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Hf-Pb isotope and trace element constraints on the origin of the Jacupiranga Complex (Brazil): Insights into carbonatite genesis and multi-stage metasomatism of the lithospheric mantle

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A B S T R A C T

The Lower Cretaceous Jacupiranga complex, in the central-southeastern portion of the South American Platform, includes carbonatites in close association with silicate rocks (i.e. strongly and mildly silica-undersaturated series). Here we document the first hafnium isotope data on the Jacupiranga complex, together with new trace element and Pb isotope compositions. Even though liquid immiscibility from a carbonated silicate melt has been proposed for the genesis of several Brazilian carbonatites, isotopic and geochemical (e.g., Ba/La ratios, lack of pronounced Zr-Hf and Nb-Ta decoupling) information argues against a petrogenetic relationship between Jacupiranga carbonatites and their associated silicate rocks. Thus, an origin by direct partial melting of the mantle is considered. The isotopic compositions of the investigated silicate samples are coherent with a heterogeneously enriched subcontinental lithospheric mantle (SCLM) source of rather complex evolution. At least two metasomatic processes are constrained: (1) a first enrichment event, presumably derived from slab-related fluids introduced into the SCLM during Neoproterozoic times, as indicated by consistently old T_{DM} ages and lamprophyre trace signatures, and (2) a Mesozoic carbonatite metasomatism episode of sub-lithospheric origin, as suggested by $\epsilon_{Nd-\epsilon_{Hf}}$ values inside the width of the terrestrial array. The Jacupiranga parental magmas might thus derive by partial melting of distinct generations of metasomatic vein assemblages that were hybridized with garnet peridotite wall-rocks.

Keywords:

Primary carbonatites
Mantle metasomatism
Alkaline rocks
Cumulates

1. Introduction

During Mesozoic and Cenozoic times, the central-southeastern region of the South American Platform was affected by extensive tholeiitic and alkaline-carbonatite magmatic activity (e.g., Almeida, 1983; Piccirillo and Melfi, 1988; Comin-Chiaramonti and Gomes, 2005). Notably, the alkaline occurrences were emplaced along the margins of the intracratonic Paraná Basin (Morbiddelli et al., 1995). Among them, the Jacupiranga complex is a prominent ultramafic-alkaline carbonatite unit (e.g., Melcher, 1966; Gaspar and Wyllie, 1983; Germann et al., 1987; Huang et al., 1995; Costanzo et al., 2006; Beccaluva et al., 2017; Chmyz et al., 2017), mainly because of an important phosphate deposit related to the carbonatite body, but also because of the particularities of some ultramafic cumulates (i.e. jacupirangites, Derby, 1891).

The origin of carbonatites has long been the subject of debate (e.g., Bell, 1994; Bell et al., 1999; Gittins and Harmer, 2003; Bizimis et al., 2003; Mitchell, 2005; Woolley and Kjarsgaard, 2008). They are attributed to two main processes (which are not necessarily in antithesis): (1) carbonatites having derived as primary melts directly generated from the mantle (e.g., Wyllie and Lee, 1998; Harmer and Gittins, 1998; Srivastava et al., 2005) and (2) carbonatite melts related to carbonated silicate parental magmas, either through extensive fractional crystallization or liquid immiscibility (e.g., Lee and Wyllie, 1994, 1997, 1998; Veksler et al., 1998a; Rosatelli et al., 2007; Stoppa et al., 2016; Doroshkevich et al., 2017). For this reason, in cases where carbonatites are spatially and temporally associated with alkaline and ultramafic rocks, such as in the Jacupiranga complex, the origin of the carbonatites cannot be properly constrained without taking into account the silicate lithotypes (Huang et al., 1995; Bell et al., 1999).

Although alkaline rocks and carbonatites are currently known to have a mantle origin (e.g., Stoppa and Schiazza, 2013; Stoppa et al., 2016), there is still no consensus on the nature or depth of their sources (Ashwal et al., 2016). While some authors consider heterogeneous subcontinental mantle as a suitable source (e.g., Comin-Chiaramonti et al.,

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2007; Omarini et al., 2016; Ashwal et al., 2016), others favor a sub-lithospheric origin (e.g., Bell and Simonetti, 2010; Bell et al., 2013). Among the incompatible element isotope systems, Lu-Hf isotope is one of the soundest methods for metasomatic overprinting (Pearson et al., 2003) and thus provides a valuable tool to constrain mantle source characteristics, particularly when dealing with the subcontinental lithospheric mantle (Griffin et al., 2000). To date, few Brazilian alkaline occurrences were studied on the basis of Hf isotope composition: kamafugites of the Goiás Province (Carlson et al., 2007) and the Catalão I ultramafic-carbonatite complex in the Alto Paranaíba Igneous Province (Guarino et al., 2017), both of Upper Cretaceous age.

The main purpose of this paper is to contribute to the understanding of the Jacupiranga complex petrogenesis, chiefly through the enhanced resolution provided by Hf and Pb isotopes. We present the first Hf isotope analyses of the alkaline magmatism that took place in central-southeastern South American Platform in Lower Cretaceous times, and new Pb isotope analyses of the Jacupiranga complex, including the first analyses of dunites and lamprophyres. The discussion also includes trace element analyses and previously published Sr-Nd isotopic data on the complex (Chmyz et al., 2017). The study focuses on (1) the Hf isotopic composition of Jacupiranga rocks, (2) better constraints to mantle sources; and (3) the petrogenetical relations, if any, between carbonatites and silicate rocks.

2. Geological setting

More than 100 alkaline occurrences located in the central-southeastern portion of the South American Platform are grouped into various provinces (Almeida, 1983; Riccomini et al., 2005). Among them, the complexes emplaced along the eastern margin of the intracratonic Paraná Basin are related to the Ponta Grossa Arch (Fig. 1A), a tectonic uplift active since Paleozoic times (Gomes et al., 2011). Two of the four NW-trending lineaments that control the Ponta Grossa Arch structural framework, the Guapiara and the São Jerônimo-Curiúva lineaments (Fig. 1B), host Lower to Upper Cretaceous complexes of alkaline affinity aligned parallel to their axis (Almeida, 1983; Ruberti et al., 2005; Gomes et al., 2011).

The Lower Cretaceous Jacupiranga complex (Fig. 1C) corresponds to a ~65 km² ultramafic alkaline-carbonatite intrusion located in the southern sector of the Guapiara Lineament (Gomes et al., 2011), emplaced into both the Neoproterozoic Itapeúna granodiorites and the Turvo-Cajati Formation. Its main lithotypes consist of ultramafic cumulates forming two bodies: (1) a northern intrusion, mostly composed of dunites, with rare wehrlites, and (2) a southern clinopyroxenite unit (~22 km²). The dunitic body is surrounded by an annular zone, with a wide variety of rock-types (i.e. gabbros, diorites, monzonites, syenites, phonolites, and lamprophyres) referred to as the Heterogeneous Zone by Chmyz et al. (2017). Associated with the clinopyroxenite body, on the other hand, are a crescent-shaped unit of banded ijolites and a small carbonatite intrusion (~1.5 km²), the latter hosting a phosphate ore deposit that has been mined for several decades.

Based on field, petrographic and mineral data, Gaspar and Wyllie (1983) describe five successive intrusion episodes within the carbonatite body (C1–C5) of the Jacupiranga complex (Fig. 1C). The southern episodes consist of sövite C1 (oldest), dolomitic sövite C2, and sövite C3, while the northern episodes consist of sövite C4 and the youngest rauhaugite C5. Based on mineralogical criteria, Hirano et al. (1987) classified the carbonatite unit into four compositional terms: calcite carbonatite (CC), magnetite-rich calcite carbonatite (CCmt), apatite calcite carbonatite (CCap), and dolomite carbonatite (DC). The southern part of the unit is made up of CC, with bands of CCap or CCmt and dikes of DC, while the northern part consists of CC with a DC core and CCmt bands.

Both the petrological model for the Jacupiranga complex and the relations between its carbonatite and silicate rocks have long been debated. While Germann et al. (1987) and Gaspar (1989) proposed a

liquid immiscibility related genesis for the carbonatites, more recent studies (e.g., Huang et al., 1995; Beccaluva et al., 2017) argue that a primary origin should be considered. In our previous work (Chmyz et al., 2017), we proposed two distinct magmatic series for the silicate rocks: (1) a strongly silica-undersaturated series including part of the clinopyroxenites and the ijolitic rocks, probably related to nephelinite melts, and (2) a mildly silica-undersaturated series that include feldspar-bearing rocks, phonolites, lamprophyres, and some of the clinopyroxenites. Repeated influxes of parental magma (for which we regard lamprophyres as good compositional proxies) evolved mainly through fractional crystallization to give rise to the mildly silica-undersaturated series. Our model differs from that of Beccaluva et al. (2017), who proposed that the entire clinopyroxenite unit derives exclusively from nephelinitic parental magmas evolved in nearly closed system conditions.

