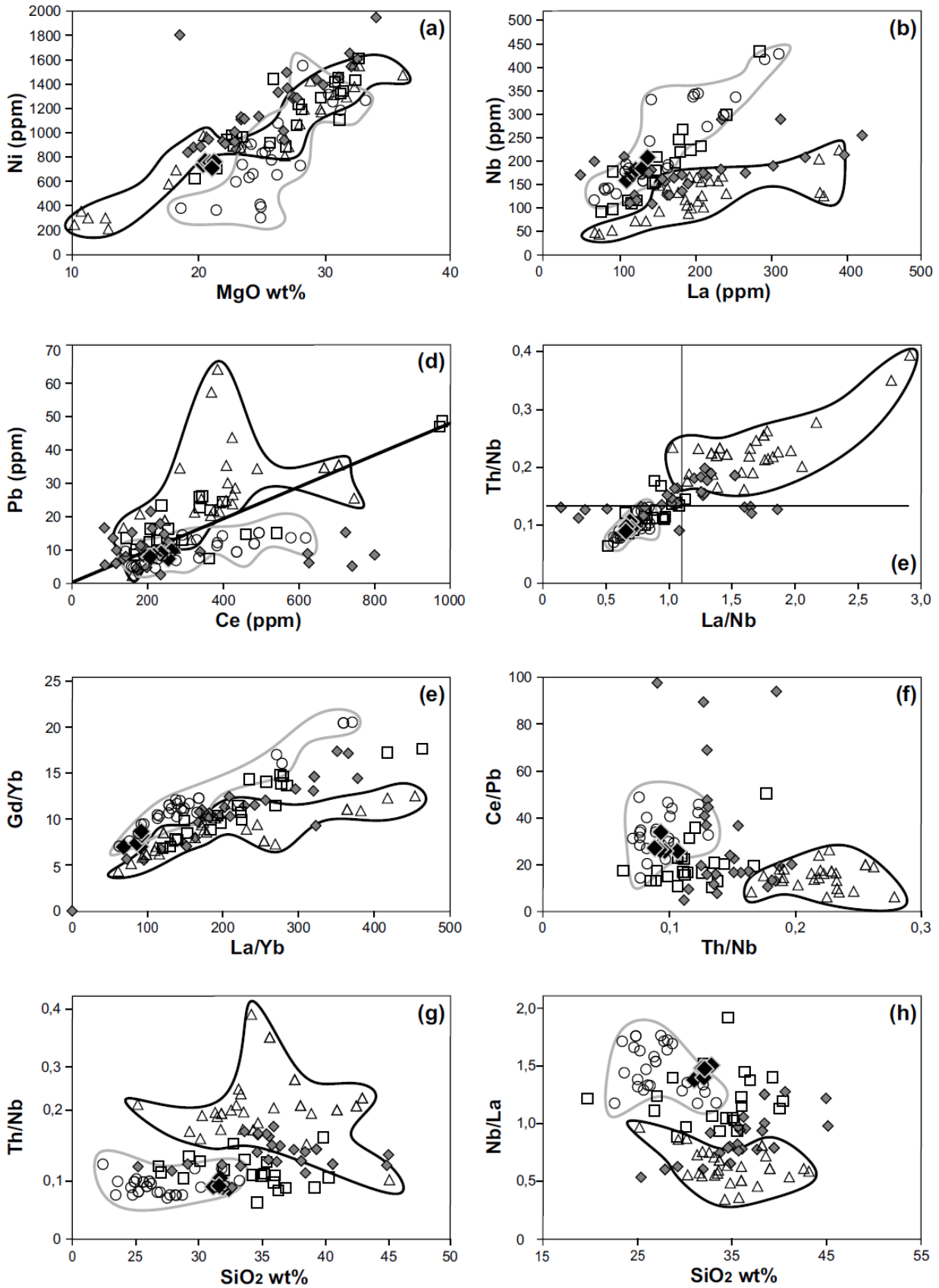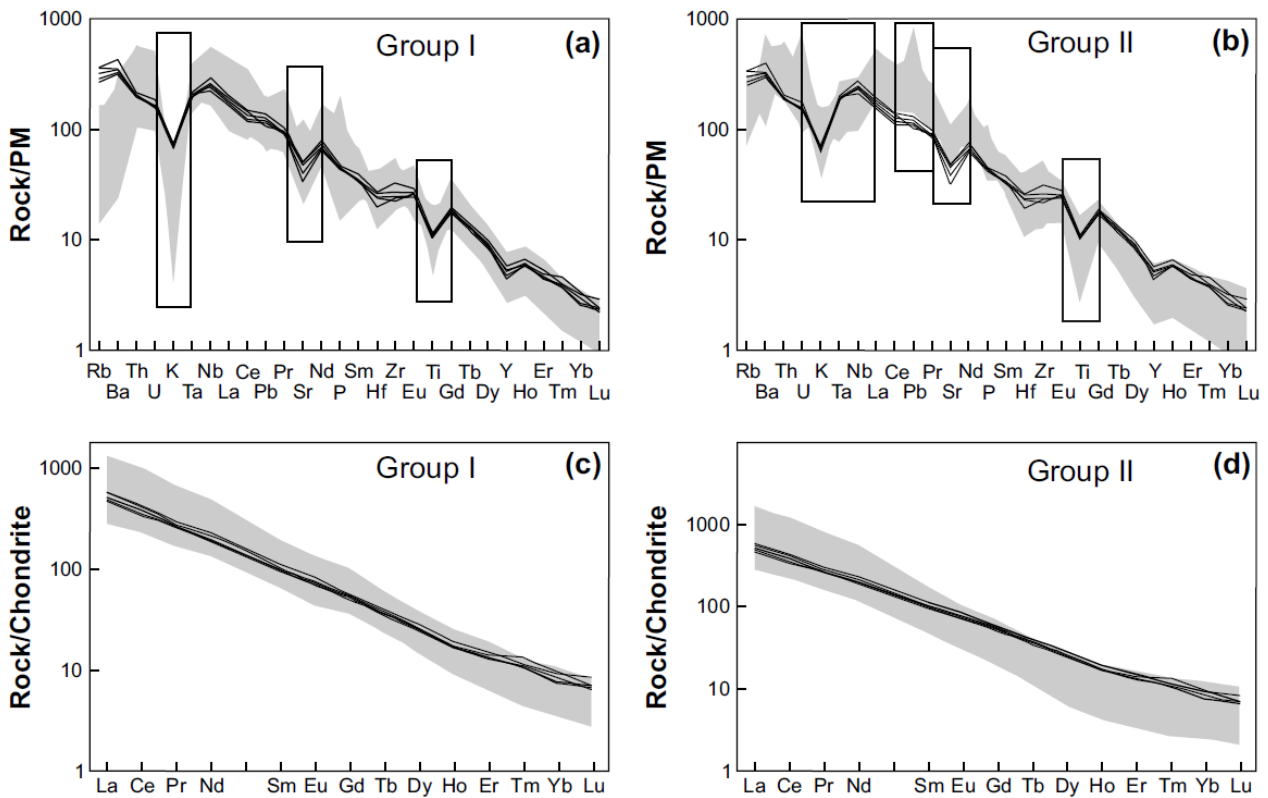| Sample	CAR-1	CAR-2	CAR-3	CAR-4	CAR-5
wt%					
SiO2	31.71	31.75	32.40	31.93	31.22
TiO2	2.37	2.29	2.40	2.24	2.37
Al2O3	7.07	6.82	6.94	6.63	6.60
Fe2O3	11.51	11.06	11.39	11.14	11.24
MnO	0.19	0.18	0.19	0.18	0.19
MgO	21.06	20.52	20.86	21.19	20.41
CaO	12.33	12.00	12.90	12.31	12.22
Na2O	0.07	0.06	0.07	0.12	0.04
K2O	2.20	1.99	2.01	2.05	2.17
P2O5	0.98	0.94	1.02	0.94	0.95
LOI	8.04	9.76	8.81	10.44	9.80
Total	88.09	88.26	89.64	90.30	88.24
Mg#	0.80	0.81	0.80	0.81	0.80
Cl	1.53	1.58	1.58	1.53	1.53
ppm					
Cs	1.89	1.81	1.95	1.89	1.30
Tl	0.17	0.16	0.16	0.18	0.13
Rb	180.22	167.85	227.78	226.28	201.90
Ba	2260.77	2187.78	2957.94	2431.18	2385.66
W	2.05	2.92	2.52	1.89	0.89
Th	16.64	16.79	18.20	16.65	17.17
U	3.35	3.40	3.85	3.41	3.23
