Alkaline-Carbonatitic magmatism

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Carbonatites from the Southern Brazilian platform: I

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Abstract: We present a comprehensive overview of the geochemical characteristics and evolution of the carbonatites from the southern Brazilian Platform (Paraná Basin). The carbonatites from different complexes display large compositional variability in terms of abundances of incompatible and rare earth elements. This is in agreement with an origin from heterogeneous lithospheric sources, as confirmed by isotopic data (see Speziale et al., this issue). The characteristic major and trace element abundances of these carbonatites present compelling evidence for invoking liquid unmixing as the main mechanism of their formation and evolution albeit few exceptions. We propose an evolutionary trend for the Brazilian carbonatites, which can be summarized as following: exsolution of the primary Ca- or Mg-carbonatitic liquids systematically takes place at the phonolite-peralkaline phonolite stage of magma differentiation; this is followed by progressive Fe-enrichment and by final emplacement of fluorocarbonatites associated with hydrothermal fluids.

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1 Introduction

The Paraná Basin is a part of the Paraná-Angola-Namibia (Etendeka) Province (PAEP [1]). It is characterized by Early Cretaceous flood basalts (tholeiites) and dyke swarms (130–135 Ma, according to refs. [2–5] and references therein) associated with alkaline and alkaline–carbonatite complexes of Early Cretaceous to Tertiary age [6–14]. The emplacement of these complexes, in and around the PAEP, occurred mainly along tectonic structures active at least since the Early Mesozoic (Figure 1), and up to present day, as indicated also by the distribution of the earthquakes in southern Brazil [15]. Molina and Ussami [16] and Ernesto et al. [3,4] pointed to a clear correlation between geoid anomalies and magmatic/tectonic provinces along southeastern Brazil and Uruguay.

The carbonatitic complexes from southern Brazilian Platform have been the subject of several studies focussing on their geology, petrology, geochemistry, and processes of liquid immiscibility [6,8–10,17–36].

The numerous carbonatitic occurrences provide additional information about the geochemical characteristics of the source regions, which are complementary to those from the silicate rocks. Carbonatitic liquids have extremely fast ascent rate and emplacement, and their peculiar chemical and physical characteristics make carbonatitic liquids better suited than silicate ones as indicators of mantle sources [36,37]. Here, we present the overall picture of the geochemical evolution of carbonatite magmatism in the southern Brazilian Platform by using an extended dataset of major and trace elements compositions (see Appendix).

This article and another article dedicated to the isotopic data (Speziale et al., this issue) can be considered a compendium of a series of specific studies from the same group of authors [11–14,31,32,38–42].

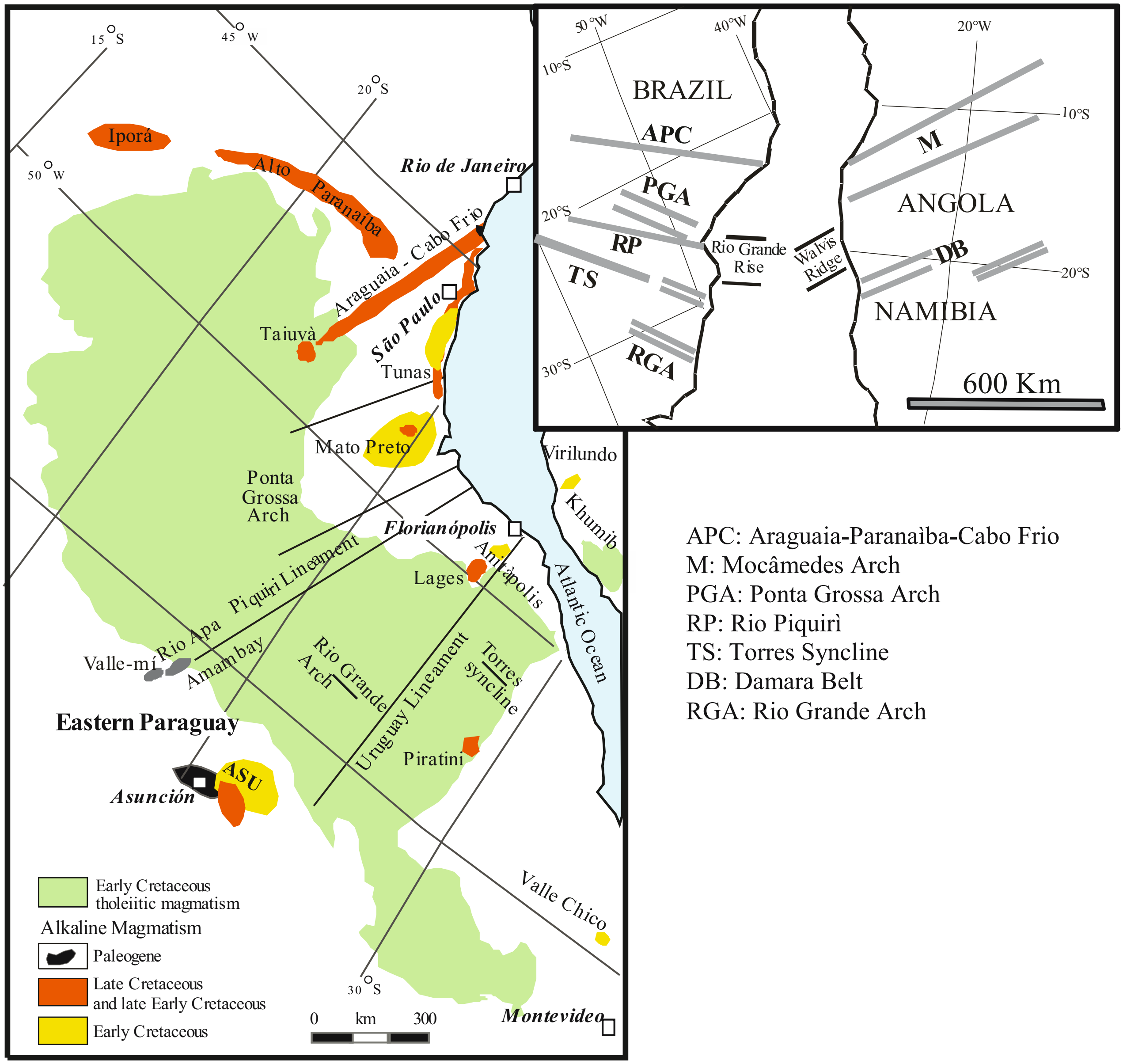

Figure 1: Distribution of the tholeiitic magmatism in the Paraná Province (South American Platform, Western Gondwana) and location of the main alkaline–carbonatitic regions in a reconstruction corresponding to 110 Ma (after refs. [39,51] and Figure 1.11 of ref. [14]), where all the single alkaline outcrops are represented. ASU, Central-Eastern Paraguay magmatic province [38]. Inset: Main lineaments in the Paraná-Etendeka System (South American and African plates, Western Gondwana) at about 110 Ma; modified after refs. [40,52] corresponding to the main lineaments of the alkaline and alkaline–carbonatitic complexes (cf. Figures 2–4 of Ref. [53]). APC, Araguaia-Paranaìba-Cabo Friom; M, Mocâmedes Arch; PGA, Ponta Grossa Arch; RP, Rio Piquirì; TS, Torres Syncline; DB, Damara Belt; RGA, Rio Grande Arch.

2 Geographic location, tectonic setting, major geolithological characteristics, and classification of the carbonatitic complexes in the Southern Brazilian Platform

The carbonatitic complexes from southern Brazil and Paraguay are found mainly along the following alignments: (1) Araguaia-Alto Paranaíba (APIP; [6])-Cabo Frio; (2) Ponta Grossa Arch (e.g., Jacupiranga, Juquiá, Barra do Itapirapuã); (3) Piquirí lineament (mainly in Eastern Paraguay); (4) Torres syncline; and (5) Rio Grande Arch (Figure 1).

Based on their age relative to the flood basalts and their associated intermediate and acid lava flows [2], these occurrences are pretholeiitic (e.g., Cerro Chiriguelo and Cerro Sarambí; 136–143 Ma), syn-tholeiitic (e.g., Anitápolis, Jacupiranga, Juquiá; 130–133 Ma), and posttholeiitic (e.g., Sapucai, 128 Ma; Ipanema, 124 Ma; Barra do Itapirapuã, 115 Ma) [cf. refs. 1,13,28,43,44]. In addition, tertiary alkaline complexes (mainly 45–65 Ma) are also present and distributed along the Taiúva-Cabo Frio lineament (Serra do Mar igneous province; cf. ref. [44]).

The geochemical characteristics of the carbonatites appear to be strictly linked to the mineral assemblages in the various evolutionary stages in carbonatites (p. 662 in ref. [31]). The mineral associations in the four main evolutionary stages are presented in Table 1.

According to refs. [22] and [27], carbonatite occurrences are believed to be produced by processes of liquid immiscibility. The rock association present in the Juquiá complex represents the prototype of all the examined carbonatites, whose evolution, reproduced by mass-balance calculations [22], follows the same sequence of stages: (1) fractionation from a parental basanite melt to a phonotephritic (basanitic) magma by crystallization of olivine clinopyroxenite and minor cumulus of olivine alkali gabbro; (2) separation of the least differentiated mafic nepheline syenite from the essexitic magma through fractionation of syenodioritic assemblages; and (3) exsolution of carbonate liquid from the CO_2-enriched nepheline syenite magma, which further fractionates producing ijolite–melteigite–urtite cumulates.

The line of evolution (alkaline gabbro to syenogabbro to nepheline syenite) is linked to the removal of large amounts of cumulitic material, mainly olivine and clinopyroxene, as indicated by the abundance of pyroxenitic and dunitic rocks in the field (cf. Figures 2 and 3 of ref. [31]). Clinopyroxene and olivine fractionation is required for the transition from olivine nephelinite/ankaratrite to phonolite/peralkaline phonolite. The exsolution of carbonatite liquids appears to be associated with the evolution of phonolite to peralkaline phonolite liquids [18].

2.1 Petrographic classification

The rock associations present in the alkaline complexes of Southern Brazil are described in detail in refs. [11,14,39]. On the basis of the petrographic associations [14], the carbonatitic occurrences of the Paraná Basin can be classified as follows:

1) Magmatic carbonatites
   (A) Occurrences associated with rock types of the urtite–ijolite–melteigite series, without the presence of extrusive nephelinites (Brazil: *Vale do Ribeira*: Anitápolis, Ipanema, Itapirapuã, Jacupiranga, Mato Preto and Juquiá; *Goiás*: Caiapó and Morro do Engenho; Paraguay: Cerro Sarambí and Sapucai).
   (B) Brazilian occurrences associated with only olivinites and pyroxenites as ultramafitites (±syenites) as Salitre I and Serra Negra, and with glimmerites as Araxá, Catalão I, Catalão II and Salitre II.
   (C) Brazilian occurrences with either intrusive ultra-melilitolites in Tapira [54] or extrusive olivine melilitites as in Lages [55] based on the classification schemes presented in refs. [56,57].
2) Hydrothermal carbonatites: those originated at temperatures ≤375°C are present at different locations in the Brazilian Platform. Barra do Itapirapuã is located in Brazil [28], Cerro Chiriguelo in Paraguay [21], and Cerro Manomó in Bolivia [52].
3) Occurrences with unusual geometric relationships: A limited number of occurrences of carbonatitic rocks in the form of small dykes (Itanhaém in Brazil [58]) or ocelli-like aggregates (Valle-mí, Cerro Canãda, Cerro E Santa Elena in Paraguay [59]) in alkaline silicate rocks.

