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ARTICLE

Cretaceous carbonatites of the southeastern Brazilian Platform: a review

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ABSTRACT: *This paper reviews general aspects of alkaline-carbonatitic rocks of Brazilian, Paraguayan and Bolivian terrains. Although 30 such occurrences are known in literature, only the major ones have been thoroughly investigated. The carbonatites are of Cretaceous age, with two well-defined Lower Cretaceous and Upper Cretaceous generation episodes. A clear tectonic control by ancient structural features such as archs, lineaments and faults characterizes most cases. The rocks exhibit a large compositional variation, in decreasing orders of abundance from calciocarbonatites to magnesiocarbonatites to ferrocarbonatites. In some complexes, they form multistage intrusions. C-O isotopes indicate that, in general, the carbonatites were affected by post-magmatic processes associated with the topographic level of emplacement and low-temperature* H_2O-CO_2 *rich fluids responsible for the increased amount of heavy carbon and oxygen. Sr-Nd isotopic compositions similar to those of coeval alkaline silicate rocks, ranging from depleted to enriched mantle sources, have been influenced by two distinct metasomatic events in Proterozoic at 2,0-1.4 Ga and 1.0-0.5 Ga. Sr-Nd-Pb-Os data seem related to an isotopically enriched source, their chemical heterogeneities reflecting a depleted mantle that was metasomatized by small-volume melts and by fluids rich in incompatible elements. Fractional crystallization and liquid immiscibility are believed to be the most effective processes in the formation of the Cretaceous carbonatites, with minor contribution of crustal contamination. Pb isotopic ratios yield evidence that HIMU and EM I mantle components played an important role in the genesis of the carbonatitic magma.*

KEYWORDS: *Carbonatites; Alkaline Rocks; Brazilian Platform.*

INTRODUCTION

Only a few review papers dealing specifically with Cretaceous carbonatites of the southeastern Brazilian Platform are known in literature. Studies by Rodrigues and Lima (1984), Berbert (1984), and Gomes *et al.* (1990) are among the first ones. More recently, papers such as those by Castorina *et al.* (1996, 1997), Comin-Chiaramonti *et al.* (2005c, 2014) and a general review by Comin-Chiaramonti *et al.* (2007a), including some African occurrences in Angola and Namibia, became available. The associated silicate alkaline rocks, on the other hand, have more frequently been reviewed (Ulbrich & Gomes 1981, Woolley 1987, Morbidelli *et al.* 1995, Comin-Chiaramonti *et al.* 2005a, 2005d, 2007b, 2015, Brod *et al.* 2005, Gomes *et al.* 2011a, 2011b, 2013, Gomes & Comin-Chiaramonti 2017, etc.).

According to Gomes and Comin-Chiaramonti (2017), a total of 30 carbonatite occurrences have been described, most of them in Brazilian terrains (23), but also in Paraguay (6) and Bolivia (1) (Table 1). Included are carbonate *ocelli* in a few occurrences of fine-grained and intrusive rocks. Carbonatites are predominantly represented by intrusive and hypabissal bodies, only two groups of volcanic occurrences having been described: the lava flows of Santo Antônio da Barra, in Goiás (Gaspar & Danni 1981, Moraes 1988), and those of Sapucai, in Paraguay (Comin-Chiaramonti *et al.* 1992). Volcanic occurrences are scarcely present, probably due to intense erosion (Morbidelli *et al.* 1995, Comin-Chiaramonti *et al.* 2005c). Carbonatites concentrate in two well-delimited areas of the Brazilian territory: the Ribeira Valley in the southeast (Ruberti *et al.* 2005, Gomes *et al.* 2011a) and the Alto Paranaíba in the central-west (Araújo *et al.* 2001, Guarino *et al.* 2013). Over the last years, these rocks have also been described near the city of Bagé (Joca Tavares and Porteira bodies; Toniolo *et al.* 2013, Monteiro *et al.* 2016) and also in

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Table 1. General information on the carbonatite occurrences of different regions of Brazil, Paraguay and Bolivia.

Locality		Occurrence	Petrography	Mineralogy	Age	References
BRAZIL						
Ribeira Valley						
1	Barra do Itapirapuã	Dike, vein, breccia	Mg-ca, Fe-ca, Si-ca, Ca-ca, Fe, S, L	Do, Ank, Cc, Phl, Pr, Qz, Ap, Bas, Pa, Syn, AB, Ga, Sph	Lower Cretaceous	1-19
2	Ipanema	Dike, vein	Ca-ca Gl, Sh, Di, S, Fe, Te	Cc, Phl, Op, Ap, Cpx, Amp, Ba, Sf	Lower Cretaceous	2-6, 12, 13, 15, 18-26, 59
3	Itanhaém (Ilha das Cabras or Givura)	Dike	Mg-ca	Do, Ap, Phl, Pv, Gr, alterated mafics	Lower Cretaceous	2, 4-6, 18, 19, 21, 23, 24, 27, 28, 59
4	Itapirapuã	Dike, vein, breccia	Ca-ca NS, I-Mel, Ti	Cc, Ap, AF, Ne, Mt, Pt	Lower Cretaceous	2, 4-6, 12, 13, 18,-19, 21, 23, 24, 29-32, 59
5	Jacupiranga	Plug, dike	Ca-ca, Mg-ca Du, Py (Ja), I-Mel, Tr, E, Mz, Fe, Sd, S, A, AB	Cc, Do, Phl, Ol, Mt, Ap, Pr, Il, Pv, Pyr, Ga, Cl, Ne, Amp	Lower Cretaceous	2-6, 12-15, 18,19, 21, 23, 24, 33-48, 59
6	Juquiá (Serrote)	Plug, dike	Mg-ca, Ca-ca Py, AG, I-Mel, NS, S, Sd, AB, Te, Pho, Fe	Do, Ank, Cc, Phl, Mt, Ba, Ap, Mo, Anc, No	Lower Cretaceous	2-6, 12-15, 18, 19, 21, 23, 24, 41, 49-52, 59
7	Mato Preto	Plug, breccia	Ca-ca, Fe-ca NS, Ti, Pho, Ga, I, Mel, L, Ta	Cc, Ank, Mt, Ap, Pr, Ba, Fl, Qz, AF, Flca	Lower Cretaceous	1, 2, 4-8, 12-19, 21, 24, 27, 53-57, 59
8	Piedade				Lower Cretaceous	12, 21, 58, 59
São Paulo Coast Line						
9	Ilhas	Dike	Mg-ca, Si-ca	Cc, Do, Phl, Ap, phyllosilicates	n.d.	60
Cabo Frio Lineament						
10.	Poços de Caldas	Dike, breccia	Si-ca, *ocelli* in lamprophyre NS, Ti, Pho, L, La, Lp,	Cc, Pr, Phl	Upper Cretaceous	2, 5, 21, 59, 61-63
Santa Catarina						
11	Anitápolis	Plug, dike, vein	Ca-ca, Mg-ca Py, Biot, I-Mel, NS, Phos, Fe, Apt, Ne, L, Pho	Cc, Do, Ap, Mt, Ol, Phl, Pr, Bd, Qz, Al, Anc, Bas, Sf	Lower Cretaceous	2-6, 13-15, 18, 19, 21, 23, 24, 59, 64-69
12	Lages	Plug, dike, vein, breccia	Fe-ca, Ca-ca NS, Pho, Ba, Ne, Meli, Te, Pht, Ki	Ank, Cc, Ap, Phl, Qz, AF, Pr, Pyr, Syn, Bas	Upper Cretaceous	2-6, 13-15, 19, 21, 23, 24, 59, 70-74
Rio Grande do Sul						
13	Joca Tavares	Plug?	Ca	Do (Cc), Ap, Op (Hm, Il), Ch	n.d.	75, 76
14	Porteira	Dike	Ca	Do, Ap., Flo, Op (Hm, Il), Ch	n.d.	75, 76
Alto Paranaíba						
15	Araxá (Barreiro)	Stock, dike	Mg-ca, Ca-ca, Fe-ca Gl, Py, Phos, Sil	Do, Cc, Ank, Str, Si, Mg, Bu, Mt Ap, Phl, AF, Anc, Pr, Mo, Sf	Upper Cretaceous	2-6, 13-15, 19, 21, 23, 24, 59, 77, 78
16	Catalão I	Dike	Mg-ca, Ca-ca, Si-ca Phl, Du, Be, Phos, NS, Nel, Sil	Do, Cc, Mg, Ap, Phl, Mt, Ba, Ti, Mo, Zr, Pr, Sf, Fl, No	Upper Cretaceous	2-6, 13-15, 19, 21, 23, 24, 59, 79-81
17	Catalão II	Stock	Ca-ca, Mg-ca Py, Gl, Phos, Apt, Mgt, Fe, S, L, Sil	Cc, Phl, Ver, AF, Mt, Pr, Ba, Pyr, REE minerals	Upper Cretaceous	2-6, 13-15, 19, 21, 23, 24, 59, 81

Continue...

Table 1. Continuation.

Locality		Occurrence	Petrography	Mineralogy	Age	References
18	Salitre	Stock, dike, vein	Ca-ca, Mg-ca Be, Py, Du, Phos, NS, S, Ti, T	Cc, Do, Ap, Mt, Phl, Ol, Pr, Zr, Ba, Sf	Upper Cretaceous	2-6, 13-15, 21, 23, 24, 59, 81-86
19	Tapira	Stock, dike, vein	Ca-ca, Mg-ca Be, Du, Pe, Py, Phos, S, T, Melil, Ka	Cc, Do, Ap, Phl, Mt, Pr, Il, Pv, Ti, Pyr	Upper Cretaceous	2-6, 13-15, 19, 21, 23, 24, 59, 81, 87-90
20	Serra Negra	Plug	Ca-ca Du, Be, Sh, Py (Ja), Ti, T, Fe	Cc, Mt, Ap, Pr, Pv, Bd	Upper Cretaceous	2-6, 13, 21, 23, 24, 59, 81, 91-93
Goiás						
21	Caiapó	Plug, breccia	Mg-ca, Ca-ca, Fe-ca I, L, Fe	Do, Cc, Ank, Si, Ap, Mt, Pr, AF, Qz, REE minerals	n.d.	4-6, 13
22	Morro do Engenho	Vein	Ca Py, Pe, AG, NS	Cc, Phl	n.d.	2, 4-6, 13, 90, 94
23	Santo Antônio da Barra (Rio Verde)	Lava, breccia, plug	Si-ca, Ca-ca Ana (?), Ka, Pho, T, Phou, Mo, Br	Cc aggregate in vitreous matrix	Upper Cretaceous	4-6, 13, 21, 24, 59, 90, 95-99
PARAGUAY						
Rio Apa						
24	Valle-mí	Dike	*Ocelli* in basanite	Cc	Lower Cretaceous	13, 14, 19, 41, 100-106
Amambay						
25	Cerro Chiriguelo (Cerro Corá)	Dike	Ca-ca, Fe-ca Fe, NS, T	Cc, Ap, AB, Qz, Phl, AF, Mt, Cpx, Zr, Ura, Syn, Hm, Pyr, Go	Lower Cretaceous	2, 5, 13, 14, 19, 21, 41, 59, 100, 102-111
26	Cerro Sarambí	Dike	Ca-ca, Si-ca Py, NS, Fe, Pho, T, L	Cc, Qz, Fl, Ver, Op	Lower Cretaceous	2, 5, 13, 14, 19, 41, 100, 102-106, 109, 111, 112
Central						
27	Cerro Cañada	Stock	*Ocelli* in ijolite AG, NS, I	Cpx, Ol, Bi, Cc	Lower Cretaceous	103-106,
28	Cerro E Santa Elena	Stock	*Ocelli* in ijolite Ga, I, Te, Ba, AB, Tph	Cpx, Ol, Mt, Amp, Bi, Cc	Lower Cretaceous	103-106-111,
29	Sapucai	Lava	Mg-ca	Do, AF, Mt, Bi, Ap	Lower Cretaceous	41, 103-106-111, 113
BOLIVIA						
Velasco						
30	Cerro Manomó	Dike	Si-ca NS, S, Gr, Tph, T	Si, Ank, Cc, Go, Li, Qz, Ap, Bas, Syn	Lower Cretaceous	2, 5, 114-116

Data sources: Barra do Itapirapuã: 1, Lapido-Loureiro & Tavares (1983); 2, Almeida (1983); 3, Berbert (1984); 4, Rodrigues & Lima (1984); 5, Woolley (1987); 6, Gomes *et al.* (1990); 7, Ruberti *et al.* (1997); 8, Speziale *et al.* (1997); 9, Andrade *et al.* (1999a); 10, Andrade *et al.* (1999b); 11, Ruberti *et al.* (2002); 12, Ruberti *et al.* (2005); 13, Comin-Chiaramonti *et al.* (2005a); 14, Comin-Chiaramonti *et al.* (2005d); 15, Biondi (2005); 16, Ruberti (1998); 17, Ruberti *et al.* (2008); 18, Gomes *et al.* (2011a); 19, Comin-Chiaramonti *et al.* (2007a); **Ipanema**: 20. Leinz (1940); 21, Sonoki & Garda (1988); 22, Davino (1975); 23, Ulbrich & Gomes (1981); 24, Morbidelli *et al.* (1995); 25, Guarino *et al.* (2012); 26, Rugenski *et al.* (2006); **Itanhaém**: 27, Coutinho & Ens (1992); 28, Mariano (1989); **Itapirapuã**: 29, Gomes & Cordani (1965); 30, Gomes & Dutra (1969); 31, Gomes (1970); 32, Gomes & Dutra (1970); **Jacupiranga**: 33, Melcher (1966); 34, Amaral (1978); 35, Gaspar (1989); 36, Ruberti *et al.* (1988); 37, Roden *et al.* (1985); 38, Germann *et al.* (1987); 39, Menezes & Martins (1984); 40, Morbidelli *et al.* (1986); 41, Castorina *et al.* (1996); 42, Santos & Clayton (1995); 43, Huang *et al.* (1995); 44, Ruberti *et al.* (1991); 45, Gomes *et al.* (1996a); 46, Azzone *et al.* (2012); 47, Beccaluva *et al.* (2017); 48, Chmyz *et al.* (2017); **Juquiá**: 49, Born (1971); 50, Beccaluva *et al.* (1992); 51, Walter *et al.* (1995); 52, Azzone *et al.* (2013);