Nb	172.95	158.68	205.80	180.17	184.52
Ta	8.25	8.47	8.76	7.97	8.30
La	116.40	110.63	137.15	121.94	130.25
Ce	217.23	206.49	262.39	234.92	254.22
Pb	8.34	8.00	9.71	8.91	7.47
Pr	24.53	25.23	28.26	25.17	26.27
Mo	0.13	0.65	0.66	0.49	0.30
Sr	834.22	697.64	1045.43	985.09	1054.64
Nd	90.48	87.34	106.70	92.49	99.78
Sm	14.67	15.51	17.27	15.29	15.50
Zr	273.99	248.83	362.58	300.04	265.45
Hf	7.45	7.29	8.22	7.99	6.10
Eu	4.09	4.41	4.84	4.39	4.27
Sn	1.61	1.98	1.65	1.51	1.60
Sb	0.22	0.40	0.43	0.24	-
Gd	10.87	11.30	11.54	10.90	10.22
Tb	1.29	1.36	1.50	1.43	1.38
Dy	6.24	6.82	7.25	6.57	6.36
Li	8.91	8.94	9.87	10.07	8.66
Y	21.61	19.98	26.30	23.12	24.25
Ho	0.95	0.98	1.08	0.99	0.98
Er	2.21	2.35	2.54	2.18	2.13
Tm	0.27	0.34	0.29	0.28	0.29
Yb	1.26	1.63	1.57	1.31	1.45
Lu	0.17	0.18	0.21	0.18	0.16