3. Sample descriptions

The general geology of Jacupiranga, which was extensively described by Melcher (1966), Germann et al. (1987), and Gaspar (1989), has been more recently summarized by Ruberti et al. (2005). A brief description of each analyzed sample is given below. For a more detailed description, the reader is referred to Chmyz et al. (2017).

Magnetite clinopyroxenite JAC45 is a coarse-grained layered mesocumulate mainly composed of subhedral cumulus diopside (~90 vol%), either normally or reversely zoned. Ti-magnetite (~10 vol%) is the main interstitial phase. Although scarce, phlogopite, apatite and perovskite (mantling the Ti-magnetite) are also present. The *nepheline-bearing clinopyroxenite* (JAC18) differs from magnetite clinopyroxenite by showing interstitial nepheline and by the higher and lower amounts of phlogopite and Ti-magnetite, respectively. *Ijolite* JAC29.2 is a coarse-grained rock composed of subhedral diopside (40 vol%), nepheline (55 vol%), phlogopite (<5% vol%), Ti-magnetite (5 vol%), apatite, and perovskite. Its main feature is a subhorizontal banding defined by variations in the amount of nepheline and clinopyroxene.

The absence of fresh outcrops and the thick regolith render a mineralogical characterization of the Jacupiranga *dunites* very difficult to obtain, hence their primary features are scarcely known. Three short drill holes samples were selected for this study: a fine-grained dunite (JAC248) essentially composed of subhedral olivine, and two medium-grained wehrlites (JAC220 and JAC243) with olivine and minor subhedral diopside (<15 vol%). Weathering and high serpentinization (30–70%) prevent primary textures and the proportions of mineral constituents to be accurately recognized that would allow for an acceptable identification of this lithotype.

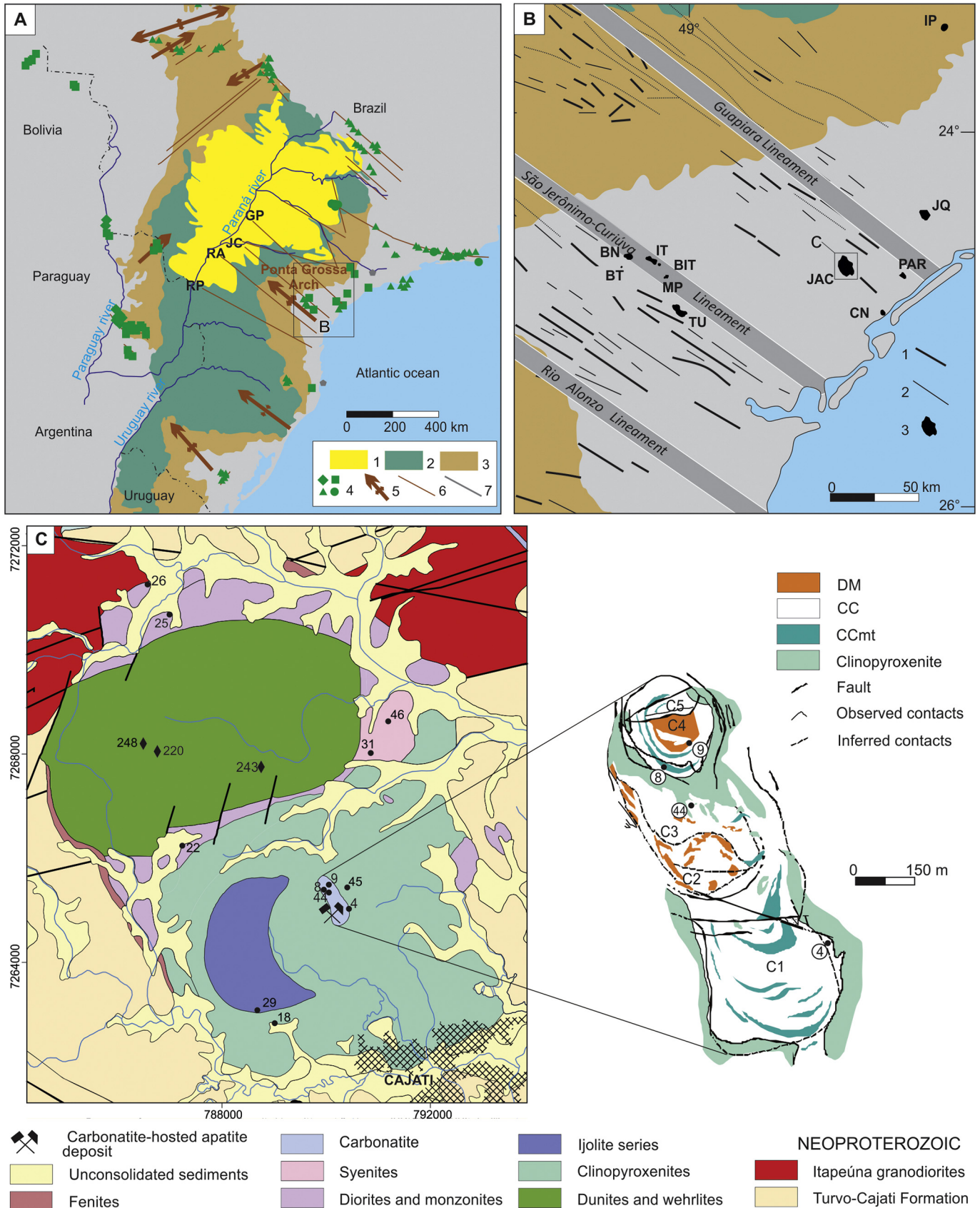
We selected a representative sample of each group of feldspar-bearing rocks that constitutes the Heterogeneous Zone (i.e. dioritic, syenitic, and monzonitic rocks), except for syenite, for which two samples were selected. *Melasyenite* JAC31 is a medium- to coarse-grained porphyritic rock with alkali feldspar phenocrysts within a matrix of mainly alkali feldspar, diopside, biotite, and minor nepheline and apatite. *Alkali-feldspar syenite* JAC46.3 is characterized by mafic aggregates (i.e. subhedral to anhedral diopside, hastingsite, titanite, biotite, and magnetite) associated with euhedral crystals of alkali feldspar. *Monzonite* (JAC25) is a medium-grained rock that outcrops in the northern part of the Heterogeneous Zone. It is composed of zoned plagioclase phenocrysts mantled by alkali-feldspar rims set in an andesine, alkali-feldspar, hornblende, biotite, titanite, magnetite matrix, with accessory zircon. *Meladiorite* JAC22 is a medium-grained rock composed of diopside and Ca-plagioclase, with minor biotite, apatite, and magnetite.

In the Heterogeneous Zone, *lamprophyres* are coarse- to fine-grained rocks that occur as dikes crosscutting alkali-feldspar syenites. Two lamprophyre samples were selected for our investigation: a coarse- (JAC46.1) and a fine-grained (JAC46.2) specimens, both from the same outcrop. Both samples present biotite and clinopyroxene macrocrysts

in a finer-grained matrix that consists of volcanic glass, clinopyroxene, biotite, alkali feldspar, plagioclase, magnetite, titanite and apatite.