Mato Preto: 53, Jenkis II (1987); 54, Santos (1988); 55, Santos *et al.* (1996); 56, Santos *et al.* (1990); 57, Comin-Chiaramonti *et al.* (2001); **Piedade**: 58, Knecht (1960); 59, Amaral *et al.* (1967); **Ilhas**: 60, Coutinho (2008); **Poços de Caldas**; 61, Ulbrich *et al.* (2002); 62, Vlach *et al.* (2003); 63, Ulbrich *et al.* (2005); **Anitápolis**: 64, Melcher & Coutinho (1966); 65, Rodrigues (1985); 66, Furtado *et al.* (1986); 67, Furtado (1989); 68, Comin-Chiaramonti *et al.* (2002); 69, Scheibe *et al.* (2005); **Lages**: 70, Scheibe & Formoso (1982); 71, Scheibe (1986); 72, Traversa *et al.* (1994); 73, Traversa *et al.* (1996); 74, Barabino *et al.* (2007); **Joca Tavares** and **Porteira**: 75, Toniolo *et al.* (2013); 76, Monteiro *et al.* (2016); **Araxá**: 77, Issa Filho *et al.* (1984); 78, Traversa *et al.* (2001); **Catalão I**: 79, Carvalho & Bressan (1981); 80, Cordeiro *et al.* (2010); 81, Gomes & Comin-Chiaramonti (2005); **Salitre**: 82, Morbidelli *et al.* (1997); 83, Barbosa (2009); 84, Barbosa *et al.* (2012a); 85, Barbosa *et al.* (2012b); 86, Haggerty & Mariano (1983); **Tapira**: 87, Guimarães *et al.* (1980); 88, Brod (1999); 89, Brod *et al.* (2000); 90, Brod *et al.* (2005); **Serra Negra**: 91, Mariano & Marchetto (1991); 92, Souza Filho (1974); 93, Grasso (2010); **Morro do Engenho**: 94, Pena (1974). **Santo Antônio da Barra**: 95, Gaspar & Danni (1981); 96, Moraes (1984); 97, Moraes (1988); 98, Sgarbi (1998); 99, Junqueira-Brod *et al.* (2002); **Valle-mí**: 100, Livieres e Quade (1987); 101, Gibson *et al.* (1995a); 102, Gomes *et al.* (1996b); 103, Castorina *et al.* (1997); 104, Comin-Chiaramonti *et al.* (2007b); 105, Gomes *et al.* (2013); 106, Comin-Chiaramonti *et al.* (2014); **Cerro Chiriguelo**: 107, Comte & Hasui (1971); 108, Censi *et al.* (1989); 109, Comin-Chiaramonti *et al.* (1999); 110, Gibson *et al.* (2006); 111, Comin-Chiaramonti *et al.* (2007c); **Cerro Sarambí**: 112, Gomes *et al.* (2011b); **Sapucai**: 113, Comin-Chiaramonti *et al.* (1992); **Cerro Manomó**: 114, Fletcher *et al.* (1981); 115, Comin-Chiaramonti *et al.* (2005b); 116, Comin-Chiaramonti *et al.* (2011). Other references consulted are listed in Gomes and Comin-Chiaramonti (2017).

Rock abbreviations: A, ankaratrite; AB, alkali basalt; AG, alkali gabbro; Ana, analcimite; Apt, apatitite; Ba, basanite; Be, bebedourite; Biot, biotitite; Ca, carbonatite; Ca-ca, calciocarbonatite; Di, diorite; Du, dunite; E, essexite: Fe, fenite; Fe-ca, ferrocarbonatite; Fou, fourchite; Ga, gabbro; Gl, glimmerite; Gr, granite; I, ijolite; Ja, jacupiranguite; Ka, kamafugite; Ki, kimberlite; L, lamprophyre; Lp, lamproite; Mel, melteigite; Meli, melilitite; Melil, melilitolite; Mgt, magnetitite; MMzd, melamonzodiorite; Mo, monchiquite; Mz, monzonite; Ne, nephelinite; Nel, nelsonite; NS, nepheline syenite; Pc, picrite; Pe, peridotite; Phl, phlogopitite; Pho, phonolite; Phos, phoscorite; Pht, phonotephrite; Py, pyroxenite; S, syenite; Sd, syenodiorite; Sh, shonkinite; Si-ca, silicocarbonatite; Sil, silexite; T, trachyte; Ta, trachyandesite; Te, tephrite; Tph, trachyphonolite; Ti, tinguaite Tr, theralite; Ur, urtite; We, wehrlite.

Mineral abbreviations: AF, alkali feldspar; Al, alstonite; Amp, amphibole; An, ancylite; Ank, ankerite; Ap, apatite; Ba, barite; Bas, bastnäesite; Bd, baddeleyite; Bi, biotite; Bu, burbankite; Caz, calzirtite; Cc, calcite; Ch, chlorite; Cl, clinohumite; Cpx, clinopyroxene; Do, dolomite; F, feldspar; Fl, fluorite; Flca, fluorocarbonates; Ga, galena; Go, goethite; Gr, garnet; Hb, hornblende; Hm, hematite; Il, ilmenite; Mg, magnesite; Mt, magnetite; Mo, monazite; Ne, nepheline; No, norsethite; Ol, olivine; Op, opaques; Pa, parisite; Phl, phlogopite; Pyr, pyrite; Pr, pyrochlore; Pt, pyrrhotite; Pv, perovskite; Sph, sphalerite; Str, strontianite; Qz, quartz; Sf, sulfide; Si, siderite; Sy, synchysite; Ti, titanite; To, thorite; Ura, uranpyrochlore; Ver, vermiculite; Zir, zirconolite; Zr, zircon.

Caçapava do Sul (Passo Feio and Picada dos Tocos) and Lavra do Sul (Três Estradas) areas (Rocha *et al.* 2013, Toniolo *et al.* 2013, Maciel 2016, Cerva-Alves *et al.* 2017), all in the Rio Grande do Sul State. Because the last three intrusions are believed to be of Proterozoic age, with U-Pb zircon data indicating a ca. value of 603.2 ± 4.5 Ma for the Picada dos Tocos beforsite (Cerva-Alves *et al.* 2017), they are excluded of this study. Other important carbonatitic occurrences are the Amambay (Cerro Chiriguelo, Cerro Sarambí; Comin-Chiaramonti *et al.* 2014) and Velasco (Cerro Manomó; Comin-Chiaramonti *et al.* 2011) regions in Paraguay and Bolivia, respectively. Figure 1 shows the distribution of alkaline and alkaline-carbonatite occurrences in the three countries.

The present paper reviews general aspects of carbonatite bodies represented by not only well-defined structures and a variety of dikes and veins, but also small aggregates (*ocelli*) in coarse and fine-grained alkaline silicate rocks.

GEOLOGICAL SETTING

The most remarkable alkaline-carbonatite complexes of the southeastern Brazilian Platform usually show intrusive/subintrusive, subcircular or oval-shaped structures that are clearly discerned in aerial photographs and are indicative of high emplacement energy. In general, carbonatites are found chiefly as stocks, plugs, dikes, dike swarms, and veins, forming occasionally complex systems (stockworks) as in Barra do Itapirapuã in the Ribeira Valley (Ruberti *et al.* 2002, 2008), where distinct events may be recognized from a network of multiple intrusions. Dikes and veins constitute single bodies or complex systems that cut associated alkaline silicate rocks or penetrate country rocks. Occasionally, dikes conform to a radial or ring-like distribution. Sometimes, they correspond to more than one rock generation phase, like in Barra do Itapirapuã (Ruberti *et al.* 2002, 2008), Juquiá (Walter *et al.* 1995) and Cerro Chiriguelo (Censi *et al.* 1989) districts, for example. Carbonatites and their associated alkaline rocks are commonly emplaced into Precambrian groups (e.g., Açungui, Araxá, Canastra, etc.) and have quartzites, schists, granites and gneisses as their main country rocks. However, some complexes also intrude sedimentary rocks of different types and ages, the regional rocks consisting, in a few cases (e.g., Lages and Santo Antônio da Barra), of tholeiitic basalts of the Paraná Basin.

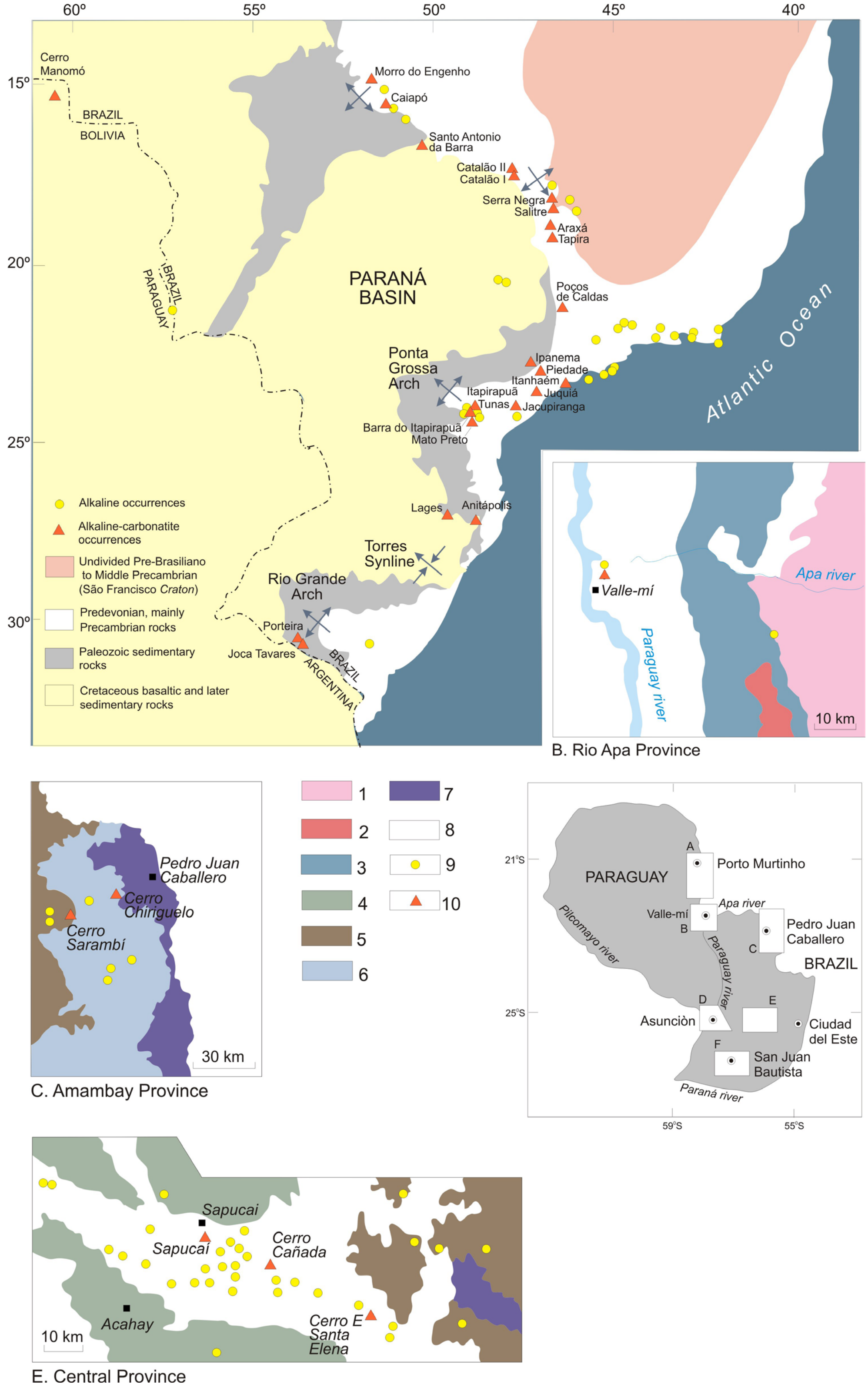
In most cases, the emplacement of alkaline-carbonatite complexes is controlled by ancient tectonic features that were reactivated in Mesozoic times, related mainly to regional structures such as arches, lineaments and rifts. These tectonic alignments have been active since Lower Cretaceous, as suggested by the distribution of earthquakes in southern Brazil (Berrocal & Fernandes 1996). The most prominent tectonic lineaments are represented by deep, NW-trending parallel fractures clearly associated with arch structures (Almeida 1971) and, apparently, in some cases, by old NE-trending fault zones as in Itanhaém (Coutinho & Ens 1992) and Cerro Manomó (Comin-Chiaramonti *et al.* 2005d). In the Ribeira Valley, emplacement was tectonically related to the Ponta Grossa Arch (Algarte 1972), a NW-trending uplift structure active since Paleozoic times that consists of four different lineaments (Guapiara, São Jerônimo-Curiúva, Rio Alonso and Piqueri; Almeida 1983). The major Jacupiranga and Juquiá complexes are related to the Guapiara Lineament, whereas Barra do Itapirapuã, Itapirapuã and Mato Preto ones associate with the São Jerônimo-Curiúva Lineament. Other occurrences in the region (Ipanema, Itanhaém and Piedade) are linked to the Piedade Lineament, a parallel structural feature lying to the south (Riccomini *et al*. 2005). The Alto Paranaíba complexes in Minas Gerais (Araxá, Catalão I and II, Salitre, Serra Negra, and Tapira) follow a NW-trending linear structure that borders the São Francisco Craton, as indicated by aeromagnetic surveys, corresponding to a well-marked regional high, the Alto Paranaíba Uplift (Hasui *et al*. 1975). In the state of Goiás, occurrences (Caiapó, Morro do Engenho and Santo Antônio da Barra) are controlled by a pronounced NW-trending alignment that shows rift tectonics characteristics (Almeida 1983). Considering the distribution of alkaline bodies in both areas along NW-trending crustal discontinuities, that extend for considerable distances, and the nature of the magmatism, Riccomini *et al*. (2005) postulated that deep lithospheric faults played a major role in the tectonic control of these carbonatitic occurrences. According to these authors, the emplacement of carbonatites in the state of Santa Catarina is still a matter of debate: Lages appears to have been subject to NW-trending faults, whereas Anitápolis does not show a clear structural control. In the specific case of Anitápolis, Melcher and Coutinho (1966) pointed out the influence of N-S-trending faults. Comin-Chiaramonti *et al*. (2005c) proposed the Uruguay Lineament to have controlled the emplacement of both complexes. The recently described occurrences in Rio Grande do Sul (Jocas Tavares and Porteira) are structurally controlled by NE-trending faults related to the Ibaré Lineament (Costa *et al*. 1995). In Amambay, northeastern Paraguay, the Cerro Chiriguelo and Cerro Sarambí complexes are tectonically related to the NE-trending Ponta Porã Arch (Livieres & Quade 1987, Comin-Chiaramonti *et al*. 1999). There, more intense magnetic anomalies at the southwestern end of the arch seem to support such a hypothesis (Velázquez *et al*. 1998). Comin-Chiaramonti *et al*. (2005c) also recall that both these Paraguayan complexes and the Valle-mí dikes are mainly found along the Piquiri Lineament. Sapucai in central-eastern Paraguay is located within the domains of the Asunción Rift and its associated faults.