Figure 10. Diagram of selected major elements of Rosário-6 kimberlite. Black diamond (this study), Grey diamond (Brazilian kimberlites from Donatti-Filho et al., 2013, Guarino et al., 2012 and Kaminsky et al., 2009), open circles and triangles (Group I and II kimberlites respectively, from Becker and Le Roex, 2006), open squares (transitional kimberlite from Becker et al., 2007). Fields comprise area of Group I (light) and II (dark) appearance. Group I–Group II dividing lines in (a) are from Smith et al., 1985.

5.3. Trace element geochemistry

Rosário-6 analyzed samples show small range in trace elements variation. They are relatively enriched in the compatible transitional metals concentrations (e.g. Ni = 717-757 ppm; Cr = 1726-2051 ppm; Co = 70-74 ppm; V = 395-471; Mo = 0.1-0.6), strongly enriched in large ion lithophile elements (LILE; Rb = 167-227 ppm; Ba = 2187-2957 ppm; Sr = 697-1054 ppm; La = 110-137 ppm) and Nb (158-205 ppm); moderately enriched in the others high field strength elements (HFSE; Zr = 248-265 ppm; Hf = 6-8 ppm; and Ta = 7-8 ppm, Th = 16-18 ppm) and in Pb (7-9 ppm). MgO vs. Ni diagram shows that Rosário-6 samples have small dispersion and similar correlation to Group I and II kimberlites, without distinction between them (Fig. 11a). Trace elements contents or ratios diagrams (Smith, 1983; Smith et al., 1985) show that Rosário-6 samples exhibit a slightly positive correlation for Nb/La vs SiO_2, Gd/Yb vs La/Yb, Pb vs Ce and Th/Nb vs La/Nb and a little dispersion for Ce/Pb vs Th/Nb and Th/Nb vs SiO_2 (Figs. 11a to h). In all these diagrams, Rosário-6 samples plot closer to the Group I kimberlites. Trace element ratios that allow the distinction between Group I from Group II kimberlites include also Ba/Nb<12, La/Nb<1.1, Ce/Pb>22 and Th/Nb<0.14 (Becker and Le Roex, 2006). For all these ratios, Rosário-6 kimberlite is in agreement with Group I kimberlites, except for Ba/Nb ratio between 12.9 and 14.3. Such high content of Ba is also followed by Sr and Rb enrichment. Multielementar diagram normalized to primitive mantle (Sun and McDonough, 1989), show that all samples have well-defined K, Sr, and Ti negative anomalies (Fig. 12a), which suggests that phlogopite, ilmenite and/or perovskite are stable phases in the source of Rosário-6 or that these minerals were severely fractionated. The absence of a strong positive Pb-anomaly in the Rosário-6 samples also suggest a good relation to Group I kimberlites. Chondrite-normalized (Sun & McDonough, 1989) rare earth element (REE) patterns for the Rosário-6 kimberlite are very similar to Group I South African Kimberlites characterized by light REE enrichment relative to the middle and heavy REE (e.g. La/Sm$_N$ = 5 ± 0.4; La/Yb$_N$ = 57 ± 10). Such behavior is well demonstrated in figure 12a to c.

Figure 11. Diagrams of selected compatible and incompatible elements of Rosário-6 kimberlite. Dividing lines for Ce/Pb, Th/Nb and La/Nb provide distinction between kimberlite groups (Becker and Le Roex, 2006). Data and symbols are the same as figure 11.
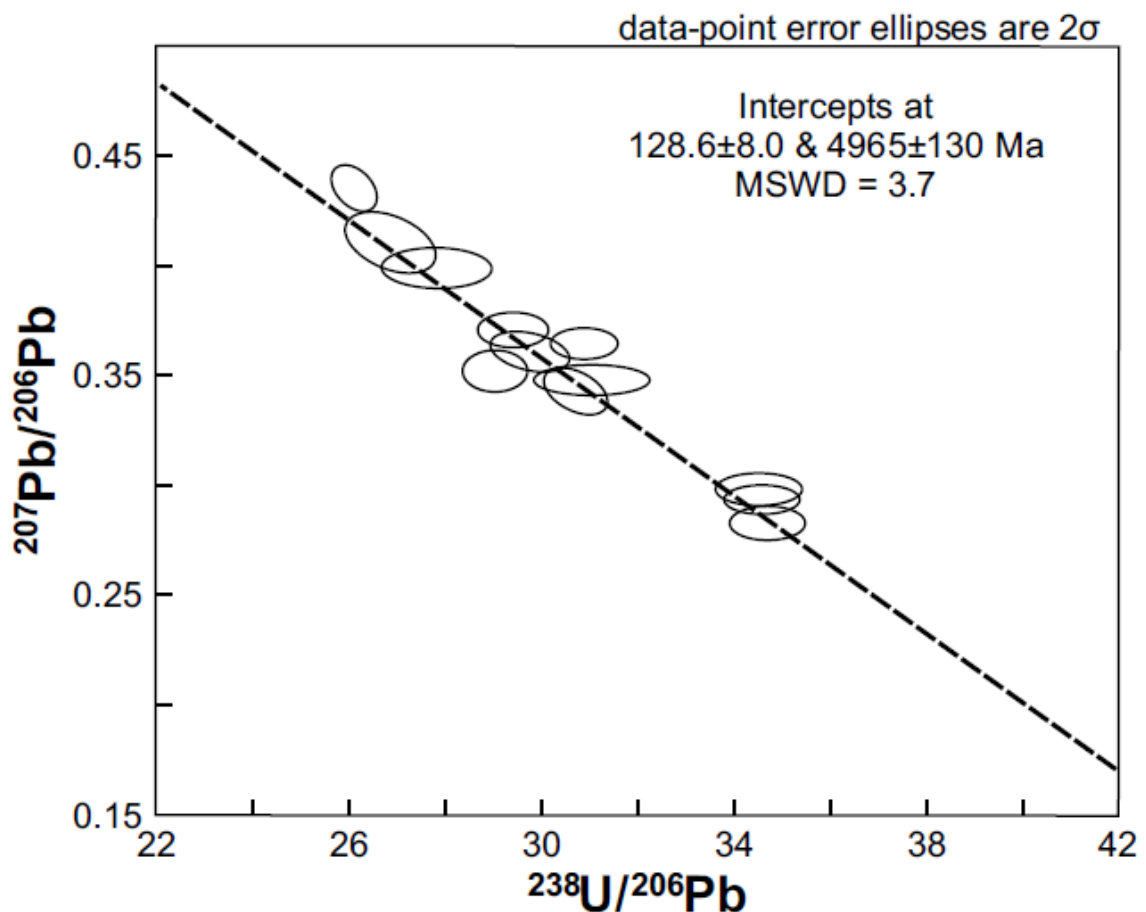
Figure 12. Primitive mantle-normalized multielementar diagrams of Rosário-6 (dark lines) compared to Kimberlites Group I (a) and II (b). In detail the characteristic anomalies from each group. Chondrite-normalized rare earth elements abundances compared with Kimberlites Group I (c) and II (d). Normalizing values from Sun and McDonough (1989). Data of Group I and II kimberlites are from Becker and Le Roex (2006).