For *carbonatites*, we selected four samples: two of apatite-calcite carbonatite (CCap), one from the southern (JAC04 – Fig. 2A) and

another from the northern part of the intrusion (JAC44); one dolomite carbonatite sample (DC, JAC09 – Fig. 2B), and a magnetite-rich calcite carbonatite sample (CCmt, JAC08 – Fig. 2C). All samples are medium to coarse-grained rocks and contain apatite, magnetite, and phlogopite



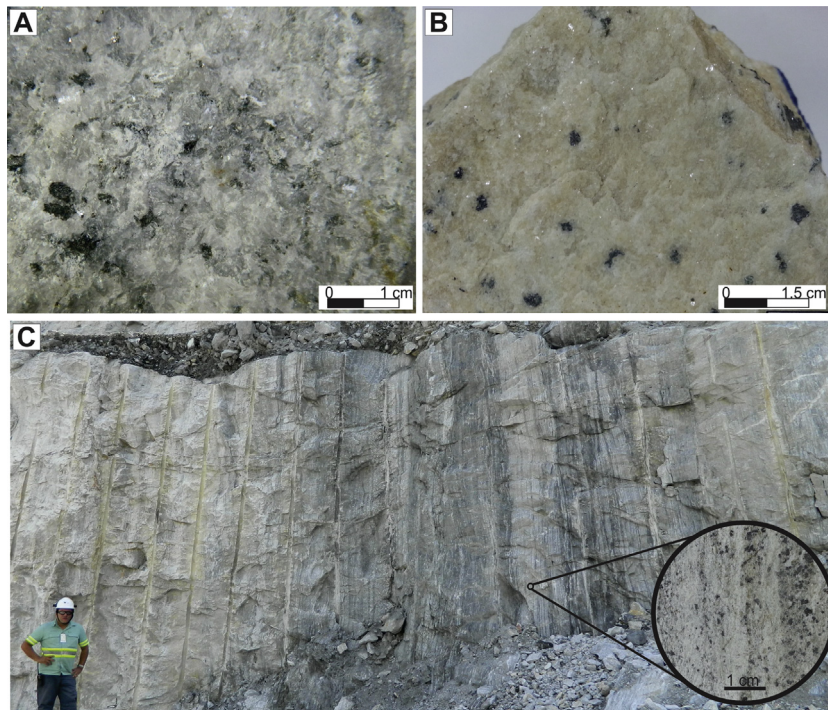


Fig. 2. Main carbonatite types of the Jacupiranga complex. (A) Apatite calcite carbonatite (CCap, JAC04). (B) Dolomite carbonatite (DC, JAC09). (C) Outcrop of magnetite-rich calcite carbonatite (CCmt) displaying vertical layering and inset showing detail of the pronounced layering in the CCmt (JAC08).

as essential phases, although in different proportions. Additionally, as ore mineral, apatite occurs in different forms: as small aggregates (JAC44), pockets (JAC09), layers (JAC08), or disseminated throughout the rock (JAC04).

4. Analytical methods

Whole-rock trace elements from selected samples were analyzed using a high resolution inductively coupled plasma mass spectrometer (ThermoFinnigan ELEMENT XR HR-ICP-MS) at the AETE technical platform (Analyse des Elements Traces dans l'Environnement, Université de Montpellier). Respectively, sixteen and eleven samples from different Jacupiranga lithotypes were selected for Pb and Hf whole-rock isotopic analyses. The sample preparation followed the procedures described by Blichert-Toft et al. (1997), Bosch et al. (2008) and Bosch et al. (2014), except for the carbonatites that did not undergo leaching treatment. Hf and Pb isotopes were determined at the École Normale Supérieure (ENS) of Lyon using a multicollector inductively coupled plasma mass spectrometer (ThermoFisher Scientific Neptune Plus). The Hf isotope ratios were normalized to $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ and, during the course of analyses, the average value for the JMC-475 Hf standard was 0.282155 ± 11 ($n = 17$). ϵ_{Hf} values were calculated with $[\text{Hf}/^{177}\text{Hf}]_{\text{CHUR}} = 0.282772$ (Blichert-Toft and Albarède, 1997). The terrestrial array from Vervoort et al. (1999) is a single coherent trend defined as $\epsilon_{\text{Hf}} = 1.36\epsilon_{\text{Nd}} + 2.95$. Hf T_{DM} was calculated considering $\lambda_{^{176}\text{Lu}} = 1.865 \times 10^{-11}$ (Scherer et al., 2001) and depleted mantle values of $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$ and $^{176}\text{Hf}/^{177}\text{Hf} = 0.28325$ (Blichert-Toft and Albarède, 1997). Routinely analyzed NBS981 Pb standards presented a reproducibility between 212 and 343 ppm ($n = 12$).

5. Results

5.1. Whole-rock trace elements

The trace element composition of the Jacupiranga rocks is reported in Table S1. All analyzed samples display LREE enrichment over HREE without marked anomalies in the chondrite-normalized REE diagram (Fig. 3A). Carbonatites yield the largest range of REE abundance, while clinopyroxenites and ijolite are close in distribution. Among the rocks from the Heterogeneous Zone, syenites show the highest (La_N/Yb_N) ratios (51.2 and 51.9), followed by lamprophyres (34.2 and 46.1). In general, the primitive mantle-normalized element patterns (Fig. 3B, C) have positive Ba anomalies and troughs at Nb for all lithotypes. Carbonatites yield peaks for Ta and Sr and troughs at K and Ti. The latter is also present in feldspar-bearing rocks, but smoother. Lamprophyres present positive anomalies for La and Sm.

5.2. Pb isotope composition

Pb isotope data are presented in Table S2. Whole-rock Th contents are extremely low in clinopyroxenites and dunites (<1.04 ppm) and quite low in carbonatites (0.3–2.3 ppm). Additionally, most of the Jacupiranga analyzed rocks show a rather low whole-rock U (<4.04 ppm) and Pb (<26.69 ppm) content. Initial isotope ratios range from 16.992 to 19.012, from 15.388 to 15.527, and from 37.362 to 39.320 for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, respectively. In the Pb/Pb isotopic diagrams (Fig. 4), the samples are in good agreement with the Jacupiranga complex domain defined by Huang et al. (1995) and Beccaluva et al. (2017). The rocks from the mildly silica-

Fig. 1. (A) Alkaline occurrences along the Paraná Basin margins in central-southeastern South American platform (after Riccomini et al., 2005): 1) Late Cretaceous Bauru Basin; 2) Early Cretaceous Paraná Magmatic Province; 3) Late Ordovician to Early Cretaceous Paraná Basin; 4) Alkaline units (diamonds, Permian-Triassic; squares, Early Cretaceous; triangles, Late Cretaceous; circles, Paleogene); 5) Axes of main arches; 6) Major fracture zones (GP, Guapiara; JC, São Jerônimo-Curiúva; RA, Rio Alonzo; RP, Rio Piquiri); 7) Lancinha-Cubatão Shear Zone. (B) Detailed tectonic setting of Cretaceous alkaline magmatism in the Ponta Grossa Arch (after Ruberti et al., 2012): (1) and (2) dikes as inferred by field geology and remote sensing and aeromagnetic survey, respectively; (3) alkaline complexes: BIT-Barra do Itapirapuã, BN-Banhado, BT-Barra do Teixeira, CN-Cananéia, IP-Ipanema, IT-Itapirapuã, JAC-Jacupiranga, JQ-Juquiã, MP-Mato Preto, PAR-Pariquera-Açu and TU-Tunas. (C) Schematic geological map of the Jacupiranga complex (compiled and modified from Faleiros and Pavan, 2013) with the location of all samples collected for this study (diamonds, core sample; circles, outcrop samples). The inset shows the detailed geological map of the Jacupiranga carbonatites as in Ruberti et al. (2005), after Gaspar and Wyllie (1983) and Hirano et al. (1987).