Deep and extensive weathering processes are characteristics of alkaline-carbonatite occurrences, rocks being usually covered by laterite layers that can reach 300 m thick. Soils originate mainly from alteration of cumulate (ultramafic) rocks and from dissolution of carbonates of carbonatites. As a result, large supergenic and residual deposits of apatite, pyrochlore, vermiculite, anatase and REE carbonates and phosphates can be present (Biondi 2005). Fresh rocks are usually scarce or even inexistent at surface, and samples for petrological studies are obtained mostly from drill cores. Jacupiranga is the only exception, presently mined for phosphate (Morro da Mina) with good local exposures that allow for sampling of fresh rock.

PETROGRAPHIC AND MINERALOGICAL CONSIDERATIONS

The carbonatites are characterized by a large variation in grain-size and texture, that grades from equi- to inequigranular and hypidiomorphic to allotriomorphic or even seriate. Other common features include structural flow with alignment of elongated crystals (e.g. apatite), presence of brecciated and xenolithic material, and typical banding from differential concentration of minerals, particularly apatite, phlogopite, olivine and magnetite, as well evidenced in Jacupiranga carbonatites (Melcher 1966, Morbidelli *et al.* 1986, Chmyz *et al.* 2017).

The carbonatites are associated (or spatially rather than genetically associated, as postulated by Gittins & Harmer 2003) with silicate rock types of varied composition, mainly cumulates of different petrographic and compositional characteristics. They are found in close contact with ultrabasic-ultramafic lithologies having dunites, peridotites and pyroxenites as their main representative variants (Tab. 1). These rocks are abundant and well-exposed at surface in the Jacupiranga (Melcher 1966, German *et al.* 1987) and Juquiá (Born 1971, Beccaluva *et al.* 1992) complexes, but are also present in a large number of occurrences. Other cumulates associated with carbonatites are glimmerites, especially in Ipanema (Guarino *et al.* 2012) and Catalão (Machado Jr. 1991, Carvalho & Bressan 1997, Cordeiro *et al.* 2010); bebedourites in Alto Paranaíba complexes, notably in Salitre (Barbosa 2009, Barbosa *et al.* 2012a, 2012b) and Tapira (Brod *et al.* 2013); phoscorites in Anitápolis (Furtado *et al.* 1986, Scheibe *et al.* 2005), Ipanema (Guarino *et al.* 2012) and several bodies in Alto Paranaíba (Cordeiro *et al.* 2010, Guarino *et al.* 2017); kamafugites, kimberlites, lamproites and picrites. All these rock types are practically restricted to occurrences in Minas Gerais and Goiás (Danni 1994, Meyer *et al.* 1994, Gibson *et al.* 1995a, 1995b, Brod *et al.* 2000, 2005, Sgarbi *et al.* 2000, Junqueira-Brod *et al.* 2000, 2002, Melluso *et al.* 2008, Guarino *et al.* 2013, 2017), except for the presence of kimberlites in Lages (Scheibe *et al.* 2005) and kimberlites and



B. Rio Apa Province

C. Amambay Province

E. Central Province

Figure 1. Schematic maps showing the distribution of alkaline and alkaline-carbonatite occurrences in Brazil (after Ulbrich & Gomes, 1981, modified) and Paraguay (after Gomes *et al.* 2013, simplified). Also, indicated is the location of the Cerro Manomó in Bolivia. Captions for the Paraguayan rocks: (1) Lower Precambrian, Rio Apa Complex; (2) Upper Precambrian, Alumiador Intrusive Suite; (3) Cambrian Sediments, Itapucumi Group; (4) Silurian Sediments, Caacupé Group; (5) Carboniferous Sediments, Cerro Corá Group; (6) Triassic Sediments, Misiones Formation; (7) Cretaceous Tholeiitic Magmatism, Alto Paraná Formation (Serra Geral Formation in Brazil); (8) Tertiary and Quaternary Sediments; (9) Alkaline occurrences; (10) Alkaline-carbonatite occurrences.

lamproites in Rio Grande do Sul (Philipp *et al.* 2005). Monomineralic cumulatic rocks (apatitites, magnetitites, phlogopitites) were described in a few complexes (e.g., Anitápolis, Ipanema and Catalão) as small segregations forming decimetric to metric irregular bands.

Association of carbonatites and alkaline gabbros of the melteiigite-ijolite-urtite series is quite frequent. It chiefly characterizes the alkaline-carbonatites of southeastern Brazil, especially in the Ribeira Valley, being particularly frequent in Jacupiranga and Juquiá and of subordinate presence in other districts (Ruberti *et al.* 2005, Gomes *et al.* 2011a). Association with lithologies of syenitic composition represented by coarse-grained (nepheline syenites, syenites) and fine-grained (phonolites, trachytes) rock types (Beccaluva *et al.* 1992, Ruberti *et al.* 2002) is also frequent. The presence of fenites, mostly of syenitic composition, is notable. Syenodioritic and dioritic fenites are scarce. Fenites are described in many carbonatitic bodies as forming irregular masses in the inner parts of the alkaline intrusions or being concentrated along their borders. Fenitization processes are occasionally responsible for aureoles in country rock that can reach tens of meters wide (e.g., 2.5 km in Araxá, Rodrigues & Lima 1984; 2.0 km in Jacupiranga, Gaspar 1989). Fenites do not usually constitute individual mappable units. They are interpreted as metasomatic bodies originated by either magmatic fluids enriched in Na and/or K and F from carbonatitic or alkaline silicatic magmas acting on the associated alkaline rocks and country rocks. Such processes can be of sodic or potassic nature, as suggested by changes in the chemical composition and texture of the rocks and by mineralogical evidences, notably the presence of sodic pyroxene and/or amphibole in the first case, and the appearance of alkali potassic feldspar in the second case (Le Bas 2008). Evidence of fenitization has been reported for a large numbers of alkaline-carbonatite complexes, especially where carbonatites are in direct contact with ultrabasic rocks (e.g., Morbidelli *et al.* 1986, Guarino *et al.* 2012). Jacupiranga is the best example of such an association, with pyroxenites (jacupirangites) and carbonatites forming reaction bands from fenitization of older ultrabasic rocks by alkali-enriched metasomatic fluids derived from carbonatite magma. This type of reaction bands was investigated in detail by Morbidelli *et al.* (1986), who distinguished among concentric, centimeter-to-decimeter layers consisting of alternating carbonate and silicate material. Amphibolitization and phlogopitization of the pyroxenitic protolith by alkali-enriched fluids associated with carbonatitic magmas seem to be a constant feature in almost all Brazilian and Paraguayan carbonatite complexes (Haggerty & Mariano 1983, Gomes *et al.* 1990).

Petrographic associations allow the major alkaline-carbonatite complexes to be identified as *primary* or *magmatic carbonatites,* as defined by Mitchell (2005) and Woolley and Kjarsgaard (2008). Yet, they allow most carbonatites to be included in at least two different clans that conform in general terms the geographic distribution areas of the occurrences.

The *nephelinite-clan carbonatites* (Mitchell 2005) or *carbonatite occurrences with melteigite-ijolite-urtite (no nephelinite extrusive rocks*, Woolley & Kjarsgaard 2008) are a classical association, ijolite being the predominant rock type. They represent about 20% of the magmatic carbonatite occurrences known to the latter authors worldwide. Ultramafic bodies (pyroxenites or olivinites or both), interpreted as cumulates, correspond to 60% of the occurrences, whereas nepheline syenites and syenites, along with rocks of the melteigite-ijolite-urtite series, are present in 84% of the cases. Considering the occurrences reviewed in the present study, this is the most abundant association, being represented mainly by the Lower Cretaceous complexes of the Ribeira Valley (Ipanema, Itapirapuã, Jacupiranga, Juquiá), Santa Catarina (Anitápolis) and Paraguay (Cerro Sarambí) and the Upper Cretaceous intrusions of Mato Preto, also in the Ribeira Valley and, apparently, Caiapó and Morro do Engenho in Goiás.

Melilite-clan carbonatites (Mitchell 2005) and *carbonatite occurrences with melilite-bearing (melilitolite) intrusive rocks* (Woolley & Kjarsgaard 2008) associations are not very common, even at global scale. Only 13 (3%) of a total 403 published occurrences are listed by the latter authors, some of them bearing rocks of the melteigite-ijolite-urtite series, nepheline syenites or syenites (or both) and, frequently, phoscorites. Mitchell (2005) included the Upper Cretaceous Alto Paranaíba complexes of Araxá, Catalão and Tapira in this clan, stressing that Minas Gerais is one of the three regions in the world characterized by extensive development of melilitolite-bearing complexes. The author also emphasized the paucity of nepheline syenite and ijolite-urtite as a representative feature that distinguishes melilitolite complexes from plutonic rocks of the nephelinite clan. Apparently, only the Tapira occurrence is known to include melilite-bearing rocks. Guimarães *et al.* (1980) reported the presence of a dike of uncompahgrite (an ultramelilitolite according to Dunworth & Bell 1998) in which the modal content of the mineral reaches up to 63%. The inclusion of Tapira in this clan was also confirmed by Woolley and Kjarsgaard (2008). However, the other Alto Paranaíba complexes were included in a new clan, the *carbonatite occurrences with only olivinite and pyroxenite as ultramafic rocks (± syenite)*. This clan is characterized by a broad spectrum of ultramafic rocks including olivinites (dunites), peridotites, pyroxenites, amphibolites and glimmerites among the carbonatite complexes. Additional rock types are phoscorites, nepheline syenites and syenites (or both). In some localities, carbonatites form km-scale diameter ore-hosting bodies with Nb (pyrochlore), phosphate and vermiculite. Rocks of the melteigite-ijolite-urtite series are missing. Guarino *et al.* (2017) emphasized the close relationship of Alto Paranaíba carbonatites and phlogopite picrites and ultramafic lamprophyres.

Although not mentioned by either Mitchell (2005) or Woolley and Kjarsgaard (2008), melilite-bearing rocks are also found in an Upper Cretaceous alkaline-carbonatite occurrence in Lages, State of Santa Catarina (Traversa *et al.* 1994, 1996, Gibson *et al.* 1999). Their occurrence is of very complex composition, consisting of large amounts of syenitic rocks (predominantly phonolites and peralkaline phonolites), carbonatites, ultrabasic types that occur mainly as dikes, and kimberlites. Outcrops of olivine melilitites are described in various places in Lages, Cerro Alto de Cima, a semiring, 50 m wide dike being the most significant body (Scheibe 1986).

More recently, Beccaluva *et al.* (2017) noticed the presence of melilite with modal content higher than 10% in ijolitic rocks of the Jacupiranga carbonatites.

Additionally, the overall petrographic association allows to distinguish a new group of carbonatites, the *hydrothermal* ones (also referred to as carbothermals by Mitchell 2005; or carbohydrothermals by Woolley & Kjarsgaard 2008). These latter authors define carbohydrothermal carbonatites as formed by precipitation at subsolidus temperatures, from a mixed CO_2-H_2O fluid that can be either CO_2-rich (i.e., carbothermal), or H_2O-rich (i.e., hydrothermal). Mitchell (2005) added variable proportions of F to the composition of the low-temperature fluids. A statistical study performed by Woolley and Kjarsgaard (2008) indicated that carbohydrothermal carbonatites amounted to 74 out of the 477 occurrences (magmatic carbonatites included) in the world, 54 of them being predominantly associated with intrusive alkali silicate rocks. Their research also made evident that syenitic rocks (feldspathoidal syenites, syenites and quartz syenites) constitute the dominant silicate rock in this association. Also according to Woolley and Kjarsgaard (2008), these occurrences typically consist of calcite ± barite ± fluorite ± quartz ± sulfides ± K-feldspar ± zeolites. However, the hydrothermal stages can also have involved enrichment in elements such as Th, REE and F, as reflected in the mineralogical assemblage, that bears REE fluorocarbonates, fluorite and other fluoride phases. Based on chemical and mineralogical evidence, notably the presence of rare accessory phases like ancylite, bastnäesite, synchysite, parisite, etc., Barra do Itapirapuã (Ruberti *et al.* 2002, 2008), Cerro Chiriguelo (Haggerty & Mariano 1983, Censi *et al.* 1989) and Cerro Manomó (Fletcher *et al.* 1981, Comin-Chiaramonti *et al.* 2005d, 2011) complexes fall within the hydrothermal group.

No data is presently available on the Piedade (SP), Jocas Tavares (RS) and Porteira (RS) carbonatites, but, considering the occurrence of alkaline rocks in Rio Grande do Sul, represented by the phonolitic suite of Piratini (Barbieri *et al.* 1987), it is possible that both bodies correlate with the aforementioned volcanism event. Woolley and Kjarsgaard (2008) described the occurrence of carbonatite with only phonolite or feldspathoidal syenite, without any ultramafic cumulates or members of the melteigite-ijolite-urtite series or melilite-bearing rocks. This association is considered to be the third most significant one, with carbonatite intrusions forming small dikes into larger bodies.

Other carbonatitic occurrences are represented by small dikes in Itanhaém (Coutinho & Ens 1992) and in an island on the coast of the State of São Paulo (Ilhas, Coutinho 2008); dikes and ultramafic silico-carbonatitic plugs and carbonatitic fragments within volcanoclastic deposits in the Poços de Caldas alkaline complex (Ulbrich *et al.* 2002, 2005, Vlach *et al.* 2003, Alves 2003); and as minor aggregates (*ocelli*) in association with fine-grained (Valle-mí) and coarse-grained (Cerro Cañada and Cerro E Santa Elena) silicate alkaline rocks in Paraguay (Castorina *et al.* 1997, Comin-Chiaramonti *et al.* 2007a, Gomes & Comin-Chiaramonti 2017).