5.4. U-Pb geochronology in CaTi-perovskite

A multi-grain groundmass CaTi-perovskite fraction from the Rosário-6 kimberlite was selected for conventional *in situ* U-Pb LA-ICP-MS analysis. Fresh and euhedral crystals of CaTi-perovskite, without visible inclusions or zonation, were picked out and mounted in resin. After polishing and metalizing, it was taken for electron microscope imagery and subsequent in situ U-Pb isotopic analysis. The U-Pb data for the CaTi-perovskites fraction are listed in Table 2. The U/Pb isotopic data were plotted in a Concordia Diagram which yield lower intercept U-Pb ages of 128±8 Ma (MSWD of 3.7) (Fig. 13). This age is believed to be the best estimate for the RSKP emplacement and overlaps the Paraná-Etendeka flood basalts final eruptions, which the main volcanic activity is assumed to be occurred in 133-132 Ma (Gibson et al., 2006; Renne et al., 1992; Turner et al., 1994). Such new data suggest a very complex and heterogeneous mantle composition and the occurrence of a great geothermal variation underneath Southern South America, at the latitudes of Paraná flood basalts, which allow an association of tholeiitic and alkaline rocks. Such association is also observed in the Paraguay alkaline-tholeiitic magmatism (Comin-Chiaramonti et al., 1997), Siberia (Arndt et al., 1995) and will be discussed latter.

Table 2. U-Pb isotopic data of Rosário-6 kimberlite CaTi-perovskite.

Sample CAR-2	Ratios					
	$^{207}Pb/^{206}Pb$	±1s	$^{207}Pb/^{235}U$	±2s	$^{206}Pb/^{238}U$	±2s
p-10	0.282007858	1.1	1.11986	2.82	0.02880	1.74
p-3	0.292555223	0.9	1.16676	2.54	0.02892	1.69
p-2	0.297041812	1.1	1.18611	2.94	0.02896	2.05
p-12	0.342073994	1.5	1.53641	2.30	0.03257	1.68
p-13	0.347402452	0.8	1.54214	3.42	0.03219	3.03
p-15	0.351208343	1.1	1.66749	2.85	0.03443	1.87
p-8	0.359580786	1.4	1.66831	2.54	0.03365	2.07
p-14	0.363466262	0.8	1.62375	2.27	0.03240	1.68
p-11	0.369418404	0.9	1.73188	2.65	0.03400	2.04
p-9	0.397608985	1.0	1.97160	3.78	0.03596	3.22
p-16	0.409393579	1.8	2.10250	3.48	0.03725	2.93
p-4	0.433623010	1.2	2.28986	1.86	0.03830	1.31