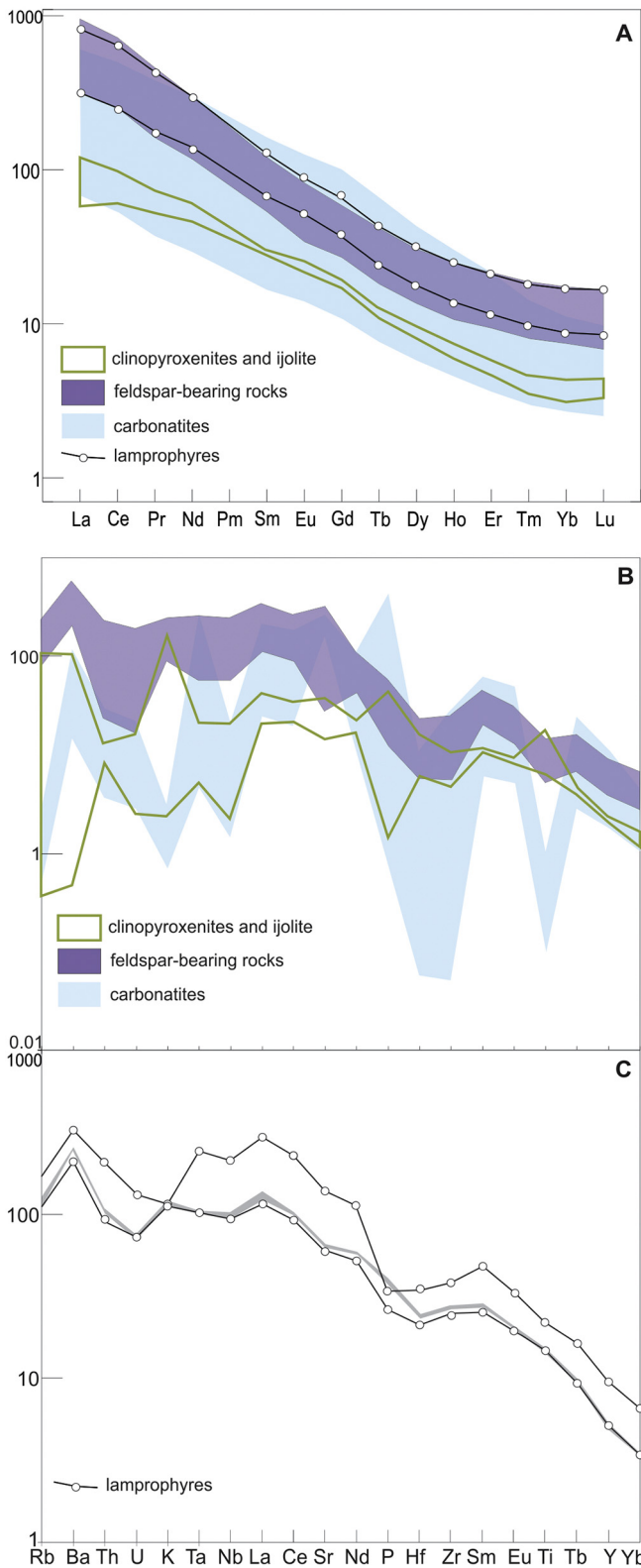


Fig. 3. (A) Chondrite-normalized REE patterns and (B, C) primitive mantle-normalized incompatible element diagrams for Jacupiranga rocks. K, P, and Ti concentrations are from Chmyz et al. (2017). Grey field represents lamprophyres from Menezes et al. (2015). Normalization values are from McDonough and Sun (1995).

undersaturated series yield a well-defined positive correlation between $^{207}\text{Pb}/^{204}\text{Pb}_{(i)}$ and $^{206}\text{Pb}/^{204}\text{Pb}_{(i)}$ ratios. In general, the analyzed carbonatites show initial Pb-isotope values similar to those obtained

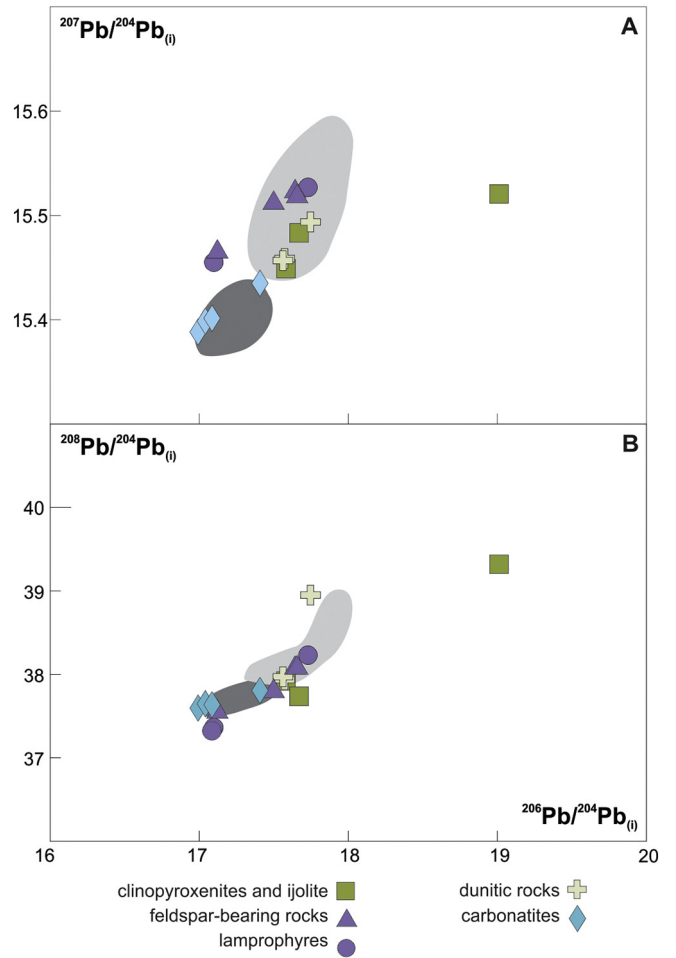


Fig. 4. Lead isotopic plots for Jacupiranga rocks. (A) Initial $^{207}\text{Pb}/^{204}\text{Pb}$ vs. initial $^{206}\text{Pb}/^{204}\text{Pb}$ and (B) Initial $^{208}\text{Pb}/^{204}\text{Pb}$ vs. initial $^{206}\text{Pb}/^{204}\text{Pb}$ for analyzed Jacupiranga samples. Dark and light grey fields respectively represent the Jacupiranga carbonatites and silicate rocks compiled from Huang et al. (1995) and Beccaluva et al. (2017).

by Huang et al. (1995) and present the lowest $^{207}\text{Pb}/^{204}\text{Pb}_{(i)}$ ratios among the analyzed lithotypes.

5.3. Hf isotope composition

The analyzed Jacupiranga samples span a rather wide range of $^{176}\text{Hf}/^{177}\text{Hf}_{(i)}$ ratios: 0.282253–0.282771 ($-18.36 < \epsilon\text{Hf}_{(i)} < -0.05$; Table S3, Fig. 5A). Clinopyroxenites and ijolite display higher Hf isotope values (0.282651–0.282754) than feldspar-bearing rocks and lamprophyre (0.282253–0.282533). Monzonite and meladorite are the least radiogenic rock-types. Dunite yields an initial Hf isotopic ratio similar to clinopyroxenite and ijolite ones, whereas wehrlite yields a composition close to the feldspar-bearing rocks. The $\epsilon\text{Hf}_{(i)}$ and $\epsilon\text{Nd}_{(i)}$ define a good correlation, with a linear expression of $\epsilon\text{Hf}_{(i)} = 0.614\epsilon\text{Nd}_{(i)} - 4.247$ ($R^2 = 0.99$) for clinopyroxenites-ijolite and $\epsilon\text{Hf}_{(i)} = 1.198\epsilon\text{Nd}_{(i)} - 1.272$ ($R^2 = 0.93$) for rocks from the Heterogeneous Zone.

6. Discussion

6.1. Constraints on the origin of the Jacupiranga carbonatites

The Jacupiranga carbonatites show a pronounced layering (Fig. 2C) defined by varying amounts of non-carbonate phases (apatite, olivine, magnetite, and phlogopite). According to Gaspar (1989), the mineral

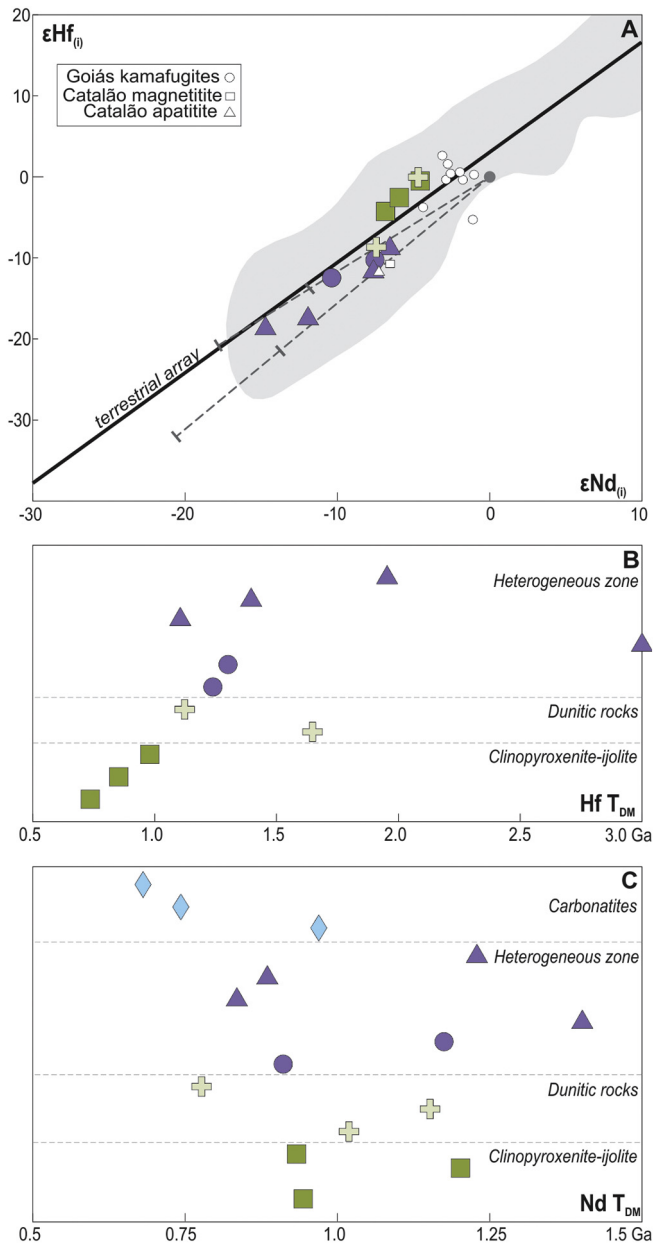


Fig. 5. (A) Initial ϵHf vs. Initial ϵNd diagram for analyzed Jacupiranga samples. Initial ϵNd values from Chmyz et al. (2017), Goiás kamafugites (Carlson et al., 2007) and Catalão rocks (Guarino et al., 2017) are shown for comparison. Grey field represents oceanic and crustal data used to define the terrestrial array of Vervoort et al. (1999). Dashed vectors are models from Nowell et al. (2004) and show the isotopic evolution of MARID metasomites from an initial BSE composition over 1–1.5 Ga. (B) Distribution of $\text{Hf } T_{\text{DM}}$ and (C) $\text{Nd } T_{\text{DM}}$ model ages for analyzed Jacupiranga samples. Symbols are as in Fig. 4.