Carbonatites are predominantly calcic (sövites-alvikites) and, even in more magnesian (beforsites) intrusions (e.g., Araxá, Barra do Itapirapuã, Juquiá, etc.), calcite is an important constituent. A more iron-rich composition with ankerite as the chief mineral form is present in Lages and Cerro Manomó, for example (Comin-Chiaramonti *et al.* 2002, 2011). The three primary end-member minerals are not usually found in the same complex, Barra do Itapirapuã and Juquiá being the most noticeable exceptions, with such phases present in different stages of intrusion. More commonly, carbonate minerals exhibit a complex and varied chemical composition, due mainly to post-magmatic changes induced by hydrothermal and deuteric-groundwater processes, as described by Comin-Chiaramonti *et al.* (2007a) in many occurrences of Lower Cretaceous (e.g., Barra do Itapirapuã, Cerro Chiriguelo) and Upper Cretaceous (e.g., Lages, Mato Preto). A secondary, hydrothermal mineralogical assemblage is the main characteristic of some complexes bearing heterogeneous and complex chemical composition phases enriched in Nb, Ti, Zr, Th, U, F, Ba, and REE. Araxá and Barra do Itapirapuã are good examples of a mineral assemblage consisting of REE-bearing carbonates, fluorocarbonates and phosphates, which was intensively investigated by Traversa *et al.* (2001) and Ruberti *et al.* (2008), respectively. Additional mineral information is also found in the studies by Fletcher *et al.* (1981, on Cerro Manomó), Haggerty and Mariano (1983, on Salitre, Cerro Chiriguelo and Cerro Sarambí) and Menezes Jr. and Martins (1984, on Jacupiranga). Table 7.1

of Gomes and Comin-Chiaramonti (2017) compiles a great number of less common and even exotic minerals related to alkaline-carbonatite complexes, including sorosilicates (*lamprophyllite, rosenbuschite, Sr-chevkinite*), cyclosilicates (*eudialyte, wadeite*), *inosilicates* (*pectolite, serandite, wollastonite*), phyllosilicates (*neptunite*), oxides and hydroxides (*baddeleyte, loparite, menezesite, perovskite, pyrochlore*, *zirconolite*), carbonates (*alstonite, ancylite, bastnäesite, breunnerite, burbankite, cordyllite, magnesite, norsethite, olekminskite, parisite, remondite, shortite, strontianite, synchysite, witherite*), and phosphates (*britholite, galgenbergite, gorceixite, monazite*). Although not cited in Table 7.1, the following should be also mentioned: carbonates (*ankerite, kutnehorite, rodochrosite, siderite*), fluorides (*fluorite*), oxides (*calzirtite, geikielite, uranpyrochlore*), phosphates (*dahlite*), sulphates (*barite, celestine*), and sulfides (*chalcopyrite, galena, phyrotite, pyrite, sphalerite*).

AGES

Except for a small number of occurrences such as Barra do Itapirapuã, Jacupiranga and Poços de Caldas (Ruberti *et al.* 1997, Chmyz *et al.* 2017, Vlach *et al.* 2003, respectively), whose ages were determined directly from carbonatites and their mineral constituents, most available data resulted from analysis of associated silicate alkaline rocks (whole-rock and mineral concentrates of different minerals). Data for all presently known alkaline-carbonatite occurrences indicates that these rocks are of Cretaceous age, with two clearly distinguished formation intervals, 120–140 Ma and 70–90 Ma, Lower Cretaceous and Upper Cretaceous (Ulbrich & Gomes 1981, Rodrigues & Lima 1984, Berbert 1984, Gomes *et al.* 1990, Gibson *et al.* 1995a, Ruberti *et al.* 2005, Comin-Chiaramonti *et al.* 2007a, 2007b, Gomes *et al.* 2011a, 2011b, 2013, Gomes & Comin-Chiaramonti 2017). Preferred ages for the occurrences are shown in Figure 2.

Lower Cretaceous

Although some results are yet to be confirmed by new analytical methods, this interval is apparently represented by three distinct generation episodes. The oldest age of ~139 Ma is suggested for the Amambay (Cerro Chiriguelo and Cerro Sarambí), Rio Apa (Valle-mí) occurrences in northern Paraguay and Cerro Manomó in southeastern Bolivia. An average approximately 130 Ma age characterizes the Ribeira Valley complexes (Barra do Itapirapuã, Ipanema, Itanhaém, Jacupiranga, Juquiá and Piedade) in southeastern Brazil and also Anitápolis to the south, in the State of Santa Catarina. Carbonatite flows cropping out nearby the village of Sapucai and ijolitic rocks of Cerro Cañada and Cerro E Santa Elena, all in central-eastern Paraguay, are probably related to the same magmatic event. The Itapirapuã massif, also in the Ribeira Valley, seems to represent the youngest Lower Cretaceous episode, with ages in the 100–110 Ma range, as suggested by old K-Ar results (Gomes & Cordani 1965) confirmed by recent Ar-Ar and U-Pb SHRIMP determinations (Gomes *et al.* 2018).

Upper Cretaceous

The Alto Paranaíba (Araxá, Catalão I and II, Salitre, Serra Negra and Tapira) and Goiás (Santo Antônio da Barra) complexes in central-western Brazil, together with Mato Preto and Lages complexes in the south, have ages that fall within the 70–90 Ma interval. The Joca Tavares and Porteira bodies in the State of Rio Grande do Sul probably belong to the same interval.

It is also important to notice that three of the above ages fit the chronogroups of 133 Ma, 108 Ma and 84 Ma proposed by Ulbrich *et al.* (1991) to define peaks of alkaline magmatism along the borders of the Paraná Basin. These chronogroups are believed to represent different phases of evolution of the basaltic and alkaline magmatism in the South Atlantic Plate. They stress the coherent relationship of this volcano-tectonic cycle to important changes in the position of rotation poles and spreading rates of the South American and African plates (Herz 1977, Sadowski 1987).

GEOCHEMISTRY

Major elements

Chemical data indicates that the carbonatites range in composition from calciocarbonatites to magnesiocarbonatites to ferrocarbonatites. However, association of these different petrographic types in a same complex is rare (e.g., Araxá, Barra do Itapirapuã, Juquiá). Plottings of whole-rock chemistry data in CaO-MgO-(FeO + MnO) classification diagrams (Woolley & Kempe 1989) are discussed in various papers (e.g., Comin-Chiaramonti *et al.* 2001, 2002, 2005c, 2007a, Gomide *et al.* 2016). They usually stress the large chemical variation of carbonatites, analyses covering the three, Ca, Mg and Fe compositional fields. Calciocarbonatites are the most abundant types, followed by magnesiocarbonatites. Calciocarbonatites constitute the main lithology in Anitápolis, Cerro Chiriguelo, Ipanema, Itapirapuã, for instance, whereas magnesiocarbonatites predominate in complexes like Araxá, Barra do Itapirapuã, and Juquiá. Ferrocarbonatites are of subordinate occurrence, being more significant only in Lages (Scheibe *et al.* 2005) and Cerro Manomó (Comin-Chiaramonti *et al.* 2002, 2011, respectively). The Bolivian Cerro Manomó complex represents the most striking occurrence of ferrocarbonatites, with 40.5 wt% of FeO, 7.7 wt%

of CaO, 0.34 wt% of MgO and 7.1 wt% of MnO (Comin-Chiaramonti *et al.* 2011). However, it is important to consider that in some complexes like Barra do Itapirapuã, Jacupiranga and Juquiá, the evolution of carbonatite magmas resulted in rocks of wide variation in chemical composition representing different stages of intrusion. Thus, early stage carbonatites of the Jacupiranga and Alto Paranaíba complexes tend to show a more calcic composition, that evolved to more magnesian in latter stages of crystallization (Gomide *et al.* 2016). This calciocarbonatites→magnesiocarbonatites evolution trend, reaching up to ferrocarbonatites in a few cases, has been described in Barra do Itapirapuã (Ruberti *et al.* 2002), Cerro Chiriguelo (Censi *et al.* 1989) and Juquiá (Walter *et al.* 1995) complexes. In some occurrences (e.g., Mato Preto, Santo Antônio da Barra, etc.), the carbonatitic association also includes silicocarbonatites, carbonatites with > 20% SiO_2 occurring mostly as dikes.

The Lower Cretaceous carbonatites of southern Brazil seem to be chemically related to a potassic magmatism of plagioleucitic composition in Foley's (1992) classification (Comin-Chiaramonti & Gomes 1996b), chiefly represented by evolved rock types of syenitic filiation. On the other

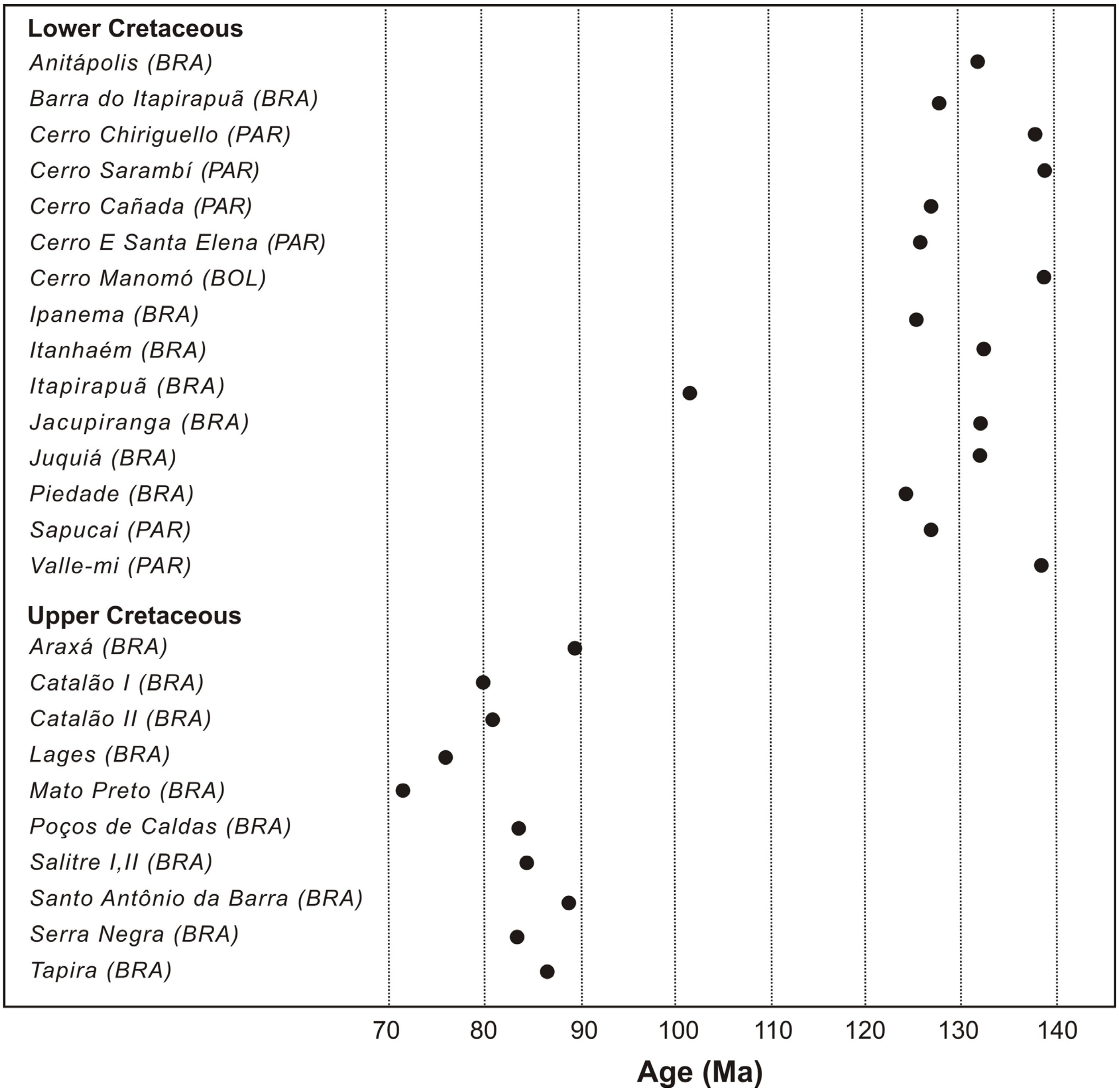


Figure 2. Reference age diagram for carbonatite occurrences in the southern Brazilian Platform. Data source follows references listed in Table 1.

hand, the Upper Cretaceous carbonatites of central-western Brazil are characterized by ultrapotassic-kamafugitic associations (Junqueira-Brod *et al.* 2002, Guarino *et al.* 2017). Usually, also included in the Lower and Upper Cretaceous occurrences are less evolved lithologies of gabbroic-basaltic affinity and cumulates of diverse nature (e.g., dunites, pyroxenites, phoscorites).

Trace and rare earth elements

Incompatible elements (IE) diagrams normalized to primitive mantle concentration (Sun & McDonough 1989) for Brazilian Lower Cretaceous carbonatites (Anitápolis, Barra do Itapirapuã, Jacupiranga, Juquiá) and Paraguay (Cerro Chiriguelo, Cerro Sarambí, Sapucai, Valle-mí) and for Upper Cretaceous Brazilian complexes (Alto Paranaíba, Lages, Mato Preto) were compiled in review papers by Comin-Chiaramonti *et al.* (2005c, 2007a). Additional multielement diagrams are also found for other areas: the Ponta Grossa Arch (Gomes *et al.* 2011a, Azzone *et al.* 2013, Beccaluva *et al.* 2017, Chmyz *et al.* 2017), Amambay (Gomes *et al.* 2011b, Comin-Chiaramonti *et al.* 2014), and the Alto Paranaíba province (Gomide *et al.* 2016).

For any given incompatible element, there is a large variation in normalized values from one carbonatite complex to another. Scatters for the different carbonatites seem to reflect, to some extent, the variable distribution and the concentration of phases, IE occurring mainly as accessory minerals such as phosphates (e.g., apatite and monazite: rare earth elements — REE), oxides (e.g, pyrochlore: Nb, Th, U; calzirtite: Nb, Zr; zirconolite: Ti, Nb, Zr; loparite: Ti, Nb, REE) and REE-carbonates and fluorocarbonates (e.g., ancylite, bastnäesite, burbankite, parisite, synchysite). In comparison to associated silicate alkaline rocks, the carbonatites follow a general tendency to higher abundances in practically all of the incompatible trace elements. Even considering variable composition and stage of intrusion, they are usually characterized by the presence of negative anomalies for Rb, K, P, Hf-Zr and Ti and positive spikes for Ba, Th-U and La-Ce. The behavior of Nb-Ta and Sr appears to be less regular, but pointing mostly to positive anomalies. Although based only on little data available (e.g., Anitápolis, Lages, Mato Preto, cf. Gibson *et al.* 1999, Comin-Chiaramonti *et al.* 2005c, 2007a), no significant difference is noticed in the chemical behavior of IE in early and late carbonatites of a same complex, except for a clear tendency of the latter rocks to be more enriched in all the elements.