Figure 13. U-Pb isotopic Concordia diagram of Rosário-6 kimberlite CaTi-perovskite.
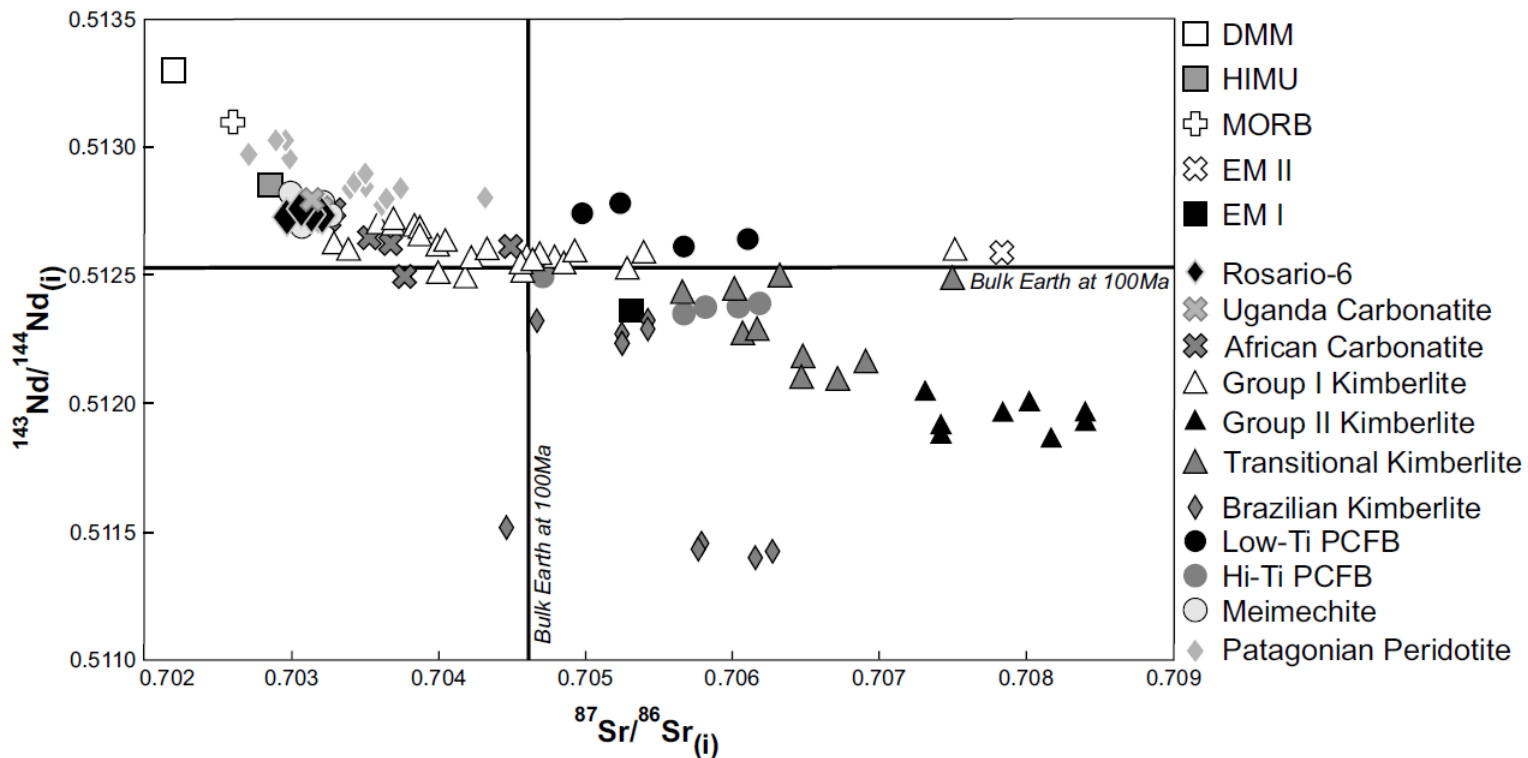
5.5. Sr-Nd isotope compositions

Whole-rock Sr and Nd isotope compositions for Rosário-6 kimberlite are given in Table 3 and displayed on Fig. 14. The samples show little variation and low initial $^{87}Sr/^{86}Sr$ ratio values (between 0.702967 and 0.703135) coupled by high and homogeneous initial $^{143}Nd/^{144}Nd$ ratios (between 0.512758 and 0.512728) calculated for 128 Ma. These results, together with lack of positive correlation between Sr isotopic ratio and SiO_2, Ba, Rb and La (not shown), indicate no crustal contamination or strong alteration, but suggest a depleted mantle re-enriched in large ion lithophile element as the source of Rosário-6 kimberlite. The Sr and Nd isotopic ratios of Rosário-6 are similar to samples of South African Group I kimberlites. Rosário-6 isotopic signature overlaps those for some South American peridotite xenoliths e.g. Gorring and Kay (2000), Stern et al. (1999) and Conceição et al. (2005) which are believed to be derived from the Sub-Continental mantle lithosphere, after some re-enrichment in LILE due to OIB-like and/or carbonatitic melts. Such metasomatism can also provide Ba, Sr and Rb enrichment, seen above. Based on the mantle reservoir defined by Hart et al. (1992), samples of Rosário-6 plot between the depleted mid-ocean ridge basalts (MORB) mantle and an the EM-I enriched mantle. The isotopic composition of Rosário kimberlite is also very similar to some carbonatites from Africa (Bizimis et al., 2003), especially the Uganda samples (see discussion section), and the initial isotopic compositions are very similar to 250 Ma meimechites from Siberia (Arndt et al., 1995), the alkaline rocks associated to the Siberian flood basalts. This intrinsic relationship between kimberlite (or meimechite) and flood basalts elsewhere suggests a parallel dynamic with the evolutionary processes for the source of both magmatism's, with generation of strongly metasomatic rocks at the end of the continental flood basalt CFB eruptions. Rosário-6 has similar Sr and Nd isotopic rations of those of Group I kimberlites, but different isotopic compositions compared to some Brazilian kimberlites e.g. Brauna and APIP (Donatti-Filho et al., 2013; Guarino et al., 2012), being less $^{87}Sr/^{86}Sr$ and higher $^{143}Nd/^{144}Nd$ radiogenic (Fig. 14).