layering is usually vertical (i.e. intrusions C2 and C4) or steep (i.e. C1 and C5), only C3 showing lower angle (between 20° and 40°) layering. Although steep angles are commonly found in the lateral zones of cumulative intrusions (e.g., Mbirney and Noyes, 1979), they are unlikely in this case due to the widespread occurrence of vertical/subvertical layers. We consider that such layers shall be interpreted as flow (as already proposed by Melcher, 1966), and that the different types of carbonatites of the Jacupiranga complex are mainly representative of melts.

Generally speaking, among the models classically invoked to explain the genesis of carbonatites, liquid immiscibility is believed to have generated most Brazilian carbonatites (Comin-Chiaramonti et al., 2005; Gomes et al., 2011). This hypothesis is based on either mass-balance calculations (Beccaluva et al., 1992) or geochemical constraints

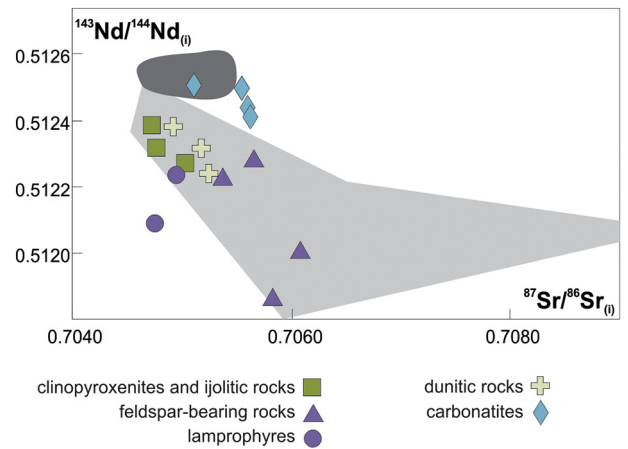


Fig. 6. Initial $^{143}\text{Nd}/^{144}\text{Nd}$ vs. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios for Jacupiranga rocks. Symbols refer to data by Chmyz et al. (2017). Dark and light grey fields respectively represent the Jacupiranga carbonatites and silicate rocks compiled from Roden et al. (1985), Huang et al. (1995), Ruberti et al. (2005) and Beccaluva et al. (2017).

(e.g., Ruberti et al., 2002; Guarino et al., 2012; Brod et al., 2013). For the Juquiá alkaline-carbonatite complex, Beccaluva et al. (1992) argue that a basanitic parental magma, by crystallization of mafic cumulates, fractionated into a nepheline syenite melt from which carbonatite separated due to immiscibility. Comin-Chiaramonti et al. (2007) referred to the Juquiá model as a suitable scenario for other Mesozoic to Cenozoic Brazilian carbonatites. Therefore, alkaline-carbonatite associations would have been generated by a combination of fractional crystallization and immiscibility processes (Gomes et al., 2011).

Indeed, liquid immiscibility is considered by Germann et al. (1987), Gaspar (1989) and Comin-Chiaramonti et al. (2007) as the mechanism that generated the Jacupiranga carbonatites. The latter suggested that ankaratrite melts evolved through fractionation of clinopyroxene and olivine (i.e. clinopyroxenite and dunite) to phonolite/peralkaline phonolite melts. The carbonatite melt separation would be associated with the transition of phonolite to peralkaline phonolite liquids. Later on, Huang et al. (1995) came to a different conclusion: not only have the carbonatites and clinopyroxenites derived from different parental magmas, but also low-degree melting of phlogopite garnet peridotites was able to reproduce the Jacupiranga carbonatites composition. Likewise, Beccaluva et al. (2017) argued that genetic links between

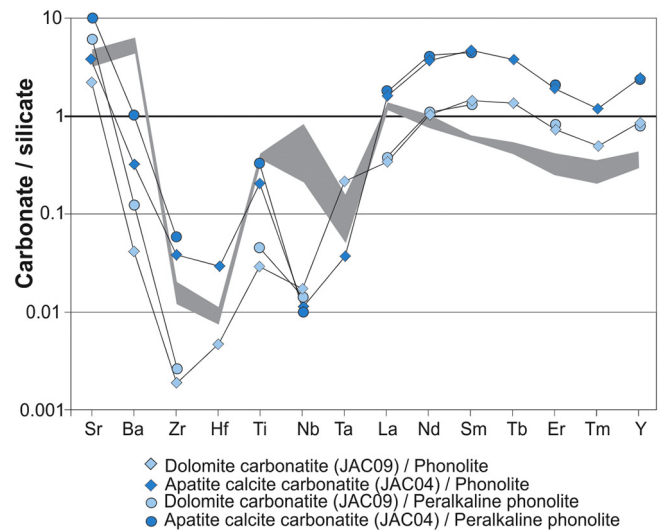


Fig. 7. Concentration ratios between Jacupiranga carbonatites and phonolites. Partition coefficients of trace elements between immiscible carbonate and silicate liquids (represented by grey field, compiled from Veksler et al., 1998b) are plotted for comparison.

Jacupiranga carbonatites and silicate rocks are not evident, as their isotopic carbon compositions suggest an independent generation.

Both strongly- and mildly alkaline silica-undersaturated series defined for the Jacupiranga complex (Chmyz et al., 2017) could have generated carbonatites by a combination of crystal fractionation and liquid immiscibility processes. Parental nephelinite magmas, such as suggested for the strongly silica-undersaturated series, have long been proposed for the generation of carbonatite magmas by liquid immiscibility (Freestone and Hamilton, 1980; Le Bas, 1987; Lee and Wyllie, 1997; Mitchell, 2005). Similarly, parental magmas such as those of the mildly silica-undersaturated series could give origin to carbonatite melts following the same evolution path proposed for Juquiá by Beccaluva et al. (1992).

Harmer and Gittins (1998) point out that, due to their common origin by liquid immiscibility, the conjugate silicate and carbonatite rocks should present similar isotopic compositions. However, this is not observed in the Jacupiranga complex: although most silicate rocks and carbonatites span a similar range in initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, carbonatites exhibit distinctly higher $^{143}\text{Nd}/^{144}\text{Nd}_{(i)}$ ratios (Fig. 6), an isotopic characteristic also noticed by Beccaluva et al. (2017). Similarly to the Nd isotopic ratio distinction, Jacupiranga carbonatites have lower initial Pb isotopic ratios than those of the silicate rocks (Fig. 4). The Jacupiranga rocks do not appear to have been significantly contaminated by crustal materials as only some lithotypes (i.e. meladiorite and monzonite) show chemical and petrographic evidences of crustal contamination (Chmyz et al., 2017). Therefore, the differences of initial Nd and Pb ratios between carbonatites and silicate rocks are regarded as a primary feature.

In order to further constrain the petrological relationship, if any, between carbonatites and silicate rocks of the Jacupiranga complex, we consider the partition coefficients (D carbonate/silicate melts at ca. 1 kbar) obtained by Veksler et al. (1998b) to assess the effects of liquid immiscibility (Fig. 7). Following Comin-Chiaramonti et al. (2007), the exsolution of carbonatite liquids in Jacupiranga may be related to the evolution from phonolite to peralkaline phonolite melts. Thus, specimens of the latter two lithotypes were selected for evaluation (Table S1). Additionally, taking into account that Jacupiranga carbonatites were emplaced from south to north (Gaspar and Wyllie, 1983), a southern CCap and a northern DC specimens were chosen.