REE display remarkable scatters even within a single complex. This is particularly evident for samples from areas that involve different stages of formation, i.e., magmatic, late-magmatic or hydrothermal conditions. Similar to the IE, scatters are mainly attributed to the presence of accessory minerals such as apatite, REE fluorocarbonates, fluorite and barite. REE fluorocarbonates are relatively abundant in late stage carbonatites (e.g., Barra do Itapirapuã, Cerro Manomó). Chondrite-normalized (Thompson 1982, Boynton 1984, McDonough & Sun 1995) REE distribution diagrams for various carbonatite complexes are discussed in several papers (e.g., Comin-Chiaramonti *et al.* 2005c, 2007a, 2014, Gomes *et al.* 2011a, 2011b, Azzone *et al.* 2013, Gomide *et al.* 2016, Beccaluva *et al.* 2017, Chmyz *et al.* 2017). Patterns are in general marked by high REE concentration and variable LREE/HREE fractionation degrees. A strong increase from Lu to La is observed in Cerro Chiriguelo, Jacupiranga, Lages (both early and late carbonatites) and Mato Preto complexes, and also Alto Paranaíba occurrences that characterizes different stages of fractional crystallization (C1 to C5, cf. Gomide *et al.* 2016). Flat REE or patterns with a smooth decrease from La to Lu are characteristic of Anitápolis, Barra do Itapirapuã (late calciocarbonatites), Ipanema, Jacupiranga (calciocarbonatites) and Juquiá (magnesio- and calciocarbonatites) rocks. In these occurrences, the REE distribution seems to be related to the apatite composition. Concave patterns with a HREE plateau and a steady increase from Dy to LREE are typical of Valle-mí and Barra do Itapirapuã carbonatitic rocks. Ferrocarbonatites are generally more enriched than calcio- and magnesiocarbonatites, mainly as evidenced in Lages. Comin-Chiaramonti *et al.* (2007a) gave especial attention to the stockwork of Barra do Itapirapuã, that includes four generations of carbonatite dikes of similar, parallel and slightly enriched LREE pattern. As a result from the presence of REE fluorocarbonate minerals, the dikes more intensely subject to hydrothermal alteration show higher LREE concentrations (Andrade 1998).

C and O isotopes

The behavior of carbon and oxygen isotopes derived mainly from carbonates of Brazilian and Paraguayan carbonatitic rocks has been discussed in detail by many authors over the last decades (e.g., Nelson *et al.* 1988, Censi *et al.* 1989, Santos *et al.* 1990, Santos & Clayton 1995, Huang *et al.* 1995, Toyoda *et al.* 1994, Walter *et al.* 1995, Castorina *et al.* 1996, 1997, Speziale *et al.* 1997, Andrade *et al.* 1999, Comin-Chiaramonti *et al.* 2001, 2002, 2005b, 2005c, 2007a, Ruberti *et al.* 2002, Gomide *et al.* 2013, 2016, Gomes & Comin-Chiaramonti 2017). In general, $\delta^{18}O$ data available in literature for such occurrences covers a wide interval, from about 5 to 25‰ (V-SMOW notation per thousand, cf. Deines 1989). For approximately 50% of the analyses, however, results lie between 6 and 10‰. In contrast, $\delta^{13}C$ values show a more restricted variation, with 91% of the analyses falling between -2‰ and -8‰ (PDB-1 notation per thousand, cf. Deines 1989). Ranges of $\delta^{18}O$ and $\delta^{13}C$ between 6 and 10‰ and between -4 and -8‰, respectively, correspond to the field defined by Taylor *et al.* (1967) and Keller and Hoefs (1995) for primary carbonatites. The plot of $\delta^{18}O$ vs. $\delta^{13}C$ (Fig. 3), including some Brazilian Lower Cretaceous and Upper Cretaceous and Paraguayan Lower Cretaceous carbonatite occurrences, makes evident that:

- a clear primary signature of the Lower Cretaceous complexes in southeastern Brazil, as exemplified mainly by the Jacupiranga rocks plotting entirely inside the range of mantle values;
- two well-distinct linear enrichment trends of heavy isotopes are present.

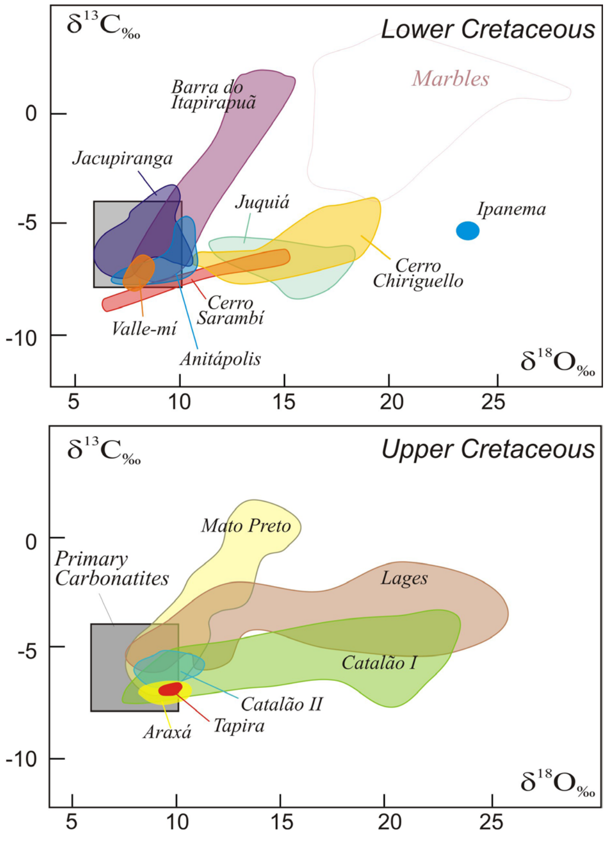


Figure 3. Fields of $\delta^{18}O$‰ (V-SMOW) vs. $\delta^{13}C$‰ (PDB-1) for Lower Cretaceous (Jacupiranga, Juquiá, Barra do Itapirapuã, Anitápolis) and Upper Cretaceous (Araxá, Catalão I, Catalão II, Tapira, Mato Preto, Lages) carbonatites of Brazil and for Lower Cretaceous carbonatites of Eastern Paraguay (Cerro Chiriguelo, Cerro Sarambí, Valle-mí). Data sources: Comin-Chiaramonti *et al.* (2005c and therein references), Cordeiro *et al.* (2011), Guarino *et al.* (2012, 2017), Gomes and Comin-Chiaramonti 2017). PC, field for primary carbonatites from Taylor *et al.* (1967) and Keller and Hoefs (1995); field for marbles is also from Comin-Chiaramonti *et al.* (2005c).

Enrichment of heavy isotopes is interpreted as resulting from mantle source heterogeneity (Nelson *et al.* 1988), contamination processes by country rocks, especially limestone (Santos & Clayton 1995), or magmatic vs. hydrothermal evolution at shallow levels (Censi *et al.* 1989). The first trend is characterized by a shift to positive values of both $\delta^{18}O$ and $\delta^{13}C$ (e.g., Barra do Itapirapuã, Jacupiranga, Mato Preto), and it appears to be an extension of the Jacupiranga carbonatites, which are believed to have a primary signature (Huang *et al.* 1995). A similar isotopic evolution from magmatic fractionation also characterizes early stage carbonatites (C1) of the Alto Paranaíba province (Gomide *et al.* 2016). Other carbonatites representing intermediate (C2, C3) and later (C4, C5) stages of the same region also show isotopic evolution consistent with magmatic fractionation, but with additional interaction with carbohydrotermal fluids and hydrothermal alteration. The second trend shows a $\delta^{18}O$ increase for similar values of $\delta^{13}C$ typical of the Juquiá, Lages, Cerro Chiriguelo and some Alto Paranaíba (e.g., Catalão I, Catalão II, Tapira) complexes.

As stressed in literature (e.g., Deines 1989), the large variation in the content of oxygen and carbon isotopes in carbonatitic complexes results from magmatic (crystal fractionation, degassing, crustal contamination) and post-magmatic (hydrothermal) processes. Systematic investigation of carbonatites of the Paraná Basin points out that most occurrences have enriched isotopic composition and negligible or absent crustal signature, and that fractional crystallization and liquid immiscibility processes cause little effect on oxygen and carbon isotopic values (Santos & Clayton 1995, Castorina *et al.* 1997, Comin-Chiaramonti *et al.* 2005b, Gomes & Comin-Chiaramonti *et al.* 2017). Also, according to these authors, the main variations in $\delta^{18}O$ and $\delta^{13}C$ could be explained by isotopic exchange between these rocks and H_2O-CO_2 rich fluids at different temperatures and H_2O/CO_2 ratios in a hydrothermal environment (e.g., below 300ºC for the first two authors, and in the range of 400–80ºC and fluids with a 0.8–1 CO_2/H_2O ratio for the others). The two paths of $\delta^{18}O$-$\delta^{13}C$ fractionation previously mentioned are attributed to different emplacement levels, that reflect subvolcanic and surface conditions, respectively. Weathering and groundwater fluids are locally important factors, as is meteoric water, that yielded samples strongly enriched in light carbon due to contamination by a biogenic component (Castorina *et al.* 1997, Comin-Chiaramonti *et al.* 2005b). Crustal contamination by limestone country rocks of the Açungui Group ($\delta^{18}O$ = +25.0 to +24.4‰ and $\delta^{13}C$ = +3.5 to -8.6‰), as suggested by Santos and Clayton (1995) for Mato Preto carbonatites, does not seem necessary to explain the enrichment in both heavy oxygen and carbon isotopes of some hydrothermally altered samples of the complex, based on considerations by Speziale *et al.* (1997) and Comin-Chiaramonti *et al.* (2005b). This interpretation is also supported by the initial $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ isotopic ratios of some selected carbonatites, that present the same values as their associated alkaline rocks (Comin-Chiaramonti *et al.* 2005c). Speziale *et al.* (1997) pointed out that, in terms of radiogenic isotopes, Barra do Itapirapuã and Mato Preto carbonatites preserve mantle source characteristics, even where original O-C isotopic signatures were in part modified by low temperature post-depositional hydrothermal fluids. A more complex situation is apparently associated with the wide $\delta^{18}O$ (between 8.58 to 23.11%) and $\delta^{13}C$ (between -3.55 and -7.88%) values shown by Catalão I carbonatitic rocks (Cordeiro *et al.* 2011, Oliveira *et al.* 2017). There, the original isotopic composition of carbonates was modified by at least two events of magmatic fractionation (1 — Rayleigh fractionation, with carbonate signatures being related to the isotopic fractionation between carbonates and other minerals as well as to the temperature and the isotopic composition of the initial melt, and 2 — degassing) and three fluid fractionation (fluid degassing, H_2O percolation and CO_2-H_2O fluid percolation) episodes.

Apparently, sulfur and carbon isotopic data from sulphides is only available in studies by Gomide *et al.* (2013, 2016) on the Alto Paranaíba complexes (Araxá, Catalão I, Catalão II, Salitre, Serra Negra and Tapira) and Jacupiranga in the Ribeira Valley. In these occurrences, almost all carbonatite intrusions present an isotopic composition of sulfur that is compatible with values for the mantle and carbonatites around the world. Exceptions are a few Catalão I and Tapira samples showing distinctly negative ^{34}S values more consistent with sulfur degassing and/or hydrothermal alteration processes (Gomide *et al.* 2013).

Gomide *et al.* (2013) also noted that in Jacupiranga sulfides have relatively narrow ^{34}S ranges and more primitive ^{34}S values than in minerals of the Alto Paranaíba occurrences for the same rock type, which suggests that the Jacupiranga magmas are less evolved and/or that they intruded deeper levels than in the aforementioned complexes.

Sr and Nd isotopes

In Brazil and Paraguay, carbonatites are characterized by initial $^{87}Sr/^{86}Sr$ (Sr_i) and $^{143}Nd/^{144}Nd$ (Nd_i) ratios similar to those of their associated alkaline rocks, even in late stages of fluid-rock re-equilibration (i.e., hydrothermal environment), as already established by Castorina *et al.* (1997) and Speziale *et al.* (1997). However, the wide ranges of Nd_i isotopes for a narrow Sr_i interval reported for the Catalão I complex by Cordeiro *et al.* (2011) are indicative that magmatic and/or carbohydrothermal processes were able to fractionate Nd, leaving Sr isotopes unaffected. Thus, caution should be taken when analyzing carbonatites submitted to post-magmatic modifications.

In general, the Sr_i and Nd_i isotopic values for Brazilian Lower Cretaceous carbonatites presented by Comin-Chiaramonti *et al.* (1999) range from 0.70425 to 0.70595 (mean Sr_i = 0.70527 ± 0.00034) and from 0.51213 to 0.51280 (mean Nd_i = 0.51224 ± 0.00011), respectively. Values of Sr_i = 0.70538 and Nd_i = 0.51253 for a sample of a carbonatite intrusion from Jacupiranga were more recently given by Beccaluva *et al.* (2017). Average values for Upper Cretaceous alkaline occurrences of different regions are: Alto Paranaíba, Sr_i = 0.70527 ± 0.00036 and Nd_i = 0.51224 ± 0.00006 (Bizzi *et al.* 1994, Gibson *et al.* 1995a, 1995b, and references therein); Taiúva-Cabo Frio and Serra do Mar, Sr_i = 0.70447 ± 0.00034 and Nd_i = 0.51252±0.00008 (Thompson *et al.* 1998); Lages, Sr_i = 0.70485 ± 0.00053 and Nd_i = 0.51218 ± 0.00022 (Traversa *et al.* 1996, Comin-Chiaramonti *et al.* 2002). Guarino *et al.* (2017) postulated that the Sr-Nd isotopic composition of the Alto Paranaíba carbonatites is markedly different from rocks of the southernmost parts of Brazil, suggesting regional-scale heterogeneity in mantle sources underneath the Brazilian Platform. In the initial $(^{87}Sr/^{86}Sr)_i$ vs. $(^{143}Nd/^{144}Nd)_I$ correlation diagram (Fig. 4A), values for Lower and Upper Cretaceous carbonatites display the same trend defined for Lower Cretaceous tholeiitic lavas of the Paraná Basin (H-Ti and L-Ti), Upper Cretaceous volcanics of the Rio Grande Rise and Paleocene alkaline rocks of the Serra do Mar province (Comin-Chiaramonti *et al.* 2005c, 2007a).