Table 3. Whole-rock Sr and Nd isotope analyses of Rosário-6 kimberlite.

Sample	Rb (ppm)	Sr (ppm)	Rb/Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	Error (SD abs)	Sm (ppm)	Nd (ppm)	Sm/Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	Error
CAR-1	116.31	616.00	0.19	0.549028	0.703966	0.000177	12.05	77.51	0.16	0.093981	0.512812	0.000009
CAR-2	112.23	572.00	0.20	0.570545	0.704103	0.000172	11.48	72.69	0.16	0.095517	0.512838	0.000001
CAR-3	113.35	629.51	0.18	0.523958	0.703986	0.000170	11.43	73.06	0.16	0.094585	0.512808	0.000001
CAR-4	95.42	647.11	0.15	0.429064	0.703906	0.000302	11.60	74.15	0.16	0.094577	0.512807	0.000003
CAR-5	86.58	686.15	0.13	0.367170	0.703803	0.000146	12.40	79.92	0.16	0.093842	0.512815	0.000005

Figure 14. $^{87}Sr/^{86}Sr_{(i)}$ vs. $^{143}Nd/^{144}Nd_{(i)}$ isotopic diagram for Rosário-6 kimberlite calculated to the emplacement age (128 Ma). Data of Mantle Reservoirs (Hart et al., 1992); Patagonian peridotite (Stern et al., 1999); Meimechite (Arndt et al., 1995); Hi and Low-PCFB (Rocha-Junior et al., 2012); Brazilian Kimberlite (Donatti-Filho et al., 2013; Guarino et al., 2012); Group I and II kimberlites (Becker and Le Roex, 2006); Transitional kimberlite (Becker et al., 2007); African carbonatites including Uganda (Bizimis et al., 2003).

6. Discussions

6.1. Rosário-6 Kimberlite classification

Kimberlites can be classified as "on-craton" and "off-craton" and the role of tectonic settings in controlling kimberlite geochemistry is ambiguous and their differences are not well constrained (Becker and Le Roex, 2006). The magnitudes of negative Rb and K anomalies in off-craton kimberlites tend to be smaller than those observed in on-craton ones, (e.g. Le Roex et al., 2003; Harris et al., 2004). Among the kimberlites from Brazil only Brauna is on-craton (located in São Francisco Craton). The RSKP is far away from the Sao Francisco Craton (Fig. 1) and the oldest rocks around it are the Paleoproterozoic Luíz Alvez and Rio de La Plata (Piedra Alta) terrains, both more than 500 km distant. These features, together with the emplacement in the Paraná sedimentary rocks, suggest that the RSKP is an off-craton kimberlite. Although Rosário-6 kimberlitic samples show similar geochemistry with all types of South African Kimberlites, its patterns suggest more affinity to the Group I type. This classification is based on petrographic characteristics, trace element and Sr-Nd isotope geochemistry.
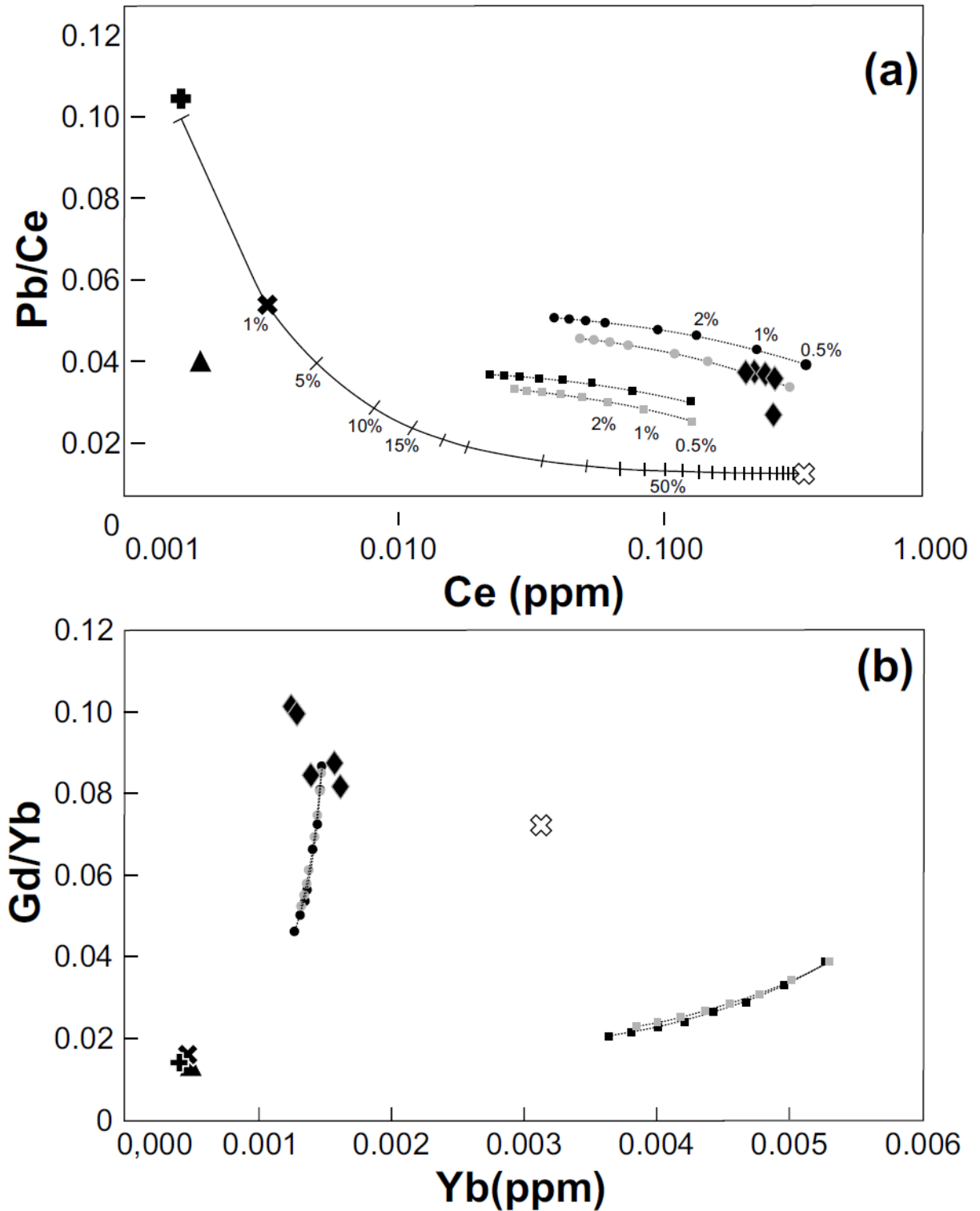
6.2. RSKP source