2.2 Major elements' chemistry

If we neglect those containing SiO_2 > 10 wt%, the investigated carbonatites vary from calciocarbonatites

Table 1: Generalized evolution of carbonatites in the Brazilian platform (cf. also ref. [45]). Data source: [14,21,28–31,38,39,46–50]

	Major minerals	Rare metal-bearing minerals
I stage	Calcite, diopside, forsterite, melilite, monticellite, nepheline, phlogopite-biotite, apatite I, Ti-magnetite	Nb-perovskite (Nb), calzirtite (Zr, Nb), monazite (Ce, REE)
II stage	Mg-calcite ± dolomite, diopside, tetraferriphlogopite, apatite II Mg-magnetite	Baddeleyite (Zr), pyrochlore-I (Nb), hatchettoloite (Nb, Ta, U, Th), zirkelite (Zr, Nb)
III stage	Calcite, dolomite (Fe-dolomite), tetrapherriphlogopite, apatite III, magnetite, titanite	Pyrochlore (Nb, Th, U), burbankite (Sr, Ba, REE)
IV stage	Dolomite (Fe-dolomite), ankerite, siderite, magnesite, fluorite rhodochrosite, K-feldspar, quartz	Pyrochlore (U, Th, Nb), bastnäesite (REE), parisite (REE), ancylite (Sr, REE), synchysite (REE), strontianite (Sr), celestine (Sr)

(CaO, 39–45; MgO, 0.4–8.1; FeO, 0.1–10.1 wt%) to magnesiocarbonatites (CaO, 0.9–29; MgO, 12.6–46.8; FeO, 1.1–10.9 wt%) and ferruginous (i.e., iron-rich) calciocarbonatites (CaO, 28–36; MgO, 4.3–13.4; FeO, 10.0–30.3 wt%; cf. ref. [11]). However, all the three rock types are rarely associated in the same complex (e.g., Araxá, Barra do Itapirapuã, Itapirapuã; cf. refs. [30,28]). Notably, the Cerro Manomó carbonatite (Bolivia) represents the only example of a ferrocarbonatite (CaO, 7.7; MgO, 0.34; FeO, 40.5; MnO, 7.1 wt% [33,52]). The molar ratio CaO/(CaO + MgO + FeO_t + MnO) used as a differentiation index (DI) of carbonatites from Southern Brazil shows a general negative correlation with (MgO + FeO_t + MnO) wt% due to Ca–Mg–Fe–Mn substitutions typical of the main carbonate minerals [11]. The data are well consistent with multistage carbonatite evolution associated with changes of the rock-forming mineral assemblages [45], with DI decreasing from the stage I to the stage 4 of Table 1.

2.2.1 Magmatic carbonatites

2.2.1.1 Carbonatites associated with rock types of the urtite–ijolite–melteigite series, without the occurrence of extrusive nephelinites

Whole-rock chemistry data were plotted in the carbonatite classification [60,61] and appear represented by calciocarbonatites followed by magnesiocarbonatites and by ferruginous carbonatites (Figure 2, IA and IB).

In the region of Vale do Ribeira, alkaline carbonatite complexes are present in Anitápolis, Ipanema, Itapirapuã, Jacupiranga, and Juquiá (Figure 2, IA: Early Cretaceous age, 132–109 Ma; cf. ref. [39] and Table 1A of the Appendix). Early-stage magnesiocarbonatites are usually rich in apatite and phlogopite and are found in the same carbonatitic complex only at Jacupiranga, which is considered to be a primary carbonatite [25]. On the opposite, the Juquiá magnesiocarbonatites (the only rock type present in this complex) are modeled as the result of fractionation from exsolved calciocarbonatite magma [22]. This model [22] may represent a suitable picture for all the examined carbonatitic complexes, where various stages of evolution are identified, together with an additional late Fe-enrichment of carbonate liquids (Figure 2, IA and II). A similar picture applies to the genesis and evolution of the Eastern Paraguay carbonatites [27].

The Late Cretaceous (70–86 Ma) Goiás carbonatites from Caiapó, Morro do Engenho, and Santo Antônio da Barra are present in Ca and Mg variants, similar to the Early Cretaceous carbonatites of Cerro Sarambí (139 Ma) and Sapucai (121 Ma) in Paraguay (Figure 2, IB and Table 1A of the Appendix).

2.2.1.2 Alkaline–carbonatite complexes with only olivinite and pyroxenites as ultramafic rocks (±syenites) or with glimmerites

All the complexes of this group belong to the Late Cretaceous (81–86 Ma) episode of alkaline carbonatite magmatism. Both Salitre [64,65] and Serra Negra [66] are without glimmerites (cf. Figure 2, III). Conversely, the complexes of Araxá [67], Catalão I [68], and Catalão II [69] contain glimmerites. Serra Negra and Catalão II calciocarbonatites and magnesiocarbonatites are found in Salitre, whereas only magnesiocarbonatites are found in Araxá and Catalão I (Figure 2, III). Notably, the evolution from phonolite to peralkaline phonolite liquids trend is shown in Figure 2, II [18] and Figure 2 of ref. [12].

2.2.1.3 Carbonatites associated with melilitolites and melilitites

The Upper Cretaceous complexes of Tapira (70 Ma; [62,54]) and Lages (82 Ma; [30]) are the only two representatives of this group. Tapira complex contains calciocarbonatites and subordinate magnesiocarbonatites associated with ultramelilitolites, while in Lages, only ferruginous calciocarbonatites are present (Figure 3, IV) associated with olivine melilitites. According to ref. [70], complete or partial separation of carbonatites from the melite-rich silicate fractions (eventually producing intrusive melilitolites or extrusive melilitites) is related to carbonate–silicate immiscibility, probably occurred under pressure less than 14 kbar and temperature higher than 1,300°C. Subsequently, carbonatites might reach the surface as a separate eruption.

2.2.2 Hydrothermal carbonatites

The carbonatitic complex of Barra do Itapirapuã (115 Ma), according to ref. [28], is represented by rare calciocarbonatites and dominant magnesiocarbonatites with subordinate ferruginous calciocarbonatites (Figure 3, V). Notably, all the rock types formed under hydrothermal conditions at temperatures between 375°C and 80°C [28,71].

The complex of Cerro Chiriguelo (Figure 3, V, 128 Ma) [21,41] shows calciocarbonatites in the central part and veins of ferruginous carbonatite cutting the carbonatitic core.

Finally, Cerro Manomó (139 Ma), in Bolivia, contains carbonate blocks, interpreted by ref. [72] as ferrocarbonatites (Figure 3, V and Table 2 of Appendix). According

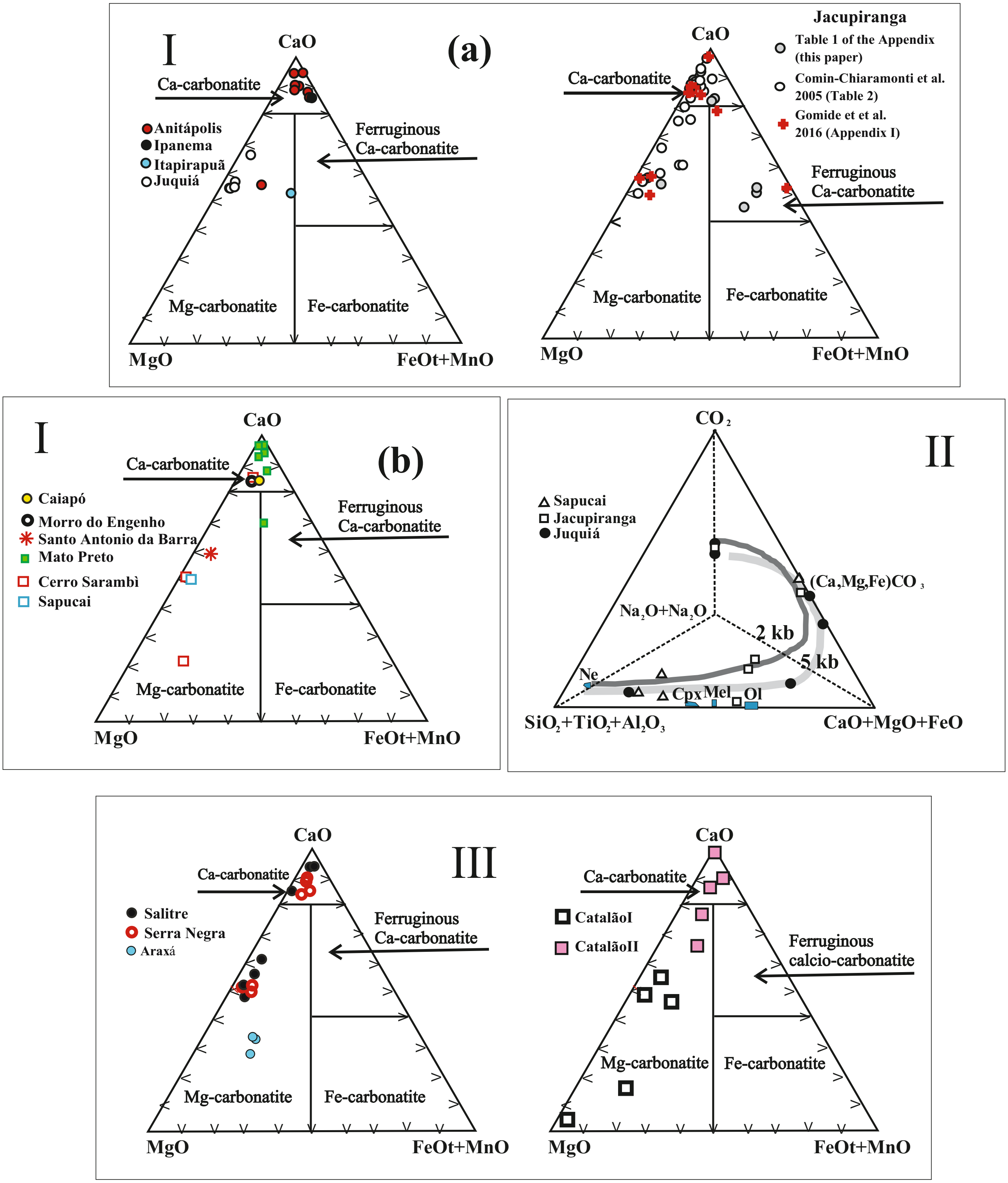

Figure 2: (I) Classification of carbonatitic associations (oxides are expressed in molar proportions, after Refs. [60,61] for the various complexes from the Brazilian Platform [31,62]). (a) Brazilian Early Cretaceous: Anitápolis, Ipanema, Itapirapuã, Jacupiranga, and Juquiá; it also includes the Early Cretaceous Paraguayan occurrences of Cerro Sarambí and Sapucai as shown in the figure IB. (b) Late Cretaceous: Caiapó, Morro do Engenho, Santo Antônio da Barra, and Mato Preto [31,62]. The full list of references is also reported in Table 1A of the Appendix. (II) Quaternary diagram showing compositional trends of exsolved carbonate liquids from a residual silicate magma [63]. The curves of 2 kb and 5 kb are theoretical isobaric-polythermal solvi [27], and the symbols are selected samples from the Appendix. Mineral abbreviations: Cpx, clinopyroxene; Mel, melilite; Ol, olivine; Ne, nepheline. (III) Classification of group B of Brazilian Late Cretaceous carbonatitic associations (Salitre, Serra Negra, Araxá, Catalão I, and Catalão II; cf. Table 1B of the Appendix).