Lower Cretaceous potassic alkaline rocks of Paraguay (both pre- and post- tholeiitic lavas) and associated carbonatites yield Sr_i and Nd_i values within 0.70612-0.70754 and 0.51154-0.51184, respectively (Fig. 4B). These higher Sr_i and lower Nd_i values are distinct when compared with those relative to late Lower Cretaceous (Misiones province) and Paleocene (Asunción province, ASV) Na-alkaline rocks, i.e., Sr_i = 0.70362-0.70524 and Nd_i = 0.51225-0.51277. Together, they define a trend similar to the Low Nd array of Hart *et al.* (1986), i.e., Paraguayan array according to Comin-Chiaramonti *et al.* (1995). Figure 4B also makes evident that sodic alkaline rocks and associated xenolith plots are close to Bulk Earth (BE) values, and that the high and low TiO_2 tholeiites are intermediate between K- and Na-alkaline rocks.

The alkaline and alkaline-carbonatite occurrences in Figure 4 follow well-defined trends involving depleted and enriched mantle components (Gomes & Comin-Chiaramonti *et al.* 2017). The Lower Cretaceous and Upper Cretaceous Brazilian complexes range from close to BE to the enriched quadrant, falling within uncontaminated tholeiitic lavas of the Paraná-Angola-Namibia (Etendeka) province

(Comin-Chiaramonti *et al.* 1997). On the other hand, isotopically Sr-enriched alkaline and alkaline-carbonatites of Paraguay are not easily explained by crustal contamination processes, because that would require high percentages of crustal components, up to 90% according to those authors. Thus, following Castorina *et al.* (1996, 1997), the Sr-Nd systematics for Paraguayan rocks seems to be related to an isotopically enriched source, where chemical heterogeneities reflect a depleted mantle metasomatized by small-volume melts and fluids rich in incompatible elements.

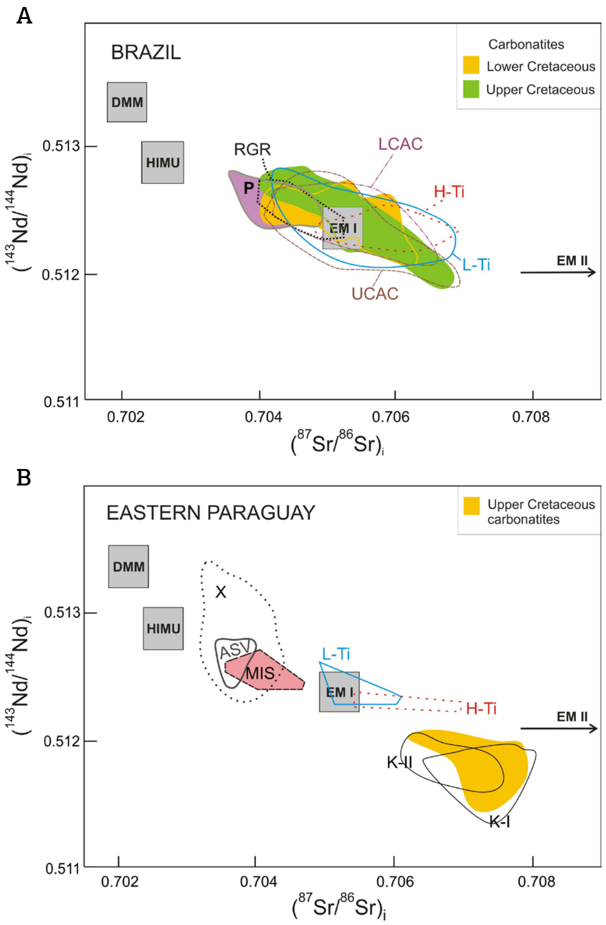


Figure 4. Correlation diagrams for ^{87}Sr/^{86}Sr (Sr)$_i$ vs. ^{143}Nd/^{144}Nd (Nd)$_i$ initial ratios for Brazilian and Paraguayan alkaline-carbonatites after Comin-Chiaramonti *et al.* (2005c, modified). Basalts and andesi-basalts are represented by poorly crustally contaminated or uncontaminated rocks (Piccirillo & Melfi 1988). (A) Brazil: H-Ti, L-Ti and LCAC, *Lower Cretaceous* high- and low-TiO_2 flood tholeiites and alkaline complexes, respectively; RGR and UCAC, *Upper Cretaceous* Rio Grande *Rise* volcanic rock types and alkaline complexes, respectively; P, *Paleocene* alkaline complexes in the Serra do Mar region. (B) Eastern Paraguay: K-I and K-II, *Lower Cretaceous* potassic alkaline complexes, pre- and post-tholeiites, respectively; H-Ti and L-Ti as in (A); MIS, late *Lower Cretaceous* sodic alkaline complexes in the Misiones province; ASV, *Paleocene* sodic alkaline complexes in the Asunción province and associated mantle xenoliths (X). Data sources for both diagrams are given in Comin-Chiaramonti *et al.* (2005c). DMM, HIMU, EM I and EM II are approximations of mantle end-members taken from Hart *et al.* (1992).

The ^{87}Sr/^{86}Sr vs. ^{143}Nd/^{144}Nd diagram in Figure 5 shows that the carbonatites extend across the field of Lower Cretaceous Hi-Ti tholeiites of northern Paraná and are intermediate between the two groups of kimberlites (Type I, Gibeon, Namibia, cf. Davies *et al.* 2001; type II, cf. Smith 1983 and Clark *et al.* 1991). In the εSr vs. εNd inset of the figure, isotopic data ranges widely in the enriched quadrant, with the kamafugite field overlapping all lithological types. In the other inset, model ages T^{DM} for the overall Alto Paranaíba population fit to 0.99 ± 0.10 Ga. The constant Sm/Nd ratio in these rocks allows considering Nd ages as indicative of the main metasomatic event that affected the lithosphere beneath the Alto Paranaíba region.

Nd-model ages

Despite their limited petrological meaning, Nd ages are useful indicators of metasomatic events that affected tholeiites and alkaline rocks of different regions of Brazil and Paraguay. Data on volcanic rocks of the Paraná Basin indicates T^{DM} (Nd) ages that range mainly from 0.5 to 2.1 Ga for Hi-Ti flood tholeiites and dikes, with a mean peak at 1.1 ± 0.1 Ga. Values for L-Ti tholeiites span between 0.7 and 2.4 Ga for L-Ti tholeiites, with a mean peak at 1.6 ± 0.3 Ga (Comin-Chiaramonti *et al.* 2014). Regarding specifically the tholeiitic rocks of Paraguay, T^{DM} (Nd) ages vary from 0.9 to 1.4 Ga for Hi-Ti and from 0.7 to 2.8 for L-Ti, respectively. Apparently, an age increase is observed from North to South and West to East (Comin-Chiaramonti *et al.* 2007a). T^{DM} (Nd) ages for the whole Paraná-Angola-Namibia (Etendeka) system reported by these authors vary from 0.8 to 2.4 Ga for Hi-Ti and from 0.8 to 2.7 Ga for L-Ti, respectively.

Age histograms for Brazilian and Paraguayan tholeiites, alkaline rocks and carbonatites are grouped together in studies by Castorina *et al.* (1997) and Comin-Chiaramonti *et al.* (1997). Nd model age values listed more recently (e.g., Gomes & Comin-Chiaramonti 2005, Bizzi & Araújo 2005, Ruberti *et al.* 2005, Scheibe *et al.* 2005, Comin-Chiaramonti *et al.* 2007a, 2014, Carlson *et al.* 2007, Gomes *et al.* 2011b) allow distinguishing among chronological events in the alkaline magmatism. Thus, the Lower Cretaceous alkaline potassic magmatism includes pre- and post-tholeiite rock types, the first group being only recognized in northern Paraguay. Nd model ages for the pre-tholeiite rocks display two peaks, one at 1.1 Ga (Valle-mí region) and the other at 1.4 Ga (Amambay region), respectively. The Lower Cretaceous syn- and post-tholeiitic magmatism Nd model ages vary from 0.6 to 0.9 Ga. The Upper Cretaceous alkaline rocks and carbonatites, represented mainly by the Alto Paranaíba complexes in Brazi, as well as the late Lower Cretaceous Misiones and Paleocene Asunción volcanics in Paraguay, yield Nd model ages within the 0.6–1.0 Ga interval. The youngest T^{DM} ages are related to the Asunción Tertiary sodic alkaline rocks.

The large variation in model ages seems related to different metasomatic events that took place from Paleoproterozoic to Neoproterozoic. The resulting isotopically distinct alkaline and tholeiitic magmas follow two main subcontinental lithospheric mantle enrichment episodes, at 2.0–1.4 and 1.0–0.5 Ga (Castorina *et al.* 1997, Comin-Chiaramonti *et al.* 1997). These metasomatic events, characterized by strong chemical differences in Ti, LILE and HFSF concentrations, may have been precursors to the genesis of tholeiitic and alkaline magmatism in the Paraná Basin.

Pb isotopes

Only a few studies present initial Pb isotopic compositions for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios in alkaline-carbonatite complexes of the southeastern Brazilian Platform (e.g., Antonini *et al.* 2005, Comin-Chiaramonti *et al.* 2005c, 2007a, Bizzi & Araújo 2005, Beccaluva *et al.* 2017, Gomes & Comin-Chiaramonti *et al.* 2017). Values are reported for Lower Cretaceous occurrences of Brazil and Paraguay and for some Brazilian Upper Cretaceous complexes in the Alto Paranaíba province (Figs. 6A and 6B). In general, isotopic values vary significantly with the different ages. Brazilian and Paraguayan Lower Cretaceous rocks values range in 17.033–19.968, 15.380–15.641 and 37.373–39.011

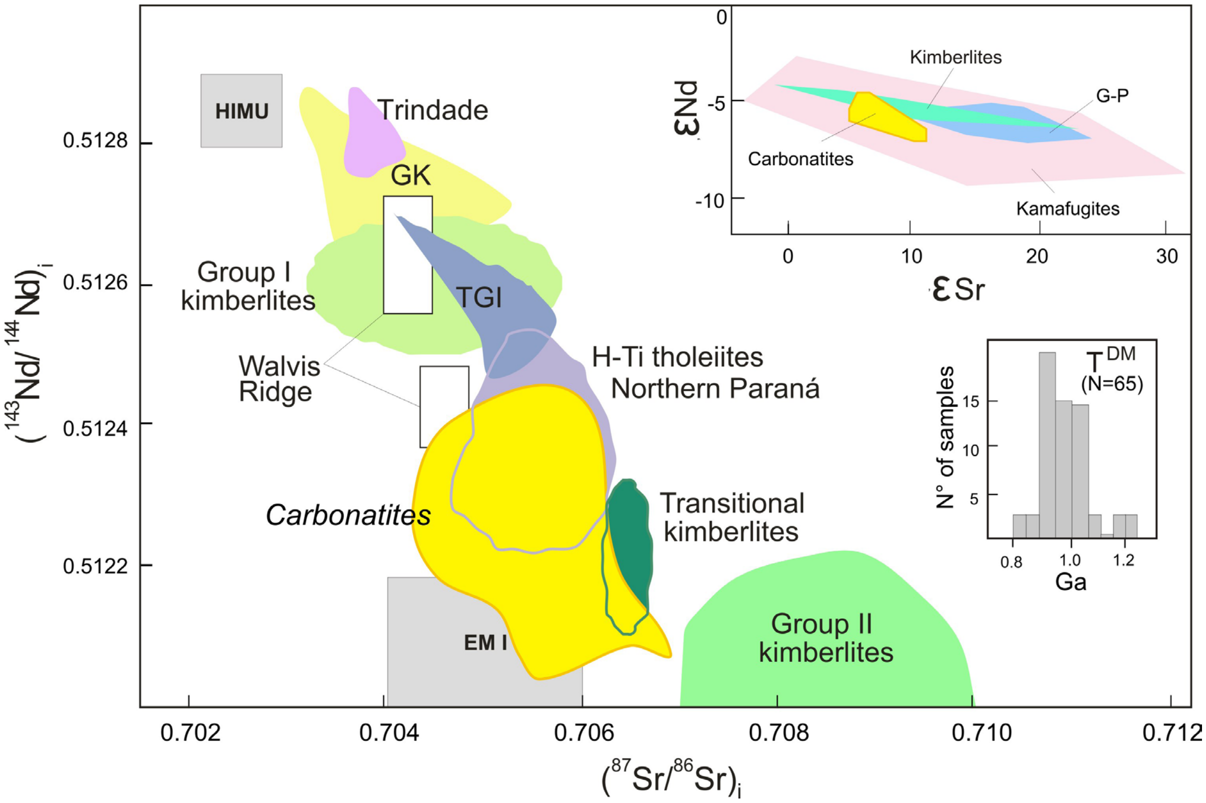


Figure 5. Correlation diagrams for ^{87}Sr/^{86}Sr (Sr)$_i$ vs. ^{143}Nd/^{144}Nd (Nd)$_i$ initial ratios of rock types from the Alto Paranaíba province after Bizzi and Araújo (2005; modified by Comin-Chiaramonti *et al.* 2005c). Data sources: GK, Gibeon kimberlites (Davies *et al.* 2001); TGI, Tristan da Cunha, Gough and Inaccessible islands (Le Roex 1985; Le Roex *et al.* 1990); Walvis Ridge (Richardson *et al.* 1984); Group I, Group II and transitional kimberlites (Smith 1983, Clark *et al.* 1991), Trindade (Siebel *et al.* 2000, Marques *et al.* 2000). Paraná uncontaminated high-Ti tholeiites (Comin-Chiaramonti *et al.* 1997). HIMU and EM I (Zindler & Hart 1986, Hart & Zindler 1989). Insets: Nd model ages (T^{DM}) histograms for Alto Paranaíba rock associations (Gomes & Comin-Chiaramonti 2005) and fields for different alkaline petrographic types (kamafugites, kimberlites, carbonatites and G-P: glimmerites and mica peridotites) in the time integrated εSr vs. εNd diagram (Bizzi & Araújo 2005, modified). T^{DM} values calculated relative to a depleted mantle: ^{143}Nd/^{144}Nd = 0.513114 and ^{147}Sm/^{144}Nd = 0.222, cf. Faure (1986).

intervals for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}$ ratios, respectively. Higher values for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios are typical of a basanite dike that crops out in the Rio Apa region (Valle-mí) in northern Paraguay (K-I, Figs. 6A and 6B). Brazilian Upper Cretaceous occurrences, in turn, show $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}$ ratios that vary within narrow intervals: 17.51–18.52, 15.44–15.55 and 38.20–38.76, respectively. These variations are well-evidenced in correlation diagrams involving $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$, and Sr_i and Nd_i vs $^{206}Pb/^{204}Pb$ initial ratios, respectively, especially for the Brazilian rocks. In the diagrams, Lower Cretaceous carbonatites superpose tholeiites of the Paraná Basin, suggesting a common geodynamic evolution for both alkaline and tholeiitic magmatisms, yet emphasizing the more Sr-enriched composition of coeval Paraguayan rocks and the scatter caused mainly by the values for samples from Valle-mí (K-I). Investigating Sr-Nd-Pb-isotopes of some selected Paraguayan Cretaceous to Tertiary alkaline-carbonatites, Antonini *et al.* (2005) postulated that two main mantle components were involved in the genesis of these rocks: an extreme and heterogeneous EM I, which was prevalent in the Lower Cretaceous potassic alkaline magmatism (K-I and K-II), and a HIMU component, which become more important in the late Lower Cretaceous and Paleocene sodic magmatism (LEC-P).