The Rosário-6 kimberlites are strongly enriched in incompatible elements. The positive anomalies of Nb, La/Nb ratios less than 1 and εNd = +3.3 suggests an asthenospheric source. However, Ba/Nb ratios and Sr and Rb contents are higher than most Group I kimberlites from South Africa kimberlites and suggest important contribution of metasomatic fluids, which could be related to fluids or melts from ancient subducted slabs. Rocha-Junior et al., 2012 also suggest some ancient slab recycled components for the Paraná CFB source. The La/Nb ratios of the Rosário-6 samples (0.67 - 0.71) are similar to those of meimechites from North Siberia (0.73 - 1.02), which is also related to a Siberian CFB province. The origin of Brazilian kimberlites has been attributed to a heterogeneous and metasomatized cratonic lithosphere with a minor input from the asthenosphere. On the other hand, the North Siberia meimechites origin is interpreted as being the result of low partial melting degree from a volatile-rich metasomatised source at the base of the lithosphere. At approximately 500 km northwest from RSKP, there is another association of alkaline rocks and continental flood basalts (CFB): the Sapucai-Villarica Magmatic Province (SVMP), Paraguay. Comin-Chiaramonti et al. (1997) and Gibson et al. (2006) suggested that the early cretaceous potassic rocks (137-118 Ma) of the SVMP are associated to Tristan da Cunha mantle plume, representing the earliest melts generated in the western part of the Paraná-Etendeka CFB. This igneous activity predates the continental break-up and probably represents melts of a phlogopite-bearing, carbonate-metasomatised peridotite in the subcontinental lithospheric mantle (Gibson et al., 2006). This type of potassic magmatism occurrences related to Paraná-Etendeka basalts implies a modified sublithospheric source and melting depth or patterns to generate alkaline and tholeiitic basalts. We suggest a similar origin for RSKP. However, due to the high Nb content, low La/Nb ratios and high εNd values for Rosário-6 samples, we suggest a stronger contribution of the asthenosphere for the RSKP source.

To summarize, the geochemical signature of Rosário-6 kimberlite, together with their moderately radiogenic Sr-Nd isotope compositions, suggest an origin from a mixed asthenospheric source with some metasomatism influence, which were most likely to be originated by a combination of ancient subducted slabs in the asthenosphere at the base of the lithosphere beneath southern Brazil during the Neoproterozoic. Thus, the geotectonic evolution proposed to RSKP formation must be very similar to that for the meimechites associated to Siberian flood basalts. These meimechites are volatile- and alkali-rich, high-magnesium lavas with origin at depths of 250 km or greater at c.a. 246 Ma ago, believed to be the result of low-degree of partial melting of an enriched deep-source at the end of a CFB volcanism (Arndt et al., 1995). For Rosário do Sul kimberlites, we infer that their magma source region was heterogeneously metasomatized prior to kimberlite magma generation. Moreover, we also suggest that the depletion in K, Sr, Ti and Pb relative to elements of similar incompatibility probably reflects the presence of metasomatic phlogopite and perovskite, which retain these elements during the partial melting.