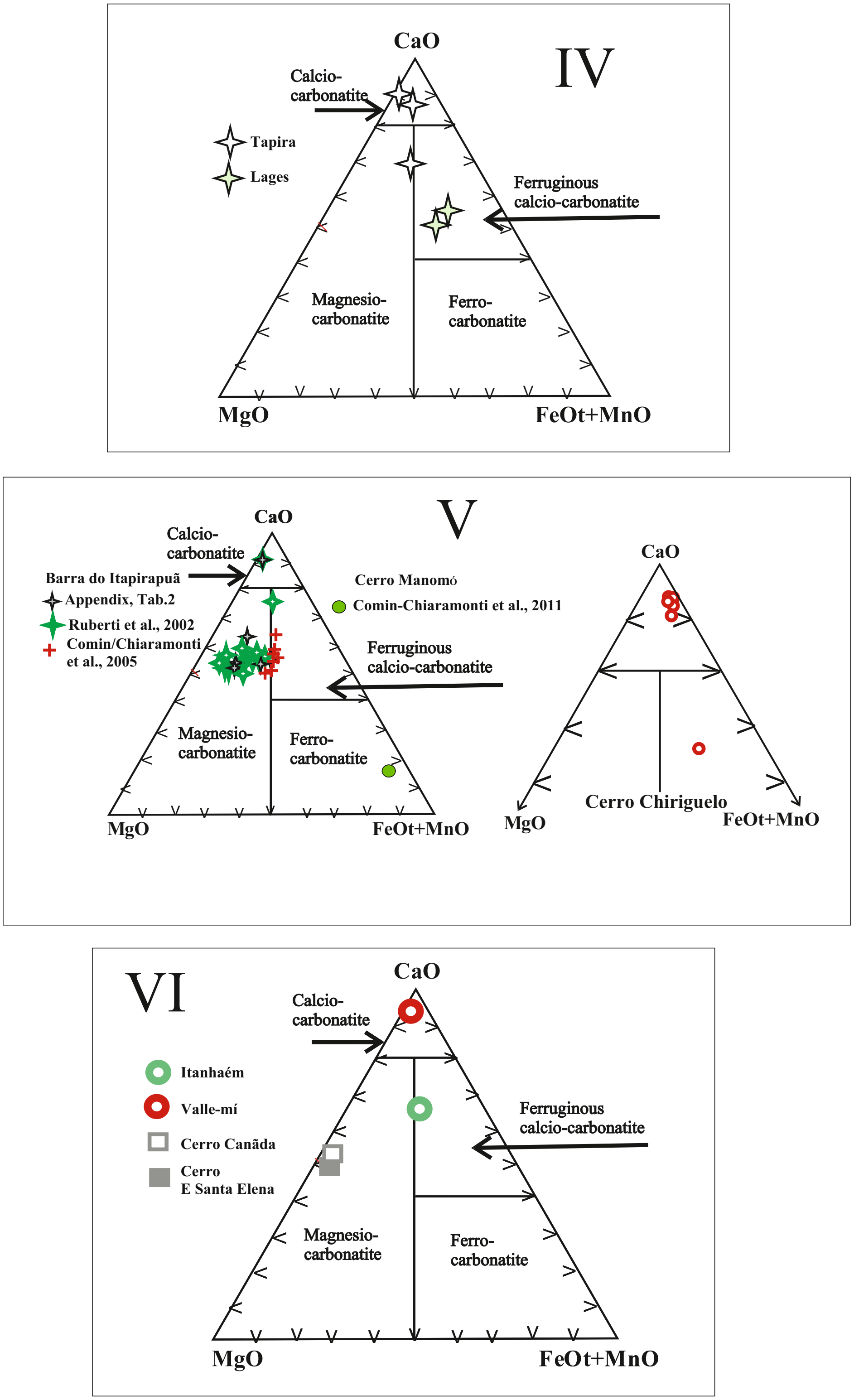

Figure 3: (IV) Classification of group C Brazilian Late Cretaceous carbonatitic associations (Tapira and Lages). Oxides are expressed as molar proportion (cf. Figure 2, and Table 1C of the Appendix). (V) Classification of the Early Cretaceous hydrothermal carbonatitic association of Barra do Itapirapuã in Brazil [28,71]. Oxides are expressed as molar proportion (cf. Table 2 of the Appendix). The plot also includes data for the complexes of Cerro Chiriguelo [21,41] and Cerro Manomó. (VI) Classification (occurrences with unusual geometric relationships) of the Early Cretaceous carbonatitic rocks from Itanhaém (129 Ma, [58]), Valle-mí (138 Ma; [37] and references therein), and Cerro Cañada and Cerro E Santa Elena (124 and 127 Ma, respectively [1,12]).

to ref. [33], the latter rock types are made up of sideritic-ankeritic carbonate, altered at hydrothermal conditions and associated mainly with rare earth elements (REE) fluorocarbonates.

2.2.3 Occurrences with unusual geometric relationships

This group consists of extremely small carbonatite occurrences with geometries that are not present in other carbonatitic complexes in Southern Brazil. A 0.3 m thick fine-grained beforsitic (ferruginous calciocarbonatitic) dyke crosses tinguatic rocks in Itanhaém (Brazil [58]). Basanitic dykes are found in Valle-mí (Paraguay) patches (probably exsolved) of calciocarbonatite[37]. In Cerro Canãda and Cerro E Santa Elena (Paraguay), ocelli made of dolomite, phlogopite, clinopyroxene, olivine, magnetite, and amphibole are contained in trachyandesitic dykes [1,11,12] (Figure 4). Representative analyses are presented in Table 3 of the Appendix and plotted in Figure 3, VI.

2.3 Incompatible elements (IEs)

The results discussed in this section is presented in the same order as the previous section, that is, (1) magmatic carbonatites, (2) hydrothermal carbonatites, and (3) occurrences with unusual geometric relationships (cf. Figures 2 and 3).

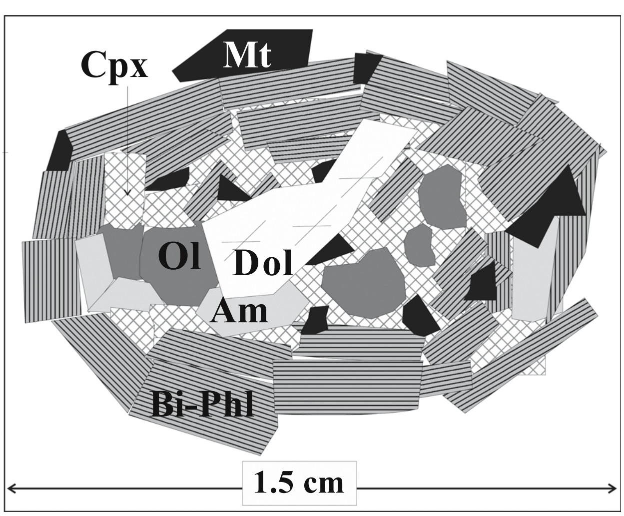

Figure 4: Mineral association representative of an *ocellus* in ijolite from the Cerro E Santa Elena alkaline complex (127 ± 8 Ma), Central Eastern Paraguay; modified after refs. [11,12]. Am, amphibole; Bi-Phl, biotite-phlogopite; Cpx, clinopyroxene; Dol, dolomite; Mt, magnetite; Ol, olivine (cf. Figure 3-VI).

2.3.1 Magmatic carbonatites

IE concentrations, which are reported in the Appendix, are shown in Figures 5 (group A) and 6 (groups B and C) as spidergrams normalized to primitive mantle concentrations [73].

The normalized values of the Early and Late Cretaceous magmatic carbonatites appear strongly enriched in La, Ce, Nd, Sm, and Eu, whereas K and Ti are systematically the least enriched elements, or they are depleted. P and Zr present very large variations probably linked to the occasional presence of apatite or phlogopite. As a matter of fact, IE in Brazilian carbonatites typically shows very large variations in the normalized values from one carbonatite complex to another for any given incompatible element [26]. The IE scatter between the different carbonatites reflects to some extent the variable distribution and concentration of mineral phases, which have high contents of selected IE such as phosphates (e.g., apatite and monazite for REE), oxides (e.g., pyrochlore for Nb, REE, Th, and U; calzirtite for Ti and Zr; zirconolite for Ti, Zr, and Nb; and loparite for REE, Ti, and Nb), REE carbonates, and REE fluorocarbonates (e.g., ancylite, bastnäsite, burbankite, and parisite).

Experiments on natural and synthetic mixtures show that carbonatite melts might be enriched in K, P, Sr, Ba, Th, and REE, as well as in F and Cl ([77] and references therein). The presence of F in silicate–carbonate systems positively influences the fractionation of Nb (Ta, U, Th, and REE) in the carbonate phase. Partitioning of IE and REE into the carbonate melt is also supported by experimental results on Nb and light rare earth element (LREE) solubility in synthetic carbonate liquids [78].

Moreover, according to ref. [79], calciocarbonatite liquids can dissolve 5–7.5 wt% of Nb_2O_5 at 950–600°C. Crystallization of these liquids at first promotes the precipitation of a perovskite-type phase followed by pyrochlore together with calcite. Phase relationships in the join calcite-La-hydroxide of the $CaCO_3$–$Ca(OH)_2$–$La(OH)_3$ system [77,80,81] show that, with the temperature variation from 610 to 700°C and increasing CO_2/H_2O ratio, the solubility of the LREE hydroxides in simplified carbonatite systems changes from 20% to 40% [81]. Bastnäsite may crystallize together with calcite from magmatic carbonate liquids with a temperature falling from liquidus (650–625°C) to eutectic (about 540°C) and

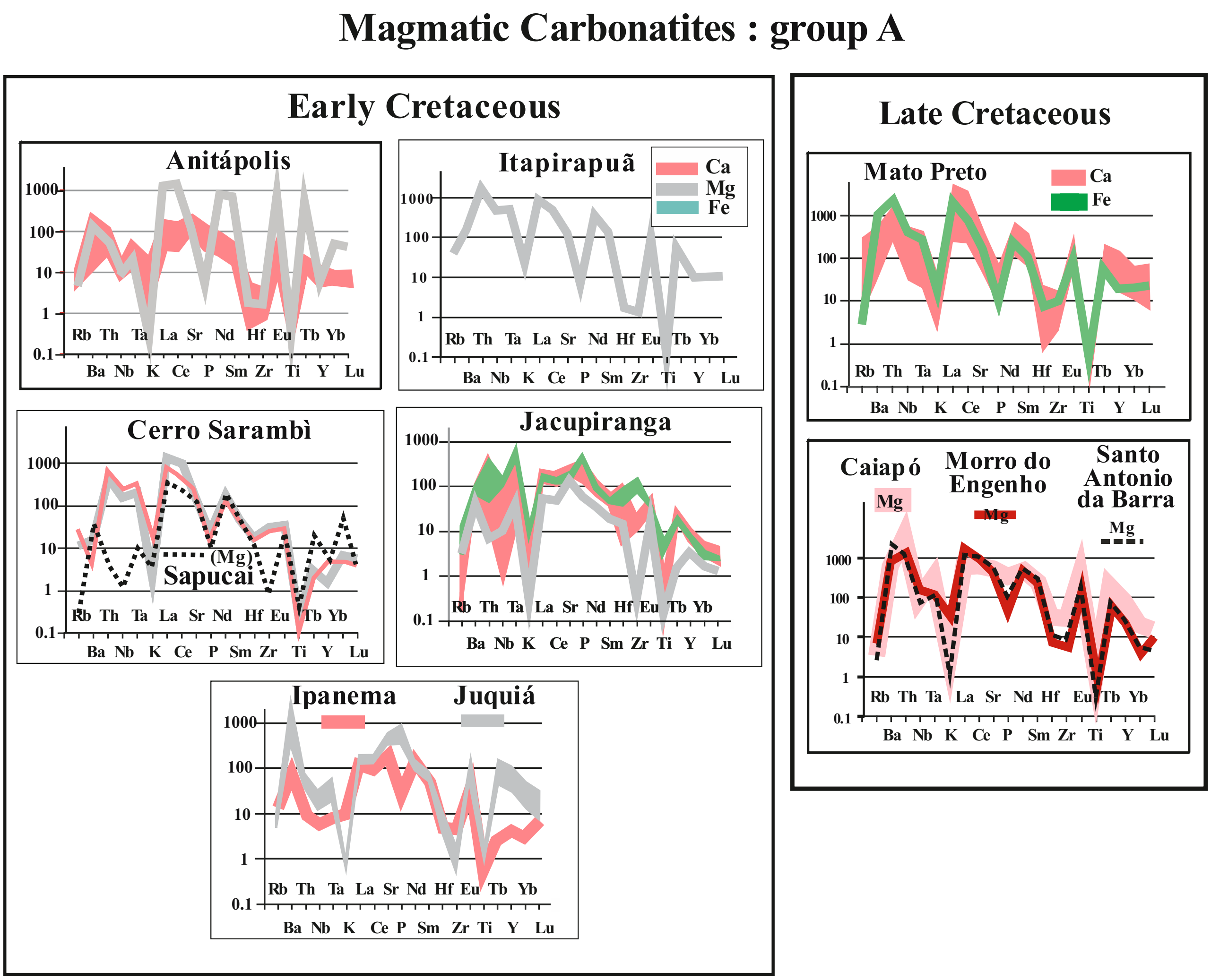

Figure 5: IE concentrations normalized to primitive mantle [73] for magmatic group A (cf. Figure 2) Early Cretaceous and Late Cretaceous carbonatites from Southern Brazil and Eastern Paraguay. Data sources in Appendix; *Early Cretaceous*: Anitápolis, [30]; Itapirapuã, [74]; Jacupiranga, [18,20,25–27,75]; Ipanema, [35]; Juquiá, [22,27]; *Late Cretaceous*: Mato Preto, [29]; Caiapó and Morro do Engenho, [46]; Santo Antônio da Barra, [6,8]. Ca, calciocarbonatite; Fe, ferruginous calciocarbonatite; Mg, magnesiocarbonatite.

under definite relations between carbon dioxide, water, and fluorine contents.