In the Jacupiranga complex, from all trace elements considered in the experiments conducted by Veksler et al. (1998b), only Sr behaviors as expected (Fig. 7). The Jacupiranga phonolites indeed have higher HFSE contents than carbonatites, however, all the tested pairs yield considerably higher ratios of Ta in comparison with Nb, and only the pair CCap/phonolite shows Zr-Hf depletion, considered as a fingerprint for silicate-carbonatite immiscibility processes (Brod et al., 2013). Besides, the Jacupiranga phonolites have higher Ba and lower Nd, Sm, and Tb contents than those of the carbonatites, while the DC presents La content lower than that of the phonolites. Therefore, following the criteria by Veksler et al. (1998b), the trace elements distribution within the Jacupiranga carbonatites speaks against a liquid immiscibility hypothesis.

A partitioning experiment from Veksler et al. (1998b) is also showed in the Nb vs. Ta diagram (Fig. 8) from Thompson et al. (2002): both initial material and silicate conjugate show Nb/Ta ratios lower than that of the separated carbonatite melt. These experimental relationships are well constrained by the carbonatites, silicate rocks and parental magma from the Tapira alkaline-silicate carbonatite complex (Brod et al., 2013), whose carbonatites are mostly attributed to an origin by liquid immiscibility. In comparison, the Jacupiranga lamprophyres (representatives of the parental magma of the mildly silica-undersaturated series) and phonolite yield Nb/Ta values (15.67–16.83 and 19.35, respectively) higher than those of the analyzed carbonatites (1.40–9.79), precluding the latter to be generated by immiscibility processes from any such melts.

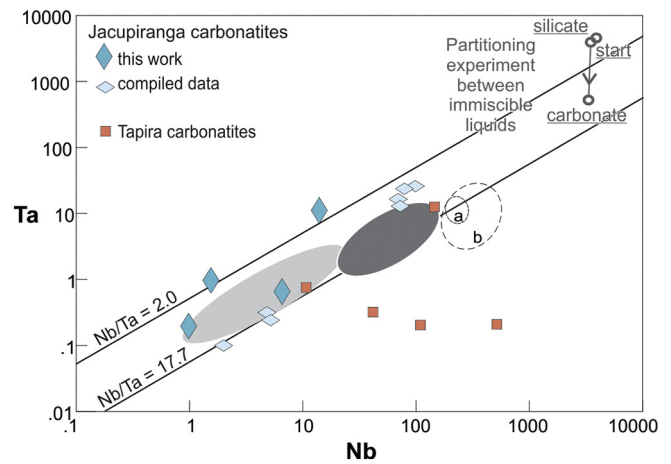


Fig. 8. Nb vs. Ta diagram (Thompson et al., 2002) for Jacupiranga carbonatites. Jacupiranga data compiled from Huang et al. (1995), Ruberti et al. (2005) and Beccaluva et al. (2017). Light and dark grey fields represent silicate rocks from strongly and mildly silica-undersaturated series, respectively. Data for Tapira carbonatites and silicate rocks from Brod et al. (2013) are plotted for comparison. Dashed fields: a, Tapira parental melt and b, Tapira bebedorites and syenite.

Ba/La ratios are considered as credible evidence for the mechanisms of carbonatite origin: during immiscibility, the carbonatite conjugate should present Ba/La ratios higher than those of its silicate counterpart under almost any pressure and temperature conditions (Hamilton et al., 1989; Harmer, 1999; Srivastava and Sinha, 2004; Srivastava et al., 2005). Jacupiranga carbonatites have Ba/La ratios lower than most silicate rocks (Fig. 9). Therefore, the higher Ba/La values of the lamprophyres and phonolites would preclude a liquid immiscibility origin from mildly silica-undersaturated series. Likewise, nepheline syenites and ijolite rocks show ratios higher and similar than those of carbonatites, respectively. Hence, it is also unlikely that the latter were generated from immiscibility processes related to the strongly silica-undersaturated series.

Based on Sr, Nd and Pb radiogenic isotopic ratios and trace element signatures, the Jacupiranga carbonatites do not derive from liquid immiscibility from any two silicate parental magmas considered for the complex. Hence, a primary origin by direct partial melting of the mantle

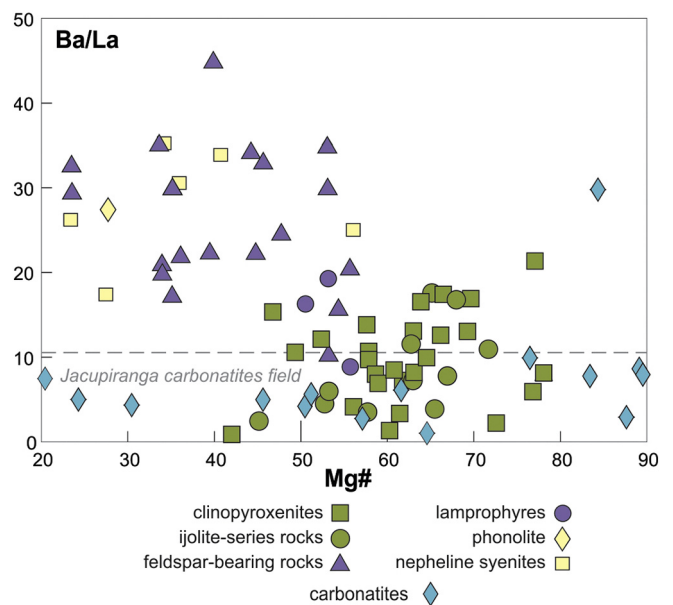


Fig. 9. Distribution of Ba/La compositions in carbonatites and silicate rocks in the Jacupiranga complex. Data compiled from Ruberti et al. (2005), Beccaluva et al. (2017), and Chmyz et al. (2017).

sounds more reasonable. Such a model is supported by both experimental (Wallace and Green, 1988; Thibault et al., 1992; Dalton and Wood, 1993; Lee and Wyllie, 1998) and natural systems (e.g., Harmer and Gittins, 1998; Harmer, 1999; Srivastava and Sinha, 2004; Srivastava et al., 2005; Beccaluva et al., 2017). According to Wyllie and Lee (1998), primary magnesio-carbonatite melts can be generated by partial melting of a carbonated peridotite at depths greater than ca. 70 km. Upon their ascent, these melts will react, crystallize and release CO₂ vapor at depths of ca. 70 km. This process is expected to generate clinopyroxene at the expense of orthopyroxene, thus converting lherzolite to wehrlite and changing the carbonatite melt to more Ca-rich compositions (Dalton and Wood, 1993; Wyllie and Lee, 1998; Harmer and Gittins, 1998). Gittins and Harmer (2003) advocated that, although of separate origins, carbonatite and alkaline melts could employ the same plumbing system in their rise through the lithosphere and, therefore, alkaline-carbonatite complexes such as Jacupiranga would solely reflect a spatial association between those lithotypes.

6.2. Metasomatism events on the mantle source of silicate rocks

Sr, Nd, and Pb isotopic ratios of carbonatites and silicate rocks of Jacupiranga plot close to EM1 (enriched mantle 1) component, with some contribution of HIMU (Fig. 10). This is in agreement with the well-defined array of depleted and enriched mantle components proposed by Comin-Chiaramonti et al. (2007) for the alkaline-carbonatite

complexes of the Paraná-Angola-Namibia system. The Jacupiranga isotopic data are also mostly consistent with the field of the Brazilian Cretaceous alkaline-carbonatite complexes, a signature interpreted as indicative of a heterogeneously enriched subcontinental lithospheric mantle (SCLM) due to metasomatic events (Ruberti et al., 2005; Comin-Chiaramonti et al., 2007; Ruberti et al., 2012).

Geochemical and isotopic constraints are used to assess the contribution of at least two metasomatic episodes in the mantle source of the Jacupiranga series: (1) a Neoproterozoic metasomatic event possibly derived from slab-derived fluids, and (2) a Mesozoic carbonatite metasomatism produced by sub-lithospheric fluids.

Basic alkaline magmas may derive by low-degree melting of a lithospheric mantle source metasomatized by fluids that generate incompatible-enriched vein networks, as supported by experimental petrology (Foley, 1992a, 1992b; Pilet et al., 2008). Such magma compositions would reflect hybridization between vein and wall-rock components. Several works have proposed vein-plus-wall-rock melting mechanisms for the origin of the Brazilian alkaline occurrences (e.g., Gibson et al., 1995; Comin-Chiaramonti et al., 1997; Gibson et al., 1999; Gibson et al., 2006; Comin-Chiaramonti et al., 2007; Ruberti et al., 2012; Azzone et al., 2013; Azzone et al., 2018). In the Jacupiranga complex, some major and trace element signatures (e.g., high CaO/Al₂O₃ and La/Zr, low Ti/Eu) of lamprophyres (the sole representative of primitive melt found in the Jacupiranga complex – also referred to as ankaratrites in previous works) and calculated melts in equilibrium with clinopyroxenites cumulus primocrysts indicate metasomatism of the mantle peridotite by carbonatite fluids in this locality (Chmyz et al., 2017). Indeed, the contribution of a carbonatite metasomatic component was proposed for the entire Ponta Grossa Arch Province (e.g., Gibson et al., 1999; Ruberti et al., 2005; Gomes et al., 2011; Ruberti et al., 2012; Azzone et al., 2013). In such a scenario, the interaction of these melts with the mantle peridotite would generate a clinopyroxene-veined network within a peridotite wall-rock, according to the reaction: dolomite + orthopyroxene = clinopyroxene + olivine + 2CO_{2fluid} (Dalton and Wood, 1993).