6.3. Metasomatism and partial melting model

Ernst and Bell (2010) have shown in their work a strong spacious and time relation of large igneous provinces (LIPs) and carbonatite. The frequency of these LIP-carbonatite associations suggests that these rocks might be considered as different evolutionary 'pathways' in a single magmatic process/system (Ernst and Bell, 2010). We suggest that this association also played an important role in RSKP source, and, although there is no evidence a carbonatitic rock in the studied area, carbonatitic liquid would have been produced in order to promote the metasomatism of the RSKP source. A carbonatitic enrichment was also proposed for source regions of African kimberlites (Becker and Le Roex, 2006; Becker et al., 2007). Experimental studies have shown that Group I kimberlite-like magmas can be produced by low degrees of partial melting of a carbonated garnet-peridotite mantle source at ~3-8 GPa (Canil and Scarfe, 1990; Dalton and Presnall, 1998; Eggler and Wendlant, 1979), which is the base of the lithosphere. Partial melting degree generally is calculated assuming a garnet–peridotite as a source mode due to the characteristic low HREE abundances and fractionated HREE patterns in

kimberlites (Le Roex et al., 2003; Rogers et al., 1992; Tainton and McKenzie, 1994). In order to estimate the mantle source composition as well as the degrees of partial melting (F) for Rosário-6 kimberlite, we performed partial melting calculations of a metasomatic peridotite estimated from a mixing line of a garnet-spinel lherzolite and a carbonatite melt in hydrous and anhydrous conditions. For that, we used a garnet-spinel lherzolite from Pali-Aike Volcanic Field (average composition from Gervasoni et al., 2013) as the peridotitic source; and carbonatites from Uganda (average composition from Bizimis et al., 2003) as the metasomatic liquid, in a proportion of 99.5% (lherzolite) for 0.5% (carbonatite). For comparison, we also tested partial melting of the Primitive Mantle (PM; McDonough, 1990) in anhydrous and hydrous condition (Fig. 15). The calculations were done using the non-modal batch melting equation reported by Shaw (2006) [$C_L = C_S/(D+F(1-P))$], with application to different degrees of partial melting (F <10%). The following trace element ratios were used due to their similar bulk partition coefficients: Ce/Pb; Sr/Ce and Gd/Yb. The bulk distribution coefficients for both the mantle source (D) and the extracted melt (P) were estimated using the mineral proportions and mineral/melt partition coefficients (McKenzie and O'Nions, 1991; Grègoire et al., 2000; Shaw, 2000; Shimizu et al., 1982; White, 2013). The melt modes are those proposed by Johnson (1998). Modal composition for PM melt trajectories are: 66% olivine, 26% opx, 5% cpx, 1% garnet, 2% phlogopite, 0.05% CaTi-perovskite for hydrated melting; and 68% olivine, 26% opx, 5% cpx, 1% garnet for anhydrous melting. For the carbonatite-peridotite mixing source, the modal composition was 66% olivine, 20% opx, 7% garnet, 5% cpx, 2% phlogopite, 0.05% CaTi-perovskite for hydrated melting; and 68% olivine, 20% opx, 5% cpx, 7% garnet for anhydrous melting. The results for the modeling indicate that Rosário-6 kimberlite could be generated from extremely small fractions of melting (F <1%) of a carbonated phlogopite-perovskite-garnet peridotite.

Figure 15. Illustrated curves representing melting and mixture trajectories of inferred source regions. Circles and lines curves are for melting calculated from a mixture of 99.5% of peridotite plus 0.5% of carbonatite. Squares and lines curves are for melting calculated from PM (dark = anhydrous; light = hydrated). Dark diamonds (Rosário-6); Dark cross (avrg. comp. from Gervasoni et al., 2012); Dark X (Rosário-6 source); Light X(avrg. comp. of Uganda carbonatites from Bizimis et al., 2003); Dark triangle (PM). Residual modal mineralogy as follows: anhydrous, ol:opx:cpx:gt:phl:prv = 0.68:0.2:0.05:0.07:0:0; hydrous, ol:opx:cpx:gt:phl:prv = 0.66:0.2:0.05:0.07:0.02:0.0005.

7. Concluding Remarks

Rosário-6 rocks are the best representative samples of Rosário do Sul cluster, due to their conservation, and their very cohesive and preserved igneous textures. Rosário-6 is a hipabyssal kimberlite with phenocrysts of olivine, CaTi-perovskite and minor apatite. Abundance of centimetrical lapillitic components and megacrysts of olivine (xenoliths) from Rosário-6 kimberlite is relatively high and are characteristic of "fluidization" in kimberlitic volcanism of root zone. Rosário do Sul cluster is off-craton, similar to Group I South African kimberlites, but with some distinctions compared to others kimberlites from Brazil (especially the moderated high content of LREE). Trace element variations and relatively low Sr and high Nd isotope compositions of Rosário-6 kimberlite are compatible with a depleted mantle source, possibly asthenospheric (εNd~3), enriched in LIL elements like Rb, Ba and K due to 0.5% of carbonatitic melts. Long-term melt/fluid ingress from ancient subducted slabs, along with thermal perturbations, may also have preconditioned the source of Rosário-6 magma at the base of the lithospheric mantle or deeper. Phlogopite and perovskite must be stable in the mantle source of RSKP magmas. U-Pb age of ~128 Ma for groundmass CaTi-perovskites is the best estimative for the timing of Rosário do Sul kimberlites emplacement. The spatial and chronological association between kimberlites and flood basalts provides what is perhaps the best constrain on their origin: Rosário-6 erupted just after the peak of the Paraná volcanism at ~132 Ma. It is highly probable that the heat source for kimberlite formation was the same that triggered the Paraná-Etendeka LIP, but in different depth of melting.

Acknowledgements

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ANEXOS

Anexo A. Carta de Submissão de artigo.

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