As shown in ref. [82], Brazilian carbonatites cover a wide range in a La versus La/Yb plot (cf. Figure 4 of ref. [37]), with the carbonate fractions of carbonatites displaying La/Yb ratios and La content two to three times higher than those of the parental rocks [11]. The La versus La/Yb trend of Rio Apa dykes was quantitatively modeled in ref. [37] by assuming that basanite was the carbonatites parental magma. The chemical evolution was described in terms of two main steps: (1) differentiation from basanite to trachyphonolite to phonolite by fractional crystallization and concentration of CO_2-rich fluids and (2) exsolution of about 20% carbonatitic liquids from the differentiated phonolitic magma (Figure 7).

Phlogopite-picrite rocks associated with carbonatites in Tapira as well as in other alkaline–carbonatitic complexes in the APIP show a strong compositional affinity to kamafugites present in the northern part of the APIP [6,62,65,83]. Notably, ref. [54] show that liquid immiscibility was a common process (from early phlogopite-picrites to late syenites) in the evolution of the Tapira complex, indicating liquid immiscibility of carbonatitic pockets at the very early stages (Figure 2 of ref. [54]). An exhaustive description of the relationships between carbonatites and associated kamafugites was presented in [39].

The overall very large variability of IE contents between primary carbonatites (formed by early-stage liquid immiscibility) from the different complexes supports the hypothesis that the alkaline–carbonatitic

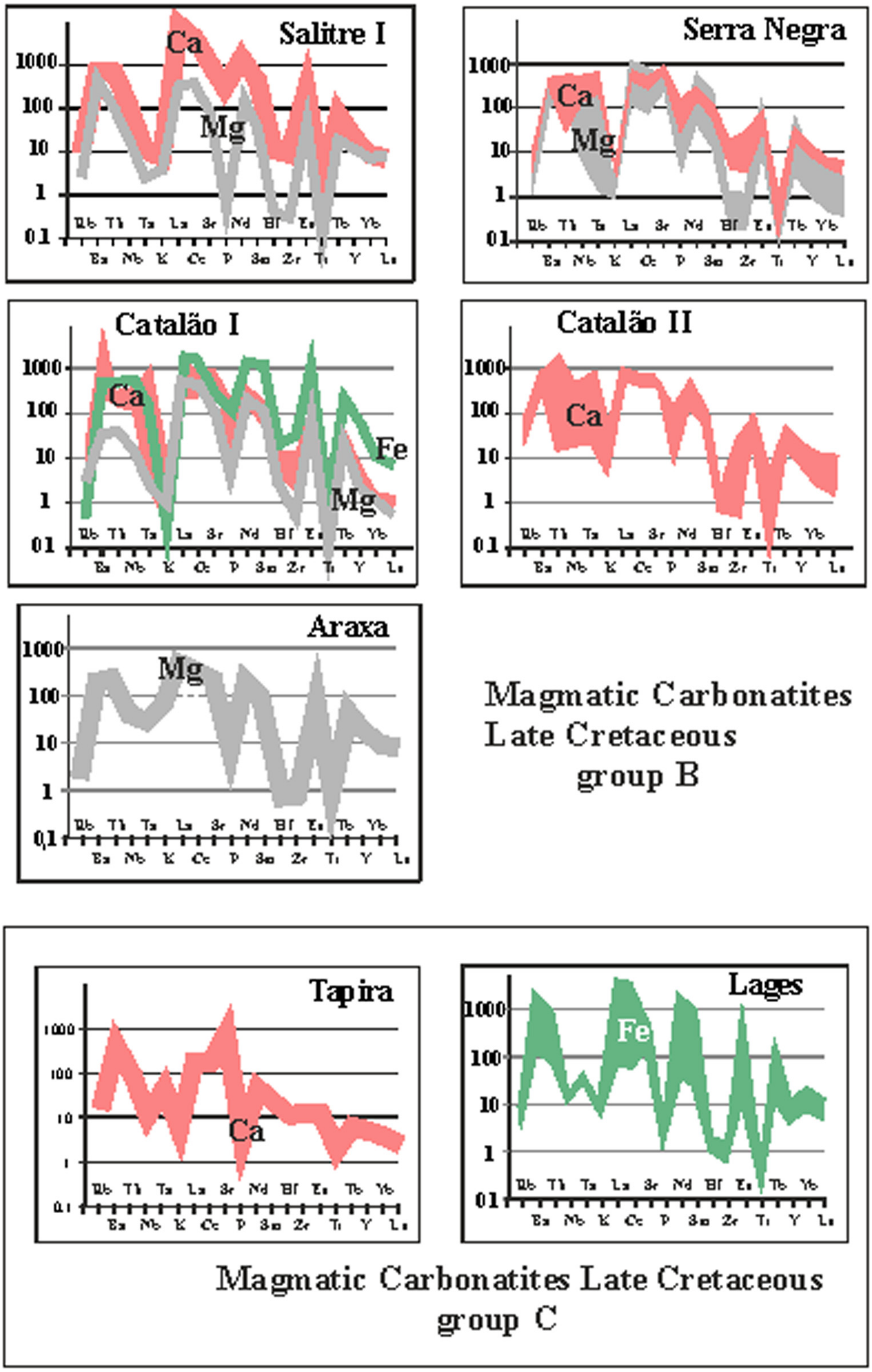

Figure 6: IE normalized to primitive mantle concentrations [73] for magmatic group B Late Cretaceous carbonatites from Southern Brazil. Data sources: Appendix. Salitre, [64,65]; Serra Negra, [66]; Catalão I, [68]; Catalão II, [69]; Araxá, [67]. Magmatic group C Late Cretaceous carbonatites from Southern Brazil (cf. Appendix): Tapira, [54]; Lages, [30,55,76]. Ca, Mg, and Fe: calciocarbonatite, ferrocarbonatite, and ferruginous calciocarbonatite.

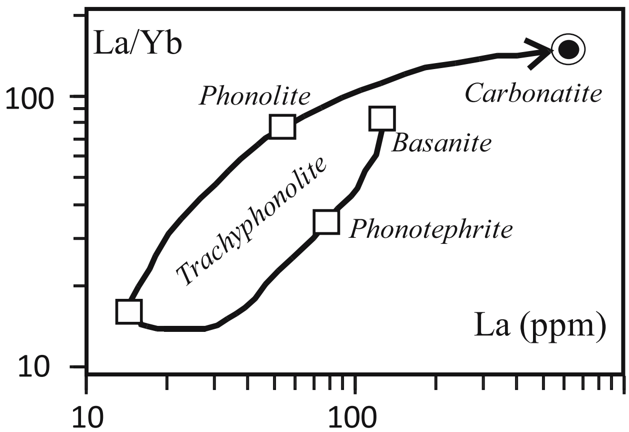

Figure 7: Evolutionary path of La/Yb ratio versus La, as determined for the Rio Apa dykes [37].

magmatism was produced by local heterogeneous subcontinental mantle sources connected to metasomatic events attributed to Neoarchean to Neoproterozoic time based on isotopic systematics ([11,12]; see also the study by Speziale et al., this issue). Some of this complexity, especially in the pattern of REE contents, can be due to the process of carbonatitic magma unmixing that produce characteristic crossing between the patterns of carbonatites and associated silicate rocks [84].

2.3.2 Hydrothermal carbonatites

REE carbonates, REE fluorocarbonates, and oxides, which are the products of hydrothermal environments, represent to some extent the individual fenitizing fluids enriched in IE rather than the primary carbonates [37]. For instance, different generations of carbonatite dykes are present in the Barra do Itapirapuã complex (Figure 3, V) [28, 85, 86]. In Barra do Itapirapuã, carbonatites are present as dykes and veins stockwork in which at least three main carbonatitic phases are recognized (Figure 3, V), that is, prevailing magnesiocarbonatites, ferruginous calciocarbonatites, and subordinate calciocarbonatites (Figure 8). These carbonatites are generally overprinted by pervasive hydrothermal events at temperatures between 375°C and 80°C during which significant amounts of REE fluorocarbonate minerals, relatively Th- and Sr-rich were deposited. Synchysite, parasite, and bastnäsite may occur as single crystals and/or polycrystals. Textural and chemical relationships between the REE fluorocarbonates provide insights into the mobility of REEs during fluid–rock interaction [28,31,85].

At Cerro Chiriguelo (Figure 8), calciocarbonatites are the prevailing rock types and show relatively high contents of Ba, Ta, Th, and Nb. The subordinate ferruginous calciocarbonatites also display high contents of Nb, Ta, and REE. Nb and Th contents of these rocks appear related to the local abundance of uranpyrochlore [21].

Cerro Manomó presents rare blocks of ferrocarbonatite made up of altered sideritic–ankeritic carbonatite with subordinate goethite–limonite, apatite, and REE-F-carbonates [52]. The latter produces a strong REE enrichment clearly shown in Figure 8.

2.3.3 Occurrences with unusual geometric relationships

The Itanhaém carbonatite (129 Ma, according to ref. [58], is represented by fine-grained Fe-dolomite veins in tinguaitic dykes, particularly enriched in Th and LREE, which make this complex a Th source of economic interest [87]).

Basanitic dykes (about 139 Ma) with a microcrystalline groundmass consisting of about 20 vol% of primary

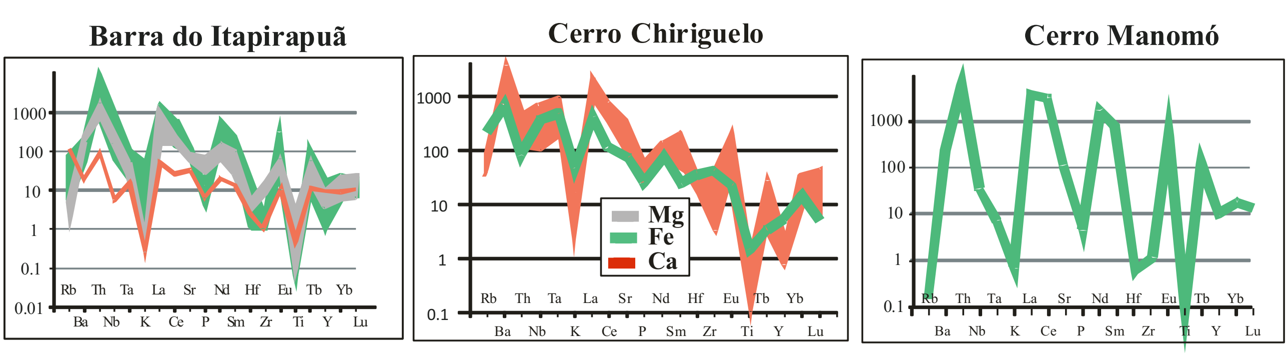

Figure 8: IE normalized to primitive mantle concentrations [73] for Early Cretaceous hydrothermal carbonatites. Data sources: Barra do Itapirapuã, [28,71]; Cerro Chiriguelo, [21]; Cerro Manomó, [52]. Ca, calciocarbonatite; Fe, ferruginous carbonatite; Mg, magnesiocarbonatite.