The timing of the carbonatite metasomatism imprint on the Jacupiranga source can be discussed on the basis of Hf and Nd isotopic signatures. Recently, both isotopic systems have been successfully applied to constrain carbonatite metasomatism events (e.g., Bizimis et al., 2003; Tappe et al., 2007; Woodhead et al., 2017). Bizimis et al. (2003) established that a carbonatite-metasomatized mantle should evolve towards radiogenic Hf and unradiogenic Nd signatures with time. According to those authors, this evolution should lead the mantle composition to transverse the width of the Nd-Hf terrestrial array within a maximum of 200–300 Ma of isolation and, because of that, the melting of an aged carbonated metasomatized mantle source would generate magmas with Nd-Hf signatures outside the range of oceanic and crustal samples of the terrestrial array after Vervoort et al. (1999) (Fig. 5A), thus indicating that the carbonatite metasomatism affected the SCLM not long before the Jacupiranga parental melts generation. A similar line of reasoning was followed by Tappe et al. (2007) for the timing of the carbonatite metasomatism imprint on the mantle source of the Aillik Bay aillikites.

Jacupiranga Hf isotope ratios may also be a hint for the role of sub-lithospheric mantle sources on the generation of the metasomatic CO₂-melts. Since the Jacupiranga magmatism (ca. 134.9–131.9 Ma, Chmyz et al., 2017) is coeval with the outpouring of Paraná Magmatic Province (PMP) tholeiitic basalts (134.7 ± 1 Ma, Thiede and Vasconcelos, 2010), εNd-εHf values inside the width of the terrestrial array indicate that the carbonatite metasomatism took place in a scenario where magmas were generated from both lithospheric and sub-lithospheric mantles. According to Bell and Simonetti (2010), while the role of lithospheric sources in the carbonatite melts formation is still under scrutiny, the close petrological relationship of carbonatites with large igneous provinces (such as PMP) is considered as “crucial

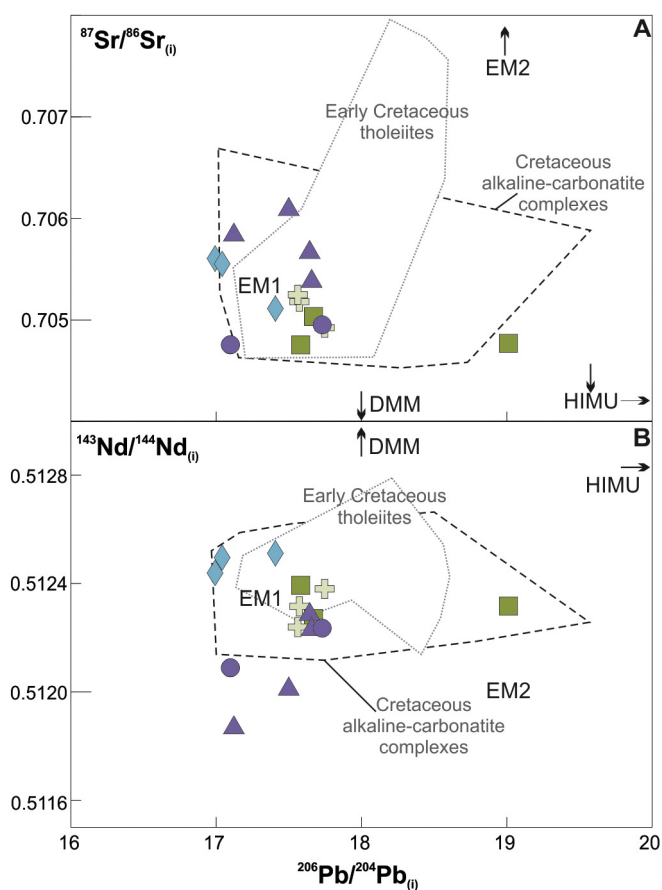
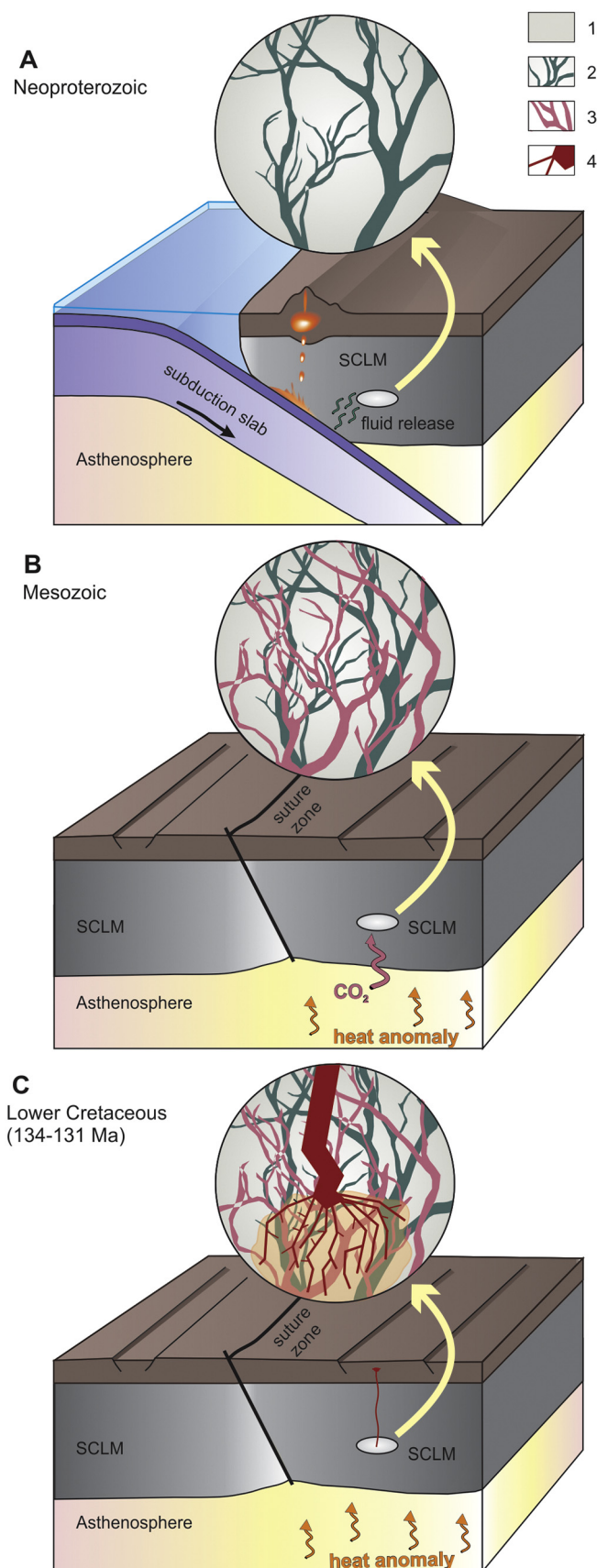


Fig. 10. (A) Initial $^{87}\text{Sr}/^{86}\text{Sr}$ vs. initial $^{206}\text{Pb}/^{204}\text{Pb}$ and (B) Initial $^{143}\text{Nd}/^{144}\text{Nd}$ vs. initial $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic ratios for analyzed Jacupiranga rocks. Parameters EM1, EM2, HIMU, and DMM are approximations of mantle end-members from Bell and Blenkinsop (2001) and Comin-Chiaramonti et al. (2005), after Hart et al. (1992). Fields of Early Cretaceous tholeiites of the Paraná Etendeka province (Comin-Chiaramonti et al., 2005 and references therein) and Brazilian alkaline-carbonatite complexes (Comin-Chiaramonti et al., 2005 and references therein) are plotted for comparison. Sr-Nd data are from Chmyz et al. (2017). Symbols as in Fig. 4.



evidence” of carbonatite sub-lithospheric origin. Therefore, carbonate metasomatizing fluids could have originated just like the PMP high-Mg picrite-basalt magmas: from asthenospheric sources owing to the trigger effect of a hot plume (Natali et al., 2018). Indeed, Gibson et al. (1999) proposed that Lower Cretaceous Tristan da Cunha plume-related melts accumulated in the SCLM might have been remobilized within a few million years to generate the Brazilian Lower Cretaceous alkaline units. The suggested scenario also resembles that of the nephelinite-carbonatite melts from Oldoinyo Lengai (Bell and Simonetti, 1996; Pirajno, 2009): 1) metasomatism of SCLM by fluids derived from an upwelling mantle plume 2) followed soon after by partial melting of said metasomatized mantle.