More recently, Beccaluva *et al.* (2017) provided isotopic data for some intrusions of the Jacupiranga complex. The northwestern body includes alkali gabbros, syenodiorites and syenites around dunites, while the southeastern body consists of clinopyroxenites and rocks of the melteigite-ijolite-urtite series and associated carbonatites. $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}$ ratios for the former petrographic association range from 17.34 to 17.94, from 15.49 to 15.59 and from 37.94 to 38.93, respectively. For the latter association, values vary from 17.70 to 17.87, from 15.47 to 15.50 and from 38.03 to 38.41, respectively. The carbonatite intrusion shows $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}$ ratios of 17.21, 15.42 and 37.87, respectively. According to these authors, the silicate and carbonatite intrusions have markedly different Sr-Nd-Pb isotopic compositions, which support derivation of the relative parental magmas from independent mantle sources.

Diagrams for Pb isotopes (Fig. 7A) define linear arrays that are subparallel to both Lower Cretaceous Paraná tholeiites (Marques *et al.* 1999a) and the Northern Hemisphere Reference Line (NHRL, cf. Hart 1984). Notably, some kimberlites appear to approach the HIMU mantle component. The Alto Paranaíba rocks fall within the Brazilian Upper Cretaceous alkaline-carbonatite complexes (Fig. 4A), which contain all the magmatic petrographic types of the Paraná Basin. Considering the $^{206}Pb/^{207}Pb$ vs. $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ initial ratio diagrams (Fig. 7B), it should be noticed that the majority of the Alto Paranaíba rocks correspond to peridotite xenoliths, some kimberlites excluded. These latter lithologies show less radiogenic Nd in comparison to other Upper Cretaceous kimberlites (e.g., Gibeon, cf. Davies *et al.* 2001).

Re-Os isotopes

Carbonatite complexes strictly associated with highly potassic mafic-ultramafic rocks of kamafugitic-kimberlitic affinity may represent useful sources of information on the behavior of platinum group elements. Analytical isotopic data on Re, Os and platinoids for rocks from the Alto Paranaíba province are discussed by Bizzi *et al.* (1994, 1995), Carlson *et al.* (1996), Araújo *et al.* (2001), Bizzi and Araújo (2005) and Comin-Chiaramonti *et al.* (2007a).

The Re-Os isotope systematics (Gomes and Comin-Chiaramonti *et al.* 2017) does not seem to allow for a clear distinction among rock types in the Alto Paranaíba province, although data provided by Comin-Chiaramonti *et al.* (2007a) indicates that glimmerites have the highest $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ ratios (Fig. 7C). Radiogenic $^{187}Os/^{188}Os$ ratios for kimberlites and kamafugites range from 0.11 to 0.13 (av. 0.122 ± 0.005) and from 0.11 to 0.15 (av. 0.134 ± 0.013), respectively. T^{RD} (Os) model ages reported by Bizzi and Araújo (2005) for the Alto Paranaíba petrographic association vary between 1.39 and 1.64 Ga, correlating these lithologies to an older event with respect to the Nd model ages (0.99 ± 0.10).

Hf isotopes

Hafnium isotopic composition is only available for baddeleyite separates from cumulatic rocks (magnetitites and apatitites) of Catalão I. Data reported by Guarino *et al.* (2017) depict a narrow range of initial $^{176}Hf/^{177}Hf$ of 0.28248 to 0.28249 and εHf_i of -10.3 to -10.9. εHf_i values are distinct with respect to those of peridotite xenoliths hosted by kamafugites of the Goiás province (Carlson *et al.* 2007), confirming mantle heterogeneities in the Alto Paranaíba province. Calculated hafnium model ages (T^{DM} Hf = 1.0–1.1 Ga) are coherent to regional tectonomagmagmatic events that affected the central-southern Brazil.

Noble gases

Only a few carbonatites in the world have been analyzed for noble gases. In Brazil, only two occurrences have so far been investigated: Lower Cretaceous Jacupiranga calciocarbonatites for forsterite and apatite, and Upper Cretaceous Tapira calciocarbonatites for apatite. Analytical data for Ar, Xe, Kr, Ne, and He is presented in Sasada *et al.* (1997) and discussed in a review paper by Comin-Chiaramonti *et al.* (2007a). A summary provided by the latter authors suggests that:

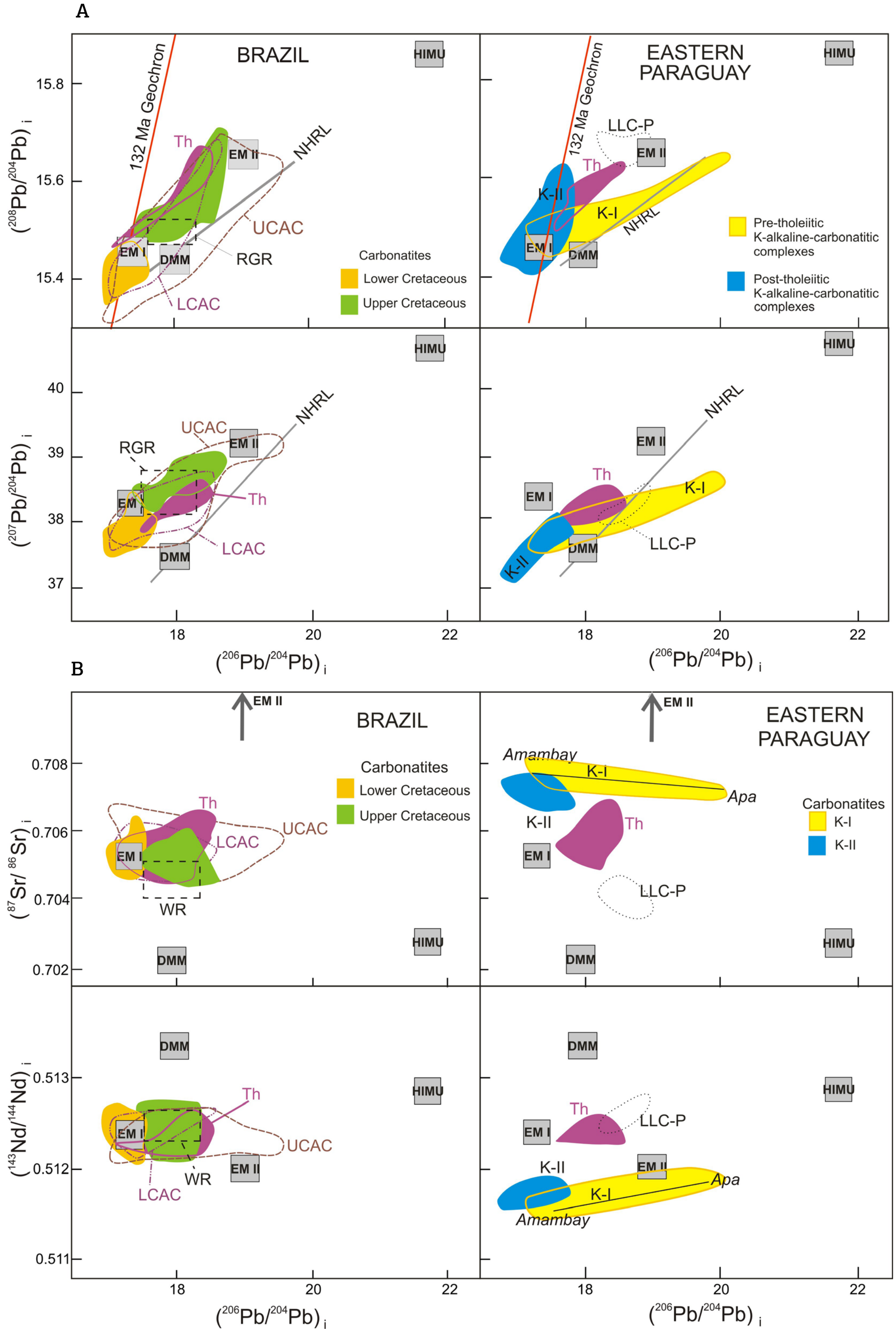


Figure 6. Correlation diagrams for (A) ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb initial ratios and for (B) ^{206}Pb/^{204}Pb initial ratios vs.Sr$_i$ and Nd$_i$ of rock types of southern Brazil and eastern Paraguay (after Comin-Chiaramonti *et al.* 2005c, modified). Brazil: LCAC and UCAC, *Lower Cretaceous* and *Upper Cretaceous* alkaline-carbonatite magmatism, respectively. Eastern Paraguay: LLC-P, late *Lower Cretaceous-Paleocene* sodic alkaline magmatism. NHRL, North Hemisphere Reference Line (Hart 1984); Th, Paraná tholeiites; WR, Walvis Ridge; 132 Ma geochron according to Ewart *et al.* (2004). Data sources are given in Comin-Chiaramonti *et al.* (2005c). Further information as in Figure 4.

- apatites from both carbonatite complexes are in the same range of possible derived sources (e.g., HIMU and MORB);
- sources are enriched in F;
- carbonatites are unlikely to derive from subduction-related carbon, whereas they support a C-O fractionation model of mantle-derived sources.

PETROLOGICAL CONSIDERATIONS

Carbonatite melts from all over the world are currently assigned to some main processes:

- immiscibility of silicate and carbonate liquids (e.g., Baker & Wyllie 1990, Kjarsgaard & Hamilton 1988, 1989, Lee & Wyllie 1996, 1997, 1998b);

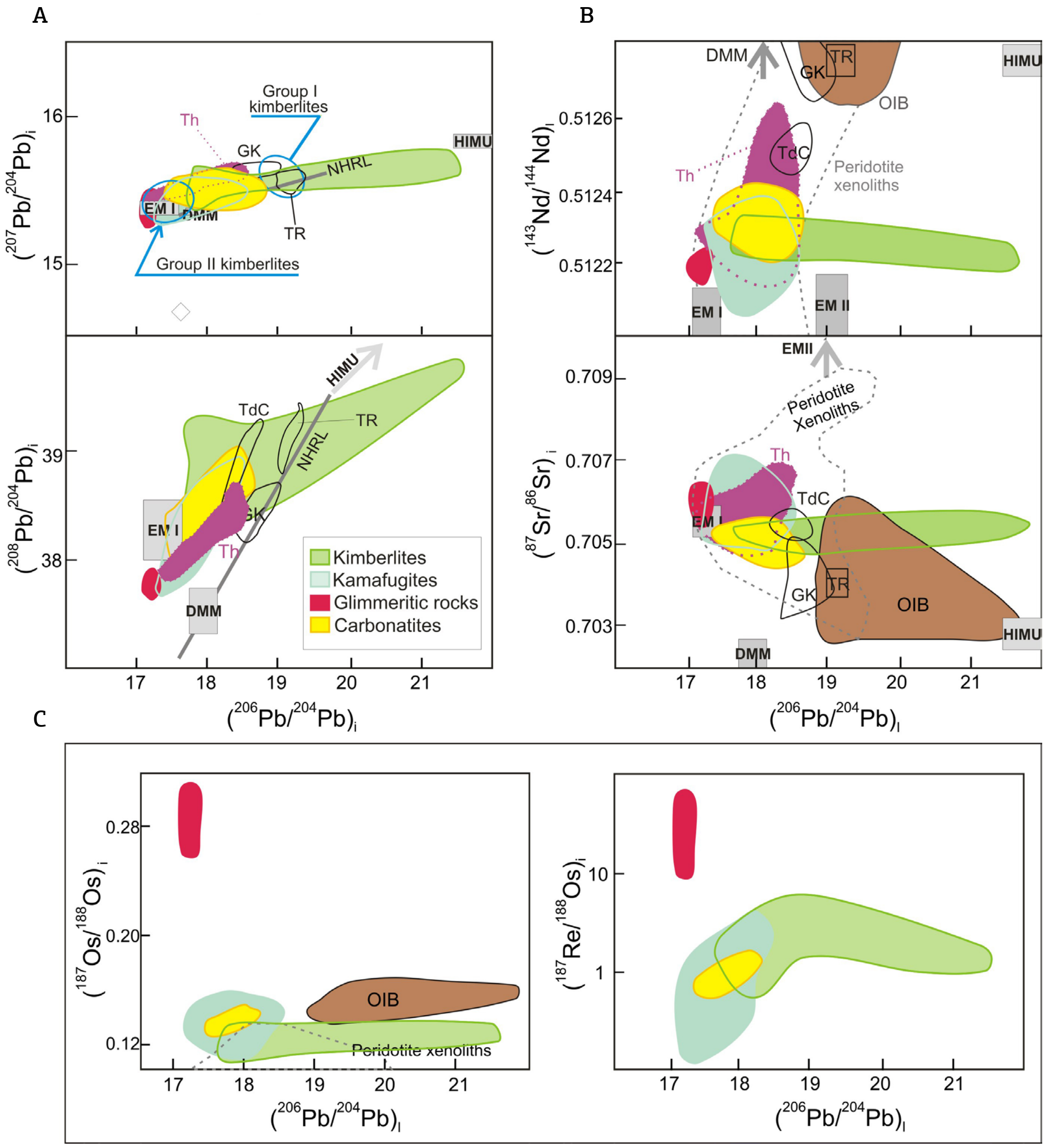


Figure 7. Graphical representation of rock samples from the Alto Paranaíba province in correlation diagrams involving isotopic ratios: (A) $(^{206}Pb/^{204}Pb)_i$ vs. $(^{207}Pb/^{204}Pb)_i$ and $(^{208}Pb/^{204}Pb)_i$; (B) $(^{206}Pb/^{204}Pb)_i$ vs. $(^{143}Nd/^{144}Nd)_i$ and $(^{87}Sr/^{86}Sr)_i$; (C) $(^{206}Pb/^{204}Pb)_i$ vs. $(^{187}Os/^{188}Os)_i$ and $(^{187}Re/^{188}Os)_i$ (after Bizzi & Araújo 2005, modified; cf. also Gomes & Comin-Chiaramonti 2017). OIB, Ocean islands basalts and peridotite xenoliths (Smith 1983; Smith *et al.* 1985; Clark *et al.* 1991); TdC, Tristan da Cunha-Gough-Inaccessible islands (Le Roex *et al.* 1990); TR, Trindade island (Marques *et al.* 2000). Further information as in Figures 4, 5 and 6.