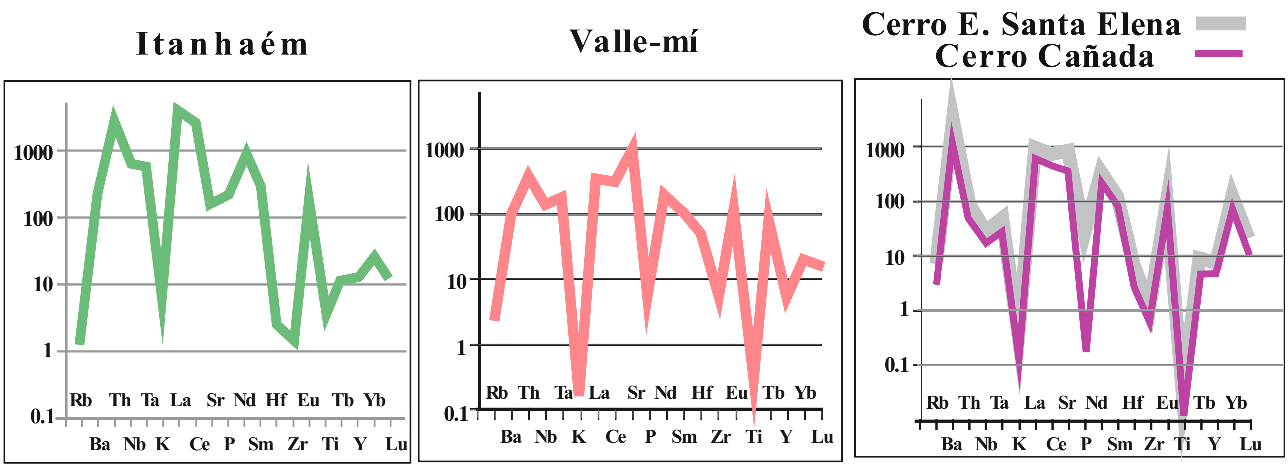

Figure 9: IE normalized to primitive mantle concentrations [73] for early cretaceous carbonatites occurrences with unusual geometric relationships. Sources of data: Itanhaém [58,87], Valle-mí [41], and Cerro Cañada and Cerro E Santa Elena [59].

calciocarbonates are present near the town of Valle-mí in Paraguay [41]. The carbonates show large enrichment of Th (Nb and Ta), REE, and Sr, and strong depletion of K and Ti with respect to mantle abundances (Figure 9).

The ijolitic host rocks in Cerro Cañada and Cerro E. Santa Elena alkaline complexes (notional age, 126 Ma [88]) are characterized by *ocelli* containing dolomite (magnesiocarbonatite; Figure 4) highly enriched in Ba, Sr, and REE ([11,37] and references therein) as shown in Figure 9.

Notably, the IE spidergrams (Figures 5–9) display remarkable scattering even within individual complexes. This is particularly evident between samples of Ca, Mg, and ferroginous calciocarbonatite belonging to different stages of crystallization of the same complex (i.e., magmatic to late-magmatic and hydrothermal conditions).

Different types of distinctive behaviors emerge if we plot REE spidergrams. In Figure 10, we grouped the different carbonatites as a function of their age of emplacement. Here, we can identify three main types of distribution [31]:

(1) Patterns with a strong decrease from La to Lu, which can be observed for instance in the rocks from Cerro Chiriguelo, Jacupiranga, and APIP [6,62] magnesiocarbonatites, Mato Preto, and Lages (both early and late carbonatites). It should be noted that the REE enrichment in Mato Preto and Lages appear to be controlled by late, secondary, carbonatite veins.
(2) Patterns with a relative weakly decrease from La to Lu, as shown in Jacupiranga (calciocarbonatites), Juquiá (magnesiocarbonatites and calciocarbonatites), Anitápolis, and Barra do Itapirapuã (calciocarbonatites).
(3) Concave patterns with a steady decrease from LREE to Dy and an HREE plateau, as found in Valle-mí and Barra do Itapirapuã occurrences. The carbonatites from the latter location contain the highest LREE concentrations due to the presence of REE fluorocarbonates [25,31,32,37,50,62]. Fluorite deposits are also present in Barra do Itapirapuã.

In conclusion, the different behaviors of the early-crystallized carbonatites, which are believed to be "primary" carbonatitic liquids (calciocarbonatites and magnesiocarbonatites), would reflect the chemical signatures of their parental melts (cf. primary calciocarbonatites and magnesiocarbonatites of the Jacupiranga and Juquiá complexes, respectively), as also outlined by ref. [89] and confirm the presence of local scale heterogeneous subcontinental mantle sources of possible due to metasomatic events dating back to the Neoarchean to Neoproterozoic based on radiogenic isotopes systematics [11,12]. The presence of late-crystallized ferruginous calciocarbonatites, variably enriched in fluorocarbonates, indicates hydrothermal processes, also supported by the observed low-temperature mineral associations (cf. [38,39]).

3 Concluding remarks

The alkaline–carbonatitic magmatism from the Southern Brazil is distributed along tectonic lineaments in both American and African continents.

The carbonatites mainly occur in the inner parts of circular/oval-shaped alkaline–carbonatitic complexes, being the rock bodies usually associated with evolved silicate rocks where liquid immiscibility processes played an important role in their genesis.

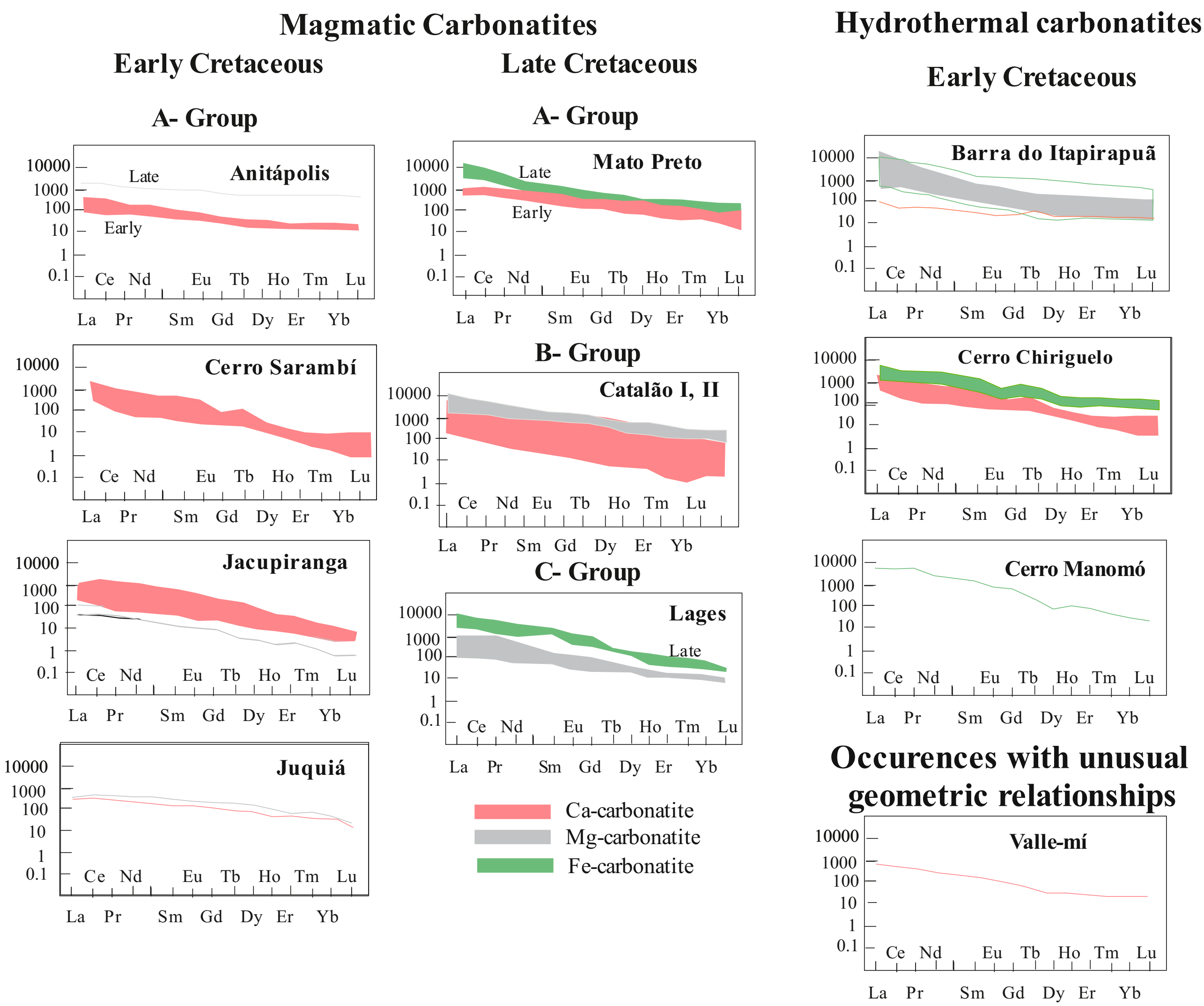

Figure 10: Spidergrams of REE normalized to chondritic contents [90] for selected Early and Late Cretaceous carbonatites (modified after ref. [31] cf. also Figures 5–9).

The geochemical data, major and trace elements, show that the genesis of the magmatism from the Southern Brazilian Platform requires heterogeneous mantle sources. As a matter of fact, the large variation of IE and REE appear related to hydrothermal processes, probably connected to metasomatic sensu lato events that occurred between Neoarchean and Neoproterozoic times [11,12].

The areal distribution of magmatism suggests that the alkaline–carbonatitic magmatism originated from large- to small-scale heterogeneous subcontinental mantle. All the results indicate that asthenospheric components derived from mantle plumes (i.e., Tristan da Cunha and Trindade hot spots [91]) did not significantly contribute to the genesis of the alkaline–carbonatitic magmatism, consistent with the conclusions reached by refs. [2–4,11,82,92] for the petrogenesis of the Paraná flood tholeiites

Regional thermal anomalies in the deep mantle, mapped by geoid and seismic tomography, support a nonplume-related heat source for the southern Brazil magmatism [4,93,96], where the hotspot tracks of Walvis Ridge and Rio Grande Rise, as well as the Victória–Trindade chain, might reflect the accommodation of stresses in the lithosphere during rifting rather than continuous magmatic activity induced by mantle plumes beneath the moving lithospheric plates (cf. also the study by Speziale et al., this issue), where the main conclusions relative to the Brazilian carbonatites are reported).