Besides the clinopyroxene-rich veins, lamprophyres, which are compositional proxies for the parental magma of the mildly silica-undersaturated series of the Jacupiranga complex (Chmyz et al., 2017), give further information on mantle source mineralogy and are indicative of other phases related to different metasomatic events. They yield high Dy/Yb ratios (2.81–3.05), coherent with melts derived from the garnet stability field (e.g., Yang et al., 2012; Yücel et al., 2017). In addition, their high phlogopite modal content (up to 35 vol %) indicates presence of K₂O- and H₂O-rich phases in the mantle source (e.g., Gibson et al., 1999). Similar phlogopite concentrations are found in minettes of the Lages alkaline-carbonatite complex (Upper Cretaceous, southern Brazil), to which Gibson et al. (1999) attributed phlogopite as the most likely metasomatic phase to host those components in the mantle. The Jacupiranga lamprophyres yield Rb/Sr and Ba/Rb ratios ranging from 0.04 to 0.06 and from 21.55 to 24.03 (Menezes et al., 2015; this work), consistent with small amounts of phlogopite and amphibole in the source (e.g., Furman and Graham, 1999). Also, primitive mantle-normalized patterns yield P and Sr troughs, indicating residual apatite (e.g., Tappe et al., 2006, 2008). Therefore, the Jacupiranga melts generation may involve the partial melting of a metasomatic vein network composed of clinopyroxene, phlogopite, amphibole, and apatite in a garnet peridotite mantle source.

Furthermore, despite the Mesozoic carbonatite metasomatism episode, the mostly Neoproterozoic Hf T_{DM} and Nd T_{DM} model ages for the Jacupiranga samples (Fig. 5B, C) imply that older enrichment processes have also affected their mantle source. Both Hf T_{DM} and Nd T_{DM} model ages for silicate rocks yield a dispersive range of values (0.7–3.0 Ga and 0.8–1.4 Ga, respectively), while the analyzed carbonatites yield systematically lower Nd T_{DM} ages (681–819 Ma). Comin-Chiaromonti et al. (1997, 2007) interpreted the large range of Nd T_{DM} model ages (0.5 to 2.0 Ga) of the carbonatite-alkaline occurrences along the margin of the Paraná Basin as related to episodes of metasomatism that affected the SCLM during Meso- to Neoproterozoic.

As the mantle reset indicated by the T_{DM} ages is mainly coeval to the Brasiliano Orogenic Cycle, a mantle source metasomatism related to slab-derived fluids is considered for the alkaline units along the Paraná Basin margins (e.g., Comin-Chiaromonti, 1997, 2014; Ruberti et al., 2005; Guarino et al., 2013; Guarino et al., 2017), and also for the high-Ti tholeiites from the PMP (e.g., Marques et al., 1999; Rocha-Júnior et al., 2013). In addition, the Jacupiranga lamprophyres yield several geochemical signatures (i.e. LREE/HREE enrichment, negative Nb-Ta anomalies, La/Th: 10.63 to 11.90) consistent with the participation of a subduction-related component in some point of the enrichment story of their mantle source. Those geochemical features are also shared

Fig. 11. Proposed model for the evolution of the Jacupiranga mantle source. (A) Neoproterozoic metasomatic process generated by slab-derived fluids related to the Gondwana assembly with formation of a vein network (phlogopite-rich) in a garnet peridotite source. (B) Carbonatite metasomatism of the SCLM and formation of clinopyroxene-rich veins during Mesozoic times. (C) Partial melting of both vein generations plus garnet peridotite wall-rock (following the vein-plus-wall-rock melting mechanism by Foley, 1992a) producing the parental magmas of the Jacupiranga series. Legend: 1, garnet peridotite; 2, metasomatic veins related to slab-derived fluids; 3, metasomatic veins related to carbonatite melts; 4, melt.

by the high-Ti tholeiites from the PMP (Marques et al., 1999; Rocha-Júnior et al., 2013).

Multi-stage metasomatism of the lithospheric mantle has been invoked to explain the genesis of K-rich alkaline magmas, as sustained by both experimental (Ulmer and Sweeney, 2002) and natural (e.g., Gibson et al., 1995; Tappe et al., 2006, 2007, 2008) systems. Gibson et al. (1995) envisaged a multi-stage process for the mantle sources of the mafic potassic rocks of the Alto Paranaíba Igneous Province (Brazil), as both silicate and carbonatite melts might have an important role in their metasomatic enrichments. Similarly, a two-stage metasomatism of the cratonic mantle has been proposed by Tappe et al. (2008) for the genesis of the Torngat ultramafic lamprophyre suite, which includes young carbonate-bearing (generated by carbonate melts derived from convective mantle) and older hydrous dominated MARID-type vein assemblages. Although the precise compositional nature of the Neoproterozoic metasomatic episode that affected the Jacupiranga mantle source is difficult to assess, Nowell et al. (2004) developed several $\epsilon\text{Hf}-\epsilon\text{Nd}$ theoretical models considering the evolution of different vein-metasomatic assemblages over 1–1.5 Ga from a starting BSE composition. The MARID assemblage models evolve to unradiogenic compositions and plot close to the terrestrial array, with an evolution that fits the signatures observed for the Heterogeneous Zone rocks from the Jacupiranga complex (Fig. 5A). A MARID- or PIC-type veined mantle source was also suggested by Ruberti et al. (2012) for the Banhadão alkaline complex from the Ponta Grossa Arch Province. Those signatures, along with the presence of phlogopite and amphibole in the Jacupiranga source, are suggestive of hydrous and/or potassic composition for the Neoproterozoic metasomatism.

Hence, our proposed model for the Jacupiranga series involves a garnet peridotite source from the SCLM subjected to at least two vein-forming metasomatic processes (e.g., Foley, 1992a). The oldest metasomatism event resulted from slab-derived fluids related to the Gondwana assembly during Neoproterozoic times (Fig. 11A). This enrichment, possibly of hydrous and/or potassic composition, generated a first vein network (phlogopite-rich) in the mantle source. Afterwards, when the Brazilian platform was subjected to an extensional setting due to the Gondwana breakup in the Mesozoic (Almeida, 1983; Comin-Chiaromonte and Gomes, 2005; Ruberti et al., 2012), carbonatite fluids from the sub-lithospheric mantle (presumably plume-related) interacted with the garnet peridotite protolith to generate a clinopyroxene veined network (Chmyz et al., 2017) (Fig. 11B), following the reactions of Dalton and Wood (1993). Then, at ca. 134–131 Ma, melting of those different vein networks and peridotite wall-rock produced the parental melts of the Jacupiranga series (Fig. 11C). A similar scenario is proposed for the magma source region of the Torngat suite, for which Tappe et al. (2008) argued that, due to persistent stretching and thinning of the cratonic lithosphere, carbonate-rich veins were remobilized and a volatile-fluxed fusion of older MARID-type veins and the peridotite wall-rock was provoked. Thus, the distensive environment prevailing during Mesozoic times in the Gondwana realm would be able to cause the low-degree melting of a multi-stage metasomatized mantle source, generating the parental melts of the Jacupiranga series.

7. Conclusions

Several lines of evidence indicate that the Jacupiranga carbonatites are not directly related to neither strongly nor mildly silica-undersaturated series. Based on isotopic and trace element signatures (e.g., Ba/La ratios, absence of pronounced Zr-Hf and Nb-Ta decoupling), we favor a primary carbonatite melt formed by direct partial melting of the mantle source. This work is the first one to report Hf isotope ratios on whole-rock samples from Lower Cretaceous alkaline-carbonatite complexes of the southern-central portion of the South American platform. In general, the Sr-Nd-Pb-Hf isotope systematics of the Jacupiranga complex imply an important contribution of a metasomatized

subcontinental lithospheric mantle to the genesis of these rocks. A multi-stage metasomatism is proposed for the Jacupiranga series mantle source, which possibly yielded different generations of vein assemblages. Two distinctive events of metasomatic imprinting are constrained, one related to slab-derived fluids of Neoproterozoic ages, and another produced by Mesozoic carbonatite melts originated in the sub-lithospheric mantle. The Hf isotope data were paramount for establishing the timing of carbonatite metasomatism in the mantle source as not long before the generation of Jacupiranga parental melts.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gr.2019.01.012>.

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