- extreme fractionation from carbonate-rich silicatic magma (e.g., Otto & Wyllie 1993, Lee & Wyllie 1994, Church & Jones 1995);
- a primary mantellic origin such as melting of metasomatized source (Chakhmouradian 2006) or melting of recycled oceanic crust components under mantle conditions (Hoernle *et al.* 2002, Song *et al.* 2017).

Petrogenetic studies performed on a selected number of prominent Cretaceous complexes, as exemplified by Barra do Itapirapuã (Ruberti *et al.* 2002), Ipanema (Guarino *et al.* 2011), Juquiá (Beccaluva *et al.* 1992, Azzone *et al.* 2013) and Lages (Traversa *et al.* 1996) in Brazil and by Cerro Chiriguelo (Castorina *et al.* 1996, 1997) and Cerro Sarambí (Gomes *et al.* 2011b) in Paraguay indicate that processes of fractional crystallization and liquid immiscibility from parental alkaline mafic magmas are the main responsible for the generation of carbonatitic liquids, as suggested by field relationships and geochemical characteristics (cf. also Comin-Chiaramonti *et al.* 2014).

A very consistent hypothetical model for the origin of the Juquiá carbonatites was discussed by Beccaluva *et al.* (1992) that considers multistage evolution under nearly closed system conditions involving:

- assemblage fractionation closely comparable to olivine clinopyroxenite and subordinate olivine alkali gabbro cumulates from parental basanitic melt leading to the formation of essexitic magma;
- derivation of least differentiated mafic nepheline syenite from essexitic magma by withdrawal of cumulitic syenodiorites;
- exsolution of carbonate fluid from a CO_2-enriched mafic nepheline syenite magma, the magma itself being also submitted to continued fractionation to form melteigite-ijolite-urtite cumulates;
- formation of residual nepheline syenitic rocks (and phonolitic dikes) leaving out orthocumulates of nepheline syenites.

Based on field, petrographic, mineralogical, chemical and isotopic evidence, Brod *et al.* (2013) consider the Tapira occurrence as resulting from the complex interplay of several petrogenetic processes: liquid immiscibility, crystal fractionation, and degassing/metasomatism. Their study strongly supports silicate-carbonate liquid immiscibility from decoupling of geochemical pairs such as Nb/Ta and Zr/Hf, rotation of REE patterns, which cross over the patterns of the primitive liquids, and matching and opposite enrichment-depletion trace elements relationships in spider diagrams of conjugate immiscible liquids.

In spite of the isotopic data support to the interpretation that the Cretaceous alkaline-carbonatites are mostly formed by processes related to immiscibilty and fractional crystallization from a common parental magma, higher $^{87}Sr/^{86}Sr$ initial ratios found in samples from a few occurrences (e.g., Barra do Itapirapuã, Ipanema, Jacupiranga, Juquiá, etc.) seem to indicate that contamination processes should not be discarded, particularly in some complexes where border facies are in contact with granitic country rocks in the latest stage of carbonatite intrusion. In the past, Roden *et al.* (1985) and Gaspar (1989), investigating the Jacupiranga complex, also interpreted isotopic heterogeneities of some rocks as due to crustal contamination. In contrast, based on isotopic data, Huang *et al.* (1995) refuted any significant contribution of contamination processes affecting the evolution of the carbonatites and clinopyroxenites. In a recent study, Chmyz *et al.* (2017) provided mineralogical, textural and geochemical evidence of crustal contamination in the formation of the weakly silica-undersaturated rocks of Jacupiranga.

A complex model combining crustal assimilation, fractional crystallization and fluid immiscibility processes was proposed for the carbonatites of Catalão I by Cordeiro *et al.* (2011). A compositional trend is assigned to multiple batches of immiscible and/or residual melts derived from fractional crystallization of a carbonated-silicate parental magma (phlogopite picrite) contaminated to a variable amount with continental crust material. A second trend involved interaction of previously-formed magmatic carbonatites with late-stage or post-magmatic carbohydrothermal fluids.

Conversely, Beccaluva *et al.* (2017) suggested that in the Jacupiranga complex carbonatitic and silicatic rocks originated from independent rather than common mantle sources. Different isotopic data trends indicate that these petrographic types do not exhibit any evidence of being genetically related among themselves. The authors mention the absence of carbonatite *ocelli* in the associated silicate rocks and the presence of fluid and melt inclusions in apatites from carbonatites (suggestive of high depth trapping) as features indicative of origin at mantle depths. Based on geochemical evidence (patterns for REE and isotopic data for sulphur and iron indicating a primitive nature), Beccaluva *et al.* (2017) also advocated that the hypothesis of carbonatites being associated with shallow level immiscibility is less plausible.

A phlogopite-bearing carbonate-metasomatized heterogeneous peridotite source is assigned to different domains of the Brazilian Platform (e.g., Gibson *et al.* 1995b, 1999, 2006, Comin-Chiaramonti *et al.* 1997, 2014, Thompson *et al.* 1998, Brotzu *et al.* 2005, Guarino *et al.* 2017). Such mantle source heterogeneities were recognized at regional scale, the isotopic signatures of the Alto Paranaíba rocks being distinct from those of the Goiás province and the Ponta Grossa Arch, as demonstrated by Guarino *et al.* (2017).

The geodynamic models regarding the Cretaceous carbonatitic and alkaline magmatism of the Brazilian Platform are related:

- to mantle plume and subcontinental lithospheric mantle (SCLM) interactions;
- to low-degree partial melts of metasomatized SCLM due to the reactivation of ancient fault zones (cf. Gomes & Comin-Chiaramonti, 2017).

Gibson *et al.* (1995a, 1995b, 1999), Thompson *et al.* (1998) and Natali *et al.* (2018) suggested for the alkaline and tholeiitic magmatism an origin associated with the interaction of melts from asthenospheric sources attributed to different mantle plumes (i.e. Tristan da Cunha and Trindade mantle plumes) with melts derived of a previously metasomatized lithosperic mantle source. On the other hand, Comin-Chiaramonti *et al.* (1997, 1999, 2002, 2005c, 2007a), Castorina *et al.* (1997), Alberti *et al.* (1999), Ernesto *et al.* (2002) and Riccomini *et al.* (2005) proposed for the alkaline-carbonatite events in the Paraná-Angola-Namíbia system an origin from metasomatized lithospheric mantle sources without the contribution of plume-derived components.

ECONOMIC ASPECTS

The economic importance of carbonatites in Brazil results from the intense weathering of alkaline rocks, mainly of ultrabasic and carbonatic composition. Lateritic soils thus formed can reach more than 200 m thick, especially in complexes of the Ribeira Valley and Alto Paranaíba regions. Mineral deposits formed by either supergene alteration or residual concentration of primary minerals during long periods (Gomes *et al.* 1990). A few sources of mineralization in contact with eluvial material and, more scarcely, fresh rocks are described. Mineral deposits of major importance include phosphate, niobium and vermiculite, whereas subordinate mineralizations are represented by titanium, rare earths, barite, bauxite, fluorspar, etc. Economic aspects of carbonatites are presented by Berbert (1984), Rodrigues and Lima (1984) and Gomes *et al.* (1990). However, such aspects are discussed in more detail in a compilation work by Biondi (2005), one of the most valuable and comprehensive sources of economic data on carbonatites. The author distinguishes among various types of alkaline rock associations containing economic or potentially economic mineral deposits. The most important mineral ores are represented by miaskitic alkaline complexes with syenites + pyroxenites + ijolites + carbonatites, and/or their effusive equivalents as main petrographic types. Recently, Oliveira *et al.* (2017) observed that the distinct evolution trends reaching late-stage rocks from Catalão I coincide with a shift from a Nb-rich to a REE- and Ba-rich mineralization environment.

Finally, in Cerro Manomó, Bolivia, extensive and important enrichments in U and Th are associated with carbonatite blocks (Fletcher *et al.* 1981, Comin-Chiaramonti *et al.* 2011).

CONCLUDING REMARKS

In the southeastern Brazilian Platform, Lower Cretaceous and Upper Cretaceous episodes of alkaline-carbonatite magmatism took place along tectonic lineaments genetically related to regional structural features like the Ponta Grossa Arch and the Alto Paranaíba Uplift in Brazil and the Ponta Porã Arch in Paraguay. The carbonatites occupy inner parts of circular/oval- shaped complexes or appear as dikes and veins that cut across associated alkaline and regional rocks. In some complexes, they result from multistage intrusions of varied composition. Carbonatites are usually found in contact with cumulates of large compositional variation such as ultrabasic (dunites, peridotites, pyroxenites) lithologies, members of the melteigite-ijolite-urtite series, nepheline syenites and syenites, glimmerites, kamafugites, kimberlites, phoscorites, and unimineralic rock types such as apatitite, magnetitite and flogopitite in a few complexes. The country rocks were in most cases deeply affected by fenitization, giving origin mainly to syenitic types. Such processes promoted flogopitization, amphibolitization and aegirinization of pyroxenitic rocks due to the action of highly concentrated alkalis, together with CO_2 and H_2O enriched fluids derived from carbonatitic and syenitic magmas, as well evidenced in Ribeira Valley and Alto Paranaíba complexes.

In an overall classification, Cretaceous carbonatites can be placed into two major groups: primary or magmatic, and hydrothermal. The major Brazilian complexes of the Ribeira Valley and Alto Paranaíba correspond to the first group, whereas Barra do Itapirapuã in Brazil, Cerro Chiriguelo in Paraguay, and Cerro Manomó in Bolivia, are included in the second group. Additional occurrences are represented by small dikes and aggregates of carbonate material (*ocelli*) present in the interior of fine- and coarse-grained alkaline silicate rocks, namely basanite and ijolite. However, it must be stressed that, in some magmatic occurrences, carbohydrothermal events were also registered.

Carbonatites vary considerably in major oxide concentrations, from calciocarbonatites to magnesiocarbonatites to ferrocarbonatites, but the three rock types are rarely associated in the same complex. Besides their richness in elements such as K, Ba, Th, U, Sr, P and REE, and F and Cl as well, and their high LREE content and La/Lu ratio, carbonatites exhibit, in general, a strongly fractionated pattern for REE, mostly controlled by the presence, concentration and variable distribution of accessory phases represented by phosphates, oxides, REE-carbonates and fluorocarbonates minerals (e.g., apatite, monazite, pyrochlore, ancylite, bastnäesite, synchysite, etc.). In spite of some scatter observed, the behavior of incompatible elements points to negative Rb, K, P, Hf-Zr and Ti anomalies, contrasting with positive Ba, Th-U and La-Ce peaks. A remarkable scattering also characterizes the REE distribution, REE-fluorocarbonates being relatively abundant in late ferrocarbonatites. Different behaviors can be distinguished: a strong increase from Lu to La, flat REE with a relative weakly decrease from La to Lu, and concave patterns with a HREE plateau followed by a steady increase from Dy to LREE.

Notably, significant differences in C-O isotope compositions are observed in primary carbonates of alkaline rocks and associated carbonatites. The variations are interpreted as due mainly to isotope exchange between carbonates and H_2O-CO_2 rich fluids, with the isotopic modifications occurring at low temperatures (400–80ºC) in a hydrothermal environment with CO_2/H_2O fluids ranging from 0.8 to 1. Two main paths of $\delta^{18}O$ and $\delta^{13}C$ fractionation associated with different emplacement levels (i.e., deep-seated up to near surface, or near-surface environments) are distinguished. Agents such as weathering and groundwater fluids, that seem to have also influenced post-magmatic changes, could explain the secondary isotopic variations, as indicated by the largest enrichment in heavy oxygen.

In general, Sr-Nd isotopes and trace-element data for the alkaline rocks shows that coeval carbonatites and primary carbonates reflect the composition of the mantle source. In particular, Sr and Nd isotopic data indicate that the carbonatite system was dominated by mantle component(s) without appreciable crustal contamination. Model ages also evidence that the alkaline rocks and associated carbonatites experienced two chemically different episodes of mantle enrichment in Proterozoic times, at 2.0–1.4 Ga and 1.0–0.5 Ga, respectively. Significant H_2O, CO_2 and F are also expected in the mantle source, as suggested by the occurrence of the carbonatitic rocks.

Combined Pb, Sr and Nd isotopic data reveal the contribution of two mantle components as source:

- an extreme and heterogeneous EM I component, which was active in the formation of the Lower Cretaceous alkaline potassic rocks;
- a depleted component, which is believed to have played an important role in the sodic magmatism, spanning in age from Permotriassic to Paleocene.

Mixing processes mainly involving HIMU and EM I end-members, DMM and EM I subordinate, as well as crustal *latu sensu* components (e.g., EM II) were also proposed. For the overall occurrences of the Paraná-Angola-Namibia system, data emphasizes carbonatite plots that fall close to EM I/DMM-HIMU mixing lines for both Pb-Sr and Pb-Nd.

Os isotopic results for silicate alkaline rocks (kamafugites, kimberlites) associated with carbonatites of the Alto Paranaíba province are indicative of lithospheric mantle sources that experienced LILE enrichment by fluid/melt metasomatism at ~1 Ga, probably during the mobile belt formation along the western border of the São Francisco Craton.

Fractional crystallization and liquid immiscibility processes from parental alkaline mafic magmas are thought to be the main responsible for the generation of Cretaceous carbonatite fluids in the Brazilian Platform, crustal contamination being considered to have played a minor role. Degassing, metasomatism and post-magmatic