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Appendix

Magmatic carbonatites

Table 1A: Selected analyses of representative carbonatites of the urtite–ijolite–melteigite series without nephelinites extrusives. References: Brazil: *Vale do Ribeira*: Anitápolis [17,94]; Ipanema [35]; Itapirapuã [74]; Jacupiranga [25,31,32,62,75]; Mato Preto [29]; Juquiá [22]. *Goiâs*: Caiapó and Morro do Engenho [46]. Paraguay: Cerro Sarambí [41,42]; Sapucai [95]

	Anitápolis age: 131 (1) Ma						Ipanema age: 124.9 (9.5) Ma
Sample	**SAN 1.0**	**14–49**	**12–78**	**11–101**	**16A–50.5**	**49–82**	**119.2**
wt%							
SiO_2	0.31	0.20	2.45	1.20	0.47	3.00	3.97
TiO_2	0.01	0.01	0.06	0.05	0.07	0.08	0.13
Al_2O_3	0.21	0.02	0.01	0.09	0.10	0.52	0.19
FeO	0.08	2.59	2.03	2.95	4.49	5.96	7.61
MnO	0.07	0.08	0.23	0.22	0.23	1.80	0.25
MgO	1.55	2.30	4.13	1.83	1.70	12.80	1.08
CaO	53.59	51.25	49.36	52.15	51.80	31.43	47.60
Na_2O	0.05	0.16	0.34	0.01	0.07	1.51	0.37
K_2O	0.49	0.78	0.07	0.02	0.06	1.01	0.30
P_2O_5	0.48	1.31	2.37	2.89	1.80	2.12	1.73
L.O.I.	42.06	40.13	38.72	38.25	38.37	38.64	35.68
Sum	98.90	98.83	99.77	99.66	100.06	99.03	98.91
IE (ppm)							
Rb	3.2	6.1	6.5	6.9	5.5	3.22	8
Ba	1052	951	1579	1121	894	1106	500
Th	5.6	3.5	0.31	0.09	0.27	5.50	0.8
Nb	5.2	8.9	7.8	10.4	8.3	6.32	4.0
Ta	1.4	0.5	1.5	1.8	1.4	1.02	0.3
K	4,068	6,475	581	166	498	83	2,491
Sr	2,462	2,983	6,849	4,462	2,779	2,462	5,950
P	20,950	5,717	10,343	12,612	7,855	524	2,550
Hf	0.4	0.4	1.8	0.8	0.38	0.67	1.4
Zr	15.8	7.7	46.2	15.5	16.4	18.74	54
Ti	60	60	360	300	420	480	779
Y	43.7	18.8	45.9	42.9	41.5	29.81	20
REE							
La	67.1	41.2	123.4	48.6	158	979	76.1
Ce	142.3	90.3	287	106.5	372	2,657	170
Pr	16.8	12.2	29.2	14.5	37.8	291	23.9
Nd	69.6	47.5	115.7	53.5	170.4	1,154	196
Sm	13.8	9.4	21.33	9.44	29.22	326	22
Eu	4.0	2.53	6.51	3.91	8.55	129.4	6.24
Gd	12.6	7.91	19.83	8.90	20.61	475	15.9
Tb	1.87	1.35	2.17	1.59	3.48	61.3	1.6
Dy	9.62	7.67	11.63	9.04	12.17	728	5.9
Ho	1.74	1.39	2.44	1.64	2.11	131.2	0.8
Er	4.81	3.17	5.90	3.74	4.43	155.7	1.9
Tm	0.63	0.56	0.81	0.67	0.71	23.76	0.25
Yb	3.74	3.09	4.83	3.48	3.07	25.00	1.5
Lu	0.59	0.44	0.65	0.51	0.36	3.21	0.19
Mol%							
CaO	96.0	90.6	95.9	91.0	89.5	56.8	86.2
FeO + MnO	0.2	3.7	3.5	4.3	6.4	11.0	11.1
MgO	3.8	5.7	0.6	4.7	4.1	32.2	2.7

Table 1A: Continued

	MatoPreto age: 70 (1) Ma						Juquiá age: 132 (3) Ma				
Sample	**I—119.3**	**I—84.0**	**II—77.0**	**III—70.0**	**III—62.2**	**III—622**	**S16C**	**S25**	**S26A**	**S26B**	**SJT**
Wt%											
SiO_2	0.30	0.23	0.52	1.91	2.28	3.22	0.24	0.30	0.27	0.36	0.29
TiO_2	0.01	0.01	0.11	0.02	0.11	0.06	0.02	0.01	0.03	0.02	0.02
Al_2O_3	0.23	0.14	0.21	0.21	0.59	0.81	0.07	0.10	0.09	0.11	0.10
FeO	1.81	0.92	2.23	1.73	10.01	4.56	1.54	1.72	1.58	1.69	1.63
MnO	0.19	0.19	0.22	0.21	0.73	0.39	0.38	0.52	0.43	0.47	0.45
MgO	0.99	0.33	1.32	0.51	6.12	1.49	12.59	17.11	17.52	17.55	16.49
CaO	54.35	54.83	53.13	55.01	39.21	49.74	37.83	30.90	31.05	30.39	32.54
Na_2O	0.03	0.01	0.02	0.01	0.10	0.06	0.89	0.45	0.45	0.46	0.56
K_2O	0.10	0.07	0.09	0.31	0.58	1.09	0.02	0.02	0.02	0.02	0.04
P_2O_5	0.52	0.17	0.51	0.16	0.28	1.67	13.25	5.47	5.57	5.28	6.14
L.O.I.	41.27	43.15	41.38	40.16	38.89	36.40	33.14	43.88	42.97	43.61	40.90
Sum	99.83	100.05	99.74	100.24	98.90	99.49	99.97	99.98	99.98	99.96	99.16
IE											
ppm											
Rb	2.9	4.3	6.8	10.2	1.6	189	4	5	6	3	4.5
Ba	175	3,798	1,134	449	8,378	2,226	1,700	3,780	12,500	4,490	5,618
Th	44.8	19.9	82	147	811	117.8	2.73	5.00	4.51	4.68	4.23
Nb	251	384	23	95	315	25.1	16	8	20	16	16
Ta	9.4	18.7	0.8	6.3	11.8	1.4	0.74	2.13	0.74	1.70	1.33
K	830	581	747	2,574	4,815	9,049	166	166	166	166	332
Sr	8,735	2,134	8,758	1,053	3,693	4,652	8,450	5,540	5,720	5,190	5,985
P	2,269	742	2,226	698	1,222	7,288	57,783	23,871	24,291	23,042	26,795
Hf	2.9	7.7	0.2	3.7	2.4	4.9	1.25	2.62	1.55	3.24	2.18
Zr	45.9	123	23	183	123	178	16	7	20	16	15
Ti	60	60	659	120	659	179	120	60	180	120	120
Y	74.3	121	192	225	96	673	339	402	119	202	266
REE											
La	198	165	241	3,686	852	1,112	99.3	99.1	68.6	85.2	88.1
Ce	377	461	717	6,510	1,577	1,808	262	257	177	221	232
Pr	44.3	69.5	101	581	155	233	34.5	30.7	24.2	31.4	30.5
Nd	156	341	461	884	350	948	164	149	97.9	120	148
Sm	25.8	73.4	91	174	52	79	31.5	29.5	18.9	23.2	26.8
Eu	8.2	22.6	22.2	56.8	17.0	25.0	17.6	21.3	7.54	11.5	12.4
Gd	24.1	76.2	71	161	48	88	66.7	72.6	21.5	32.1	49.9
Tb	3.74	12.0	8.3	23.1	6.9	14.4	12.3	12.2	4.1	7.6	9.2
Dy	17.3	67.3	39.9	86	30.2	90	59.7	70.3	21.6	36.8	53.0
Ho	2.81	12.3	6.7	9.7	5.1	18.2	11.3	12.9	4.1	6.0	9.7
Er	7.3	24.0	16.0	26.5	10.4	47	27.6	32.2	10.5	17.0	25.8
Tm	1.07	2.83	2.6	3.8	1.7	6.9	3.8	4.3	1.0	1.7	3.7
Yb	4.78	10.2	8.5	22.6	11.3	34.1	17.3	21.7	5.93	9.69	16.8
Lu	0.42	1.53	2.20	3.34	1.8	5.7	1.65	2.07	0.52	0.64	1.60
Mol%											
CaO	94.9	97.6	93.4	96.1	69.9	89.3	66.6	54.7	54.5	53.8	57.0
FeO + MnO	2.7	1.6	3.4	2.6	15.0	7.0	2.6	3.1	2.8	3.0	2.8
MgO	2.4	0.8	3.2	1.3	15.1	3.7	30.8	42.2	42.7	43.2	40.2

Table 1A: Continued

Goiás	Caiapó age: 86 (6) Ma	Morro do Engenho age: 86 (6) Ma	Santo Antônio da Barra age: 86 (6) Ma	Paraguay Cerro Sarambí age: 138.9 (0.9) Ma			Paraguay Sapucai age: 128.6 (2) Ma
	CR-09	**ME-C**	**SAB-12**	**GL-SA**	**GL-SA**	**SA-958 Trachyphonolite**	**PS72 Phonotephrite**
			Glimmerite-Carbonatite (whole rock)	**Carbonate Fraction (dolomite)**	**Carbonate Fraction (dolomite)**	**Carbonate Fraction (calcite 7%)**	**Carbonate Fraction (24.3 wt%)**
Wt%							
SiO_2	2.26	0.62	0.88	28.82	—	—	—-
TiO_2	0.27	0.15	0.07	3.22	0.06	0.05	—
Al_2O_3	0.10	0.05	0.05	7.37	—	—	—
FeO	4.71	3.14	3.53	8.71	1.49	4.25	2.51
MnO	0.26	0.23	0.28	0.11	—	—	0.26
MgO	3.78	4.71	14.85	19.27	20.83	3.95	20.17
CaO	45.94	46.30	32.85	9.23	30.21	48.12	30.04
Na_2O	0.28	0.19	0.05	0.29	—	—	0.25
K_2O	0.10	0.12	0.04	3.35	0.08	0.07	—
P_2O_5	7.70	1.01	2.29	0.31	0.39	0.33	—
L.O.I.	33.02	41.04	42.39	16.21	47.19	43.37	46.77
Sum	98.42	97.56	97.28	97.99	100.00	100	100.00
IE							
ppm							
Rb	2.0	4.0	2.3	138.1	6.7	16.9	0.21
Ba	4,454	4,872	16,469	2,082	101	36	262
Th	301	103	104	12.5	26	37	0.32
Nb	53.1	113	50.1	94	93	112	0.90
Ta	12.9	4.4	4.5	7.7	6.8	9.2	0.76
K	830	996	332	27,812	664	581	—
Sr	11,669	10,542	10,851	1,387	2,860	4,066	268
P	33,603	4,408	5,014	1,353	1,702	1,444	—
Hf	8.9	2.23	2.23	7.1	6.6	5.4	—
Zr	324	125	171	289	370	292	—
Ti	1,619	899	420	19,304	360	300	—
Y	377	107	129	23	8.6	23	23.75
REE							
La	455	1,011	909	167	513	343	239
Ce	1,093	1,647	1,725	319	980	654	420
Pr	147	162	103	35.6	45.3	41	46.8
Nd	637	513	682	123	139	138	159.9
Sm	119	92.8	133	14.7	20.1	18.3	19.1
Eu	59.5	25.0	33.7	3.9	6.1	5.25	3.90
Gd	140	64.7	82.9	10.1	19.3	10.4	14.90
Tb	19.8	6.54	7.96	1.03	2.14	1.65	2.12
Dy	89.4	26.5	32.4	7.6	12.9	8.7	10.57
Ho	14.9	4.89	4.99	1.1	2.51	1.9	2.05
Er	22.7	6.04	7.22	2.9	6.27	4.8	5.40
Tm	2.88	0.45	0.54	0.40	0.68	0.53	3.16
Yb	10.0	2.07	2.55	1.70	3.28	2.53	24.7
Lu	1.11	0.92	0.35	0.23	0.43	0.34	0.32
Mol%							
CaO	83.4	83.5	59.0	21.5	50.1	84.5	49.9
FeO + MnO	7.1	4.7	5.4	16.0	1.9	5.8	3.6
MgO	9.5	11.8	35.6	62.5	48.0	9.7	46.5

Table 1B: Carbonatites associated with ultramafic rocks (olivinites and pyroxenites) ± syenites as Salitre I and Serra Negra and with glimmerites as Araxá, Catalão I, and Catalão II. References: Salitre [64,65], Serra Negra [66], Araxá [67], Catalão I [68], and Catalão II [69]

Sample	Salitre I Age: 86.3 (4.2) Ma						
	C1	C4	ASL013	ASL031	ASL034	ASL036	09A-60A
Wt%							
SiO_2	0.06	1.34	0.22	0.33	0.42	0.24	0.26
TiO_2	0.01	0.38	0.17	0.06	0.01	0.01	0.01
Al_2O_3	0.01	0.09	0.17	0.32	0.19	0.23	0.01
FeO	1.46	2.35	2.88	3.09	0.66	1.67	0.18
MnO	0.12	0.56	0.39	0.19	0.15	0.22	0.08
MgO	0.79	14.65	18.48	14.88	5.17	19.35	1.57
CaO	53.84	28.75	25.13	35.40	46.11	29.72	53.94
Na_2O	0.17	0.17	0.10	0.19	0.46	0.50	0.13
K_2O	0.11	0.22	0.03	0.05	0.01	0.16	0.11
P_2O_5	0.01	6.69	0.43	10.16	0.01	0.66	0.99
L.O.I.	40.70	32.20	46.14	34.77	44.70	46.04	41.20
Sum	97.25	99.04	94.14	99.47	97.89	98.77	98.49
IE							
ppm							
Rb	1.6	4.4	15.3	3.3	6.5	10.7	5.7
Ba	3,178	5,007	28,394	32	32.6	266	326.5
Th	10.5	57.8	164	1.5	80.2	20.5	155
Nb	14.2	88.9	77.3	629	695	161	524
Ta	0.10	0.5	1.13	n.a.	n.a.	2.9	23.9
K	913	1,826	249	415	83	1,328	913
Sr	17,560	26,480	10,147	6,683	6,661	7,100	3,180
P	44	29,195	1,877	44,338	83	2,880	4,320
Hf	0.11	3.0	0.24	n.a.	n.a.	0.37	25.1
Zr	3.50	97.3	4.2	44.1	14.9	6.7	1,071
Ti	60	2,278	1,019	360	60	60	60
Y	53.9	95	66.5	54	20.5	15.6	79.1
REE							
La	373	6,354	1,846	264	107	85.1	431
Ce	701	8,541	3,486	684	283	181	1,203
Pr	68.8	700	400	n.a.	n.a.	7.8	149
Nd	242	2,204	1,452	319	128	79	566
Sm	38.8	201	202	44	17.7	11.0	72.3
Eu	7.28	44.8	55.4	n.a.	n.a.	2.7	19.2
Gd	21.16	82.0	125	n.a.	n.a.	6.4	41.6
Tb	2.27	8.74	10.34	n.a.	n.a.	0.70	5.66
Dy	10.04	30.4	26.04	n.a.	n.a.	2.70	18.14

Table 1B: Continued

Sample	Salitre I Age: 86.3 (4.2) Ma						
	C1	C4	ASL013	ASL031	ASL034	ASL036	09A-60A
Ho	1.66	2.98	2.73	n.a.	n.a.	0.32	2.51
Er	4.02	6.66	4.91	n.a.	n.a.	0.61	4.82
Tm	0.60	0.76	0.70	n.a.	n.a.	0.09	0.61
Yb	3.48	4.27	4.84	n.a.	n.a.	0.42	3.27
Lu	0.53	0.45	0.68	n.a.	n.a.	0.09	0.41
Mol%							
CaO	95.8	55.9	47.1	60.3	85.5	51.2	95.8
FeO + MnO	2.2	4.4	4.8	4.4	1.2	2.5	0.4
MgO	2.0	39.7	48.1	35.3	13.3	46.3	3.8

Sample	Serra Negra age: 83(5) Ma						
	LG-03-70	LG-14-28	LG-06-32	LG-13-125	LG20-91.5	LG32-63.80	LG38-46-142
wt%							
SiO_2	0.54	0.88	0.65	0.74	0.20	0.92	0.14
TiO_2	0.02	0.20	0.04	0.05	0.01	0.11	0.01
Al_2O_3	0.01	0.09	0.04	0.03	0.02	0.34	0.01
FeO	1.98	5.29	1.80	4.19	1.11	2.96	1.69
MnO	0.13	0.14	0.11	0.14	0.25	0.60	0.40
MgO	3.60	3.15	2.97	4.51	19.44	18.98	19.50
CaO	48.82	45.94	48.61	45.87	29.36	27.71	29.23
Na_2O	0.03	0.06	0.10	0.07	0.06	0.09	0.13
K_2O	0.09	0.12	0.16	0.15	0.03	0.05	0.05
P_2O_5	0.48	3.32	3.62	2.59	0.35	0.26	0.09
L.O.I.	43.11	39.52	40.21	39.69	46.70	45.90	47.82
Sum	98.81	98.70	98.31	98.03	97.53	97.93	99.07
IE							
ppm							
Rb	2.10	5.00	5.30	7.50	1.30	2.70	0.80
Ba	2,768	2,314	2,391	3,515	930	1,502	2,187
Th	2.30	38.8	44.4	7.30	31	41.2	11.6
Nb	97.3	373	292	129	280	299.4	5.30
Ta	22.0	28.0	23.3	8.60	16.7	3.30	0.05
K	747	996	1,329	1,245	249	415	415
Sr	13,268	18,833	16,122	11,354	12,051	5,517	10,003
P	2,095	14,488	15,798	11,303	1,527	1,134	393
Hf	6.40	1.60	1.20	2.10	0.40	0.10	0.05

Table 1B: Continued

Sample	Serra Negra age: 83(5) Ma						
	LG-03-70	LG-14-28	LG-06-32	LG-13-125	LG20-91.5	LG32-63.80	LG38-46-142
Zr	326.2	73.2	46.2	89.2	13	9.20	1.80
Ti	120	1,199	240	300	60	659	60
Y	35.3	54.8	73.9	40.9	4.90	72.4	9.10
REE							
La	290	414	498	374	82.4	818	135
Ce	517	783	959	699	152.9	1,511	201
Pr	60.04	93.82	122.66	85.61	17.41	215	21.14
Nd	202.6	321.6	427.9	291.2	59.30	805	66.90
Sm	24.39	41.25	54.93	36.54	6.23	103.32	7.80
Eu	6.52	10.89	15.25	9.58	1.56	27.30	2.36
Gd	16.31	28.04	38.42	24.09	3.67	68.44	6.93
Tb	1.80	3.03	4.24	2.53	0.37	7.02	0.93
Dy	8.28	12.79	17.99	10.54	1.44	25.30	3.56
Ho	1.26	1.93	2.60	1.45	0.18	2.77	0.38
Er	2.74	4.21	5.76	3.00	0.35	4.10	0.53
Tm	0.35	9.56	0.76	0.41	0.04	0.45	0.07
Yb	2.03	3.27	4.12	2.23	0.27	2.19	0.32
Lu	0.27	0.41	0.50	0.27	0.03	0.20	0.04
Mol%							
CaO	88.0	84.2	89.6	82.6	51.1	48.7	50.4
FeO + MnO	3.0	7.8	2.8	6.1	1.8	4.9	2.8
MgO	9.0	8.0	7.6	11.3	47.1	46.4	46.8

Sample	Araxá age: 88 (10) Ma			Catalão I age: 87 (4) Ma					Catalão II age: 85 (6) Ma				
	AE 891 Phlo-rich	AR 892 Phlo- rich	AR 893	C1- L1250	C1CB02	C1C4	C1C12B	C1C14	C2-AA 165907	C2A2	C2B19	C2B18	C2B17
wt%													
SiO_2	9.74	9.93	2.15	1.75	0.25	0.64	4.67	0.22	8.95	4.02	3.46	14.89	0.21
TiO_2	2.86	2.90	1.92	0.08	0.01	0.02	0.25	0.01	0.44	0.05	0.88	0.12	0.01
Al_2O_3	2.76	2.81	2.79	0.08	0.11	0.05	0.13	0.02	0.20	0.06	0.03	0.28	0.01
FeO	11.13	9.75	10.34	8.89	5.40	1.80	10.89	1.23	9.45	2.29	4.65	7.58	0.21
MnO	0.19	0.16	0.18	0.28	0.22	0.37	0.85	0.61	0.25	0.10	0.11	0.09	0.07
MgO	18.10	16.54	18.31	14.60	17.36	19.26	31.30	46.81	2.56	2.82	2.51	8.12	0.56
CaO	13.70	14.61	16.16	23.23	33.59	25.41	10.35	0.92	39.90	46.49	46.02	32.99	53.56
Na_2O	0.21	0.11	0.14	0.05	0.06	0.07	0.01	0.01	0.82	0.10	0.06	0.14	0.11
K_2O	5.21	4.45	2.29	0.31	0.14	0.01	0.01	0.03	0.63	1.10	0.84	3.42	0.14
P_2O_5	0.22	0.19	0.18	4.34	0.10	1.04	2.59	0.09	1.49	1.08	2.71	14.79	0.25

Table 1B: Continued

Sample	Araxá age: 88 (10) Ma			Catalão I age: 87 (4) Ma					Catalão II age: 85 (6) Ma				
	AE 891 Phlo-rich	AR 892 Phlo- rich	AR 893	C1- L1250	C1CB02	C1C4	C1C12B	C1C14	C2-AA 165907	C2A2	C2B19	C2B18	C2B17
L.O.I.	35.07	38.85	44.64	31.20	41.20	41.95	34.35	50.89	31.70	38.52	35.11	13.91	42.78
Sum	99.19	100.30	99.18	99.24	99.06	90.60	95.39	100.07	96.41	96.65	96.39	96.36	97.89
IE													
ppm													
Rb	149	138	1.1	19.5	1.7	3	6	2	24.6	51	56	233	4
Ba	1,299	1,203	1,648	7,622	1,573	52,300	3,936	233	4,174	5,305	3,036	1,430	4,531
Th	18.21	16–97	23.1	18.3	12.1	26	44.8	3.2	158	7.5	4.6	29.5	1.4
Nb	2,750	2,514	32.1	306	203	231	434	9	310	109	127	238	14
Ta	16.5	14.9	1.22	73.5	48.7.	0.1	6.9	0.1	31.6	0.70	3.4	7.5	0.20
K	43,253	36,944	19,812	2,784	1,162	83	83	249	5,230	9,132	6,974	28,393	1,162
Sr	1,150	1,230	5,937	18,975	10,723	>10,000	6,176	2,120	13,981	>10,000	>10,000	8,377	>10,000
P	960	829	786	18,940	436	4,539	11,303	393	6,502	4,713	11,826	10,8913	1,091
Hf	4.14	2.44	0.19	4.5	1.00	0.2	10.3	0.2	4.0	0.50	1.01	0.60	0.20
Zr	170	100	7.8	171	30.4	21	393	6	313	17	28	15	6
Ti	17,146	17,386	11,510	480	60	120	1,499	60	2,638	300	5,276	719	60
Y	54	44	90	24.1	10.7	31	271	19	93.5	34	27	56	28
REE													
La	506	351	413	398	154	729	2,000	326	643	388	398	485	398
Ce	1,083	657	751	860	375	1,660	3,000	727	1,200	750	784	1,060	742
Pr	131	79	91	95.7	46.0	189	1,000	85.4	121	81.1	85.7	123	76.2
Nd	320	225	324	362.7	181.6	569	2,000	273	422.5	269	224	329	189
Sm	50.6	35.1	50.1	64.9	25.75	86.3	537	46.8	50.76	32.9	32.5	48	27.3
Eu	12.5	7.74	15.50	11.48	6.31	23.1	121	11.5	12.1	8.74	8.22	11.7	7.13
Gd	35.16	24.39	34.81	34.05	11.36	53.8	277	26.2	35.88	21.8	21.3	32.8	18.7
Tb	4.60	2.81	4.53	2.60	1.08	4.6	24.3	2.3	4.66	2.3	2.0	3.2	1.8
Dy	22.00	13.44	21.67	8.26	3.34	14.4	76.7	7.0	21.87	8.9	7.3	13.5	7.2
Ho	3.39	2.07	3.34	0.92	0.31	1.6	9.8	0.8	3.35	1.4	1.0	2.2	1.0
Er	6.68	4.40	8.55	1.26	0.58	2.6	22.7	1.5	7.49	3.4	2.4	5.5	2.5
Tm	0.79	0.52	1.01	0.15	0.08	<0.05	<0.05	<0.06	0.93	0.41	0.26	0.68	0.29
Yb	3.72	2.46	4.78	0.89	0.45	0.7	5.2	0.5	5.29	2.0	1.2	3.5	1.4
Lu	0–47	0.26	0.74	0.10	0.06	0.04	0.05	0.04	0.72	0.25	0.12	0.43	0.16
Mol%													
CaO	28.7	32.2	32.4	45.7	54.1	47.1	16.4	1.4	78.2	88.9	86.8	65.6	98.2
FeO + MnO	18.5	17.1	16.5	14.3	7.1	3.2	14.7	2.1	14.8	2.6.	7.0	11.9	0.4
MgO	52.8	50.7	51.1	40.0	38.8	49.7	68.9	96.5	7.0	7.5	6.5	22.5	1.4

na = not available.

Table 1C: Carbonatites with associated intrusive melilitic rock types, as Tapira and Lages. References: Tapira [54,62] and Lages [30]

Sample	Tapira age: 70 (9) Ma			Lages age: 82 (6) Ma	
	T 1	T 2	TPTAPS	SB05A	SB02
Wt%					
SiO_2	0.70	0.02	1.16	2.53	1.46
TiO_2	0.33	0.05	0.10	0.05	0.04
Al_2O_3	0.20	0.07	0.06	0.87	0.83
FeO	10.13	0.12	3.96	10.28	17.74
MnO	0.17	0.06	0.11	1.06	2.39
MgO	6.35	3.85	2.44	14.16	12.72
CaO	38.48	51.00	50.78	34.27	29.41
Na_2O	0.04	0.02	0.09	0.02	0.02
K_2O	0.12	0.13	0.11	0.26	0.20
P_2O_5	0.05	0.10	4.25	0.03	0.04
L.O.I.	45.14	44.56	37.00	35.33	33.16
Sum	101.71	99.99	100.06	98.86	98.01
IE					
ppm					
Rb	7.4	0.1	2.3	6.1	3.5
Ba	2,360	11,600	1,971	951	13,528
Th	5.73	0.68	437	3.5	5.0
Nb	6.14	2.02	997	8.9	8.4
Ta	1.40	0.53	105	1.5	2.0
K	996	1,079	913	2,159	1,660
Sr	12,200	9,570	13,364	2,983	8,057
P	248	486	21,097	131	175
Hf	2.7	0.50	3.6	0.3	0.1
Zr	110	18.4	112	7.7	14.3
Ti	1,978	399	600	300	240
Y	17.0	11.0	74	18.8	45.5
REE					
La	90.2	62.2	472	41.2	2,569
Ce	112	90	1,104	90.3	5,236
Pr	12.33	8.32	122	12.24	551
Nd	47.0	31.7	477	47.54	2,184
Sm	7.11	4.68	62.5	9.43	376
Eu	1.56	1.25	15.9	2.53	80.1
Gd	2.74	1.71	45.5	7.91	225
Tb	0.55	0.33	4.28	1.35	16.92
Dy	2.72	1.63	18.0	7.67	56.91
Ho	0.54	0.33	2.62	1.39	18.92
Er	1.85	1.08	5.41	3.17	22.45
Tm	0.17	0.06	0.67	0.56	8.29
Yb	1.37	0.53	3.73	3.09	8.72
Lu	0.13	0.06	0.49	0.44	0.86
Mol%					
CaO	69.5	90.2	88.5	54.5	50.4
FeO + MnO	14.5	0.3	5.5	14.1	19.3
MgO	16.0	9.5	6.0	31.4	30.3

Table 2: Hydrothermal carbonatites

Sample	Barra do Itapirapuã age: 115 (10) Ma					
	I.A; I.B; II.A	IV.A 3	IV.B 5	IV B 3	II A 2	IV A 5
wt%						
SiO_2	0.54 (0.37)	1.46	12.76	5.21	2.27	6.67
TiO_2	0.01 (0.00)	0.51	0.49	0.15	0.01	0.01
Al_2O_3	0.02 (0.01)	0.22	1.20	1.69	0.23	1.83
FeO	7.76 (1.32)	7.64	5.80	1.36	14.48	12.28
MnO	1.08 (0.16)	0.94	0.30	0.08	1.91	1.19
68MgO	15.23 (1.15)	15.06	14.82	2.64	10.55	10.51
CaO	30.54 (1.18)	28.99	27.64	51.56	31.49	27.23
Na_2O	0.08 (0.01)	0.09	0.03	0.42	0.08	0.06
K_2O	0.02 (0.01)	0.01	0.01	1.03	0.03	1.48
P_2O_5	1.27 (0.14)	0.59	2.11	0.15	0.22	0.10
L.O.I.	42.30 (2.20)	43.33	34.19	35.56	37.11	37.26
Sum	98.85	98.84	99.35	99.85	98.38	98.62
ppm						
Rb	1.9 (0.6)	3.0	2.96	83.5	5.1	47.2
Ba	1,252 (29)	1,730	1,828	145.7	1,927	456
Th	122.5 (25.0)	64.5	185	7.9	246	114
Nb	165 (48)	—	38.1	4.3	48	721
Ta	1.5 (0.4)	—	1.9	0.7	0.8	41.5
Sr	1,743 (382)	1,150	3,016	782	2,955	2,052
Hf	0.51 (0.02)	0.5	3.1	0.9	1.0	0.3
Zr	145 (32)	88.4	27.5	10.4	19.2	7.0
Y	20.1 (1.4)	43.5	291.8	45.6	76	4.3
La	150 (45)	734	633	35.44	1,070	294
Ce	347 (65)	923	935	47.71	1,397	457
Pr	46 (14)	78.4	110	6.57	184	51
Nd	123 (12)	208	383	29.74	826	167
Sm	25.4 (14.0)	24.20	58.74	6.36	117	16.67
Eu	8.25 (2.92)	6.79	22.46	1.81	30.2	4.02
Gd	27.00 (10.2)	18.0	77.37	7.88	91.3	8.47
Tb	4.15 (2.05)	2.10	14.10	1.39	11.7	0.87
Dy	25.2 (11.7)	10.90	84.03	6.80	37.4	4.06
Ho	3.46 (2.68)	1.92	17.23	1.40	3.72	0.86
Er	4.22 (2.23)	4.71	44.20	4.04	12.5	3.15
Tm	0.78 (0.25)	0.64	6.50	0.67	1.75	0.42
Yb	6.74 (4.16)	3.04	38.85	4.46	10.1	2.98
Lu	0.97 (0.53)	0.53	5.63	0.70	1.38	0.48
Mol%						
CaO	52.1	51.2	62.5	91.5	53.4	52.0
FeO + MnO	11.8	11.8	10.8	2.0	21.7	20.1
MgO	36.1	37.0	26.7	6.5	24.9	27.9

Sample	Cerro Chiriguelo age: 128 (5) Ma						Cerro Manomó age: 139 (3) Ma
	3,411	3,414	3,422	3,434	3,440	3,443	PV-69C
wt%							
SiO_2	2.26	5.44	5.05	7.18	10.55	6.25	3.02
TiO_2	0.05	0.05	0.01	0.10	3.41	0.30	0.02
Al_2O_3	0.22	0.25	0.30	0.56	1.44	0.53	0.11
FeO	3.25	2.84	3.19	2.99	15.20	0.40	40.49
MnO	0.60	0.45	0.28	0.15	0.64	0.40	7.13
MgO	0.10	0.15	0.41	0.50	2.80	1.00	1.34
CaO	48.45	47.15	47.00	46.98	30.89	44.62	7.68
Na_2O	0.08	0.08	0.03	0.04	0.03	0.10	0.08

Table 2: Continued

Sample	Cerro Chiriguelo age: 128 (5) Ma						Cerro Manomó age: 139 (3) Ma
	3,411	**3,414**	**3,422**	**3,434**	**3,440**	**3,443**	**PV-69C**
K_2O	0.07	0.15	0.28	0.50	1.61	0.42	0.02
P_2O_5	0.80	0.95	0.69	0.48	0.54	1.20	0.10
L.O.I.	40.99	40.07	38.29	38.05	31.94	39.08	35.28
Sum	96.87	97.59	95.53	97.53	99.05	97.15	95.27
ppm							
Rb	24	32	39	36	151	59	0.1
Ba	25,885	23,989	22,123	10,390	5,464	19,532	1,560
Th	40	29.7	11	28	8	12	481
Nb	109	81	178	100	260	495	25
Ta	—	—	13.5	7.6	20	37.6	0.29
K	581	1,245	2,325	4,151	13,366	3,487	166
Sr	2,875	2,031	5,243	7,441	1,776	7,103	2,342
P	3,971	4,716	3,425	2,383	2,681	5,957	496
Hf	—	—	5.1	10.0	11.6	—	0.19
Zr	133	87	219	430	506	39	15
Ti	300	300	60	600	20,442	1,799	120
Y	4	3.9	3.7	10	29	5.0	49
REE							
La	1,336	1,257	1,169	590	312	889	2,570
Ce	1,305	1,240	1,102	633	227	1,022	5,328
Pr	120	128	101	63.1	22.6	79	787
Nd	151	181	178	120	110	151	2,142
Sm	94	31.5	30.0	20.1	12	29.2	369
Eu	32	10.8	10.2	6.9	4.1	9.8	79
Gd	101	34.1	32.4	21.8	13.0	29.9	221
Tb	16.3	5.5	5.20	3.6	2.1	4.8	13
Dy	96	32.8	31.0	21.2	—	28.9	60
Ho	18.3	6.09	5.87	4.06	—	5.66	10
Er	44	14.7	14.2	9.9	—	14.5	24
Tm	5.3	1.77	1.71	1.23	0.84	1.80	3
Yb	17.1	8.68	8.04	6.03	4.42	9.02	9
Lu	3.3	1.13	0.77	0.68	0.45	1.02	1
Mol%							
CaO	93.5	94.4	93.5	93.7	65.5	90.4	16.4
FeO + MnO	6.2	5.2	5.4	4.9	26.2	6.8	79.6
MgO	0.3	0.4	1.1	1.4	8.3	2.8	4.0

References: Barra do Itapirapuã [28,71], Cerro Chiriguelo [21], and Cerro Manomó [52]. Values for Barra do Itapirapuã I.A, I.B, II.A are averaged, with standard deviations in parentheses.

Table 3: Occurrences with unusual geometric relationships

Sample	Itanhaém Age:129 (5) Ma	Valle-mí Age: 138.7 (0.2) Ma	Cerro Cañada Age: 124.6 (0.7) Ma	Cerro E Santa Elena Age: 127 (8)
	IA-2	VM1 Carbonate Fraction (15.56 wt%)	Dolomite Fraction (15.5 wt%) In ijolite	
wt%				
SiO_2	5.58	—	—	0.29
TiO_2	0.92	0.05	0.01	0.02
Al_2O_3	1.84	0.01	—	0.89
FeO	11.79	0.29	2.25	1.63
MnO	0.62	0.01	0.20	0.45
MgO	6.23	0.20	18.20	16.23
CaO	36.06	6.67	31.30	32.54
Na_2O	0.37	0.01	0.25	0.40
K_2O	0.18	0.01	0.01	0.02
P_2O_5	4.64	0.08	0.01	0.44
L.O.I.	30.70	8.13	47.79	46.92
Sum	98.91	15.56	100.02	100.00
ppm				
Rb	0.8	0.90	2.36	4.5
Ba	1,546	435	2,950	5,618
Th	233	20	2.82	4.23
Nb	448	64	10.3	15.0
Ta	24.4	4.8	1.11	1.32
K	1,494	83	81	166
Sr	3,248	128	3,246	6,225
P	20,249	349	41	1,920
Hf	0.8	10	1.05	1.71
Zr	17.0	39	12	18.8
Ti	5,515	300	59	118
Y	57	16.0	24.2	25.5
REE				
La	2,773	155	164	188
Ce	4,902	340	325	409
Pr	337	43.5	36.5	30.2
Nd	1,181	168	146.3	184
Sm	132	27.7	22.45	25.8
Eu	29.7	10.66	8.2	14.4
Gd	79	33.12	31.4	48.2
Tb	6.4	5.24	3.3	5.1
Dy	37	30.0	30.5	47.1
Ho	7.2	5.95	5.7	8.9
Er	14.8	12.27	13.6	21.8
Tm	1.61	1.34	2.1	2.7
Yb	11.7	5.95	21.7	31.1
Lu	0.90	0.67	0.77	1.22
Mol%				
CaO	66.2	92.8	53.5	49.9
FeO + MnO	17.8	3.3	3.3	3.6
MgO	16.0	3.9	43.2	46.5

References: Itanhaém [34], Valle-mí [37], and Cerro Cañada and Cerro E Santa Elena [11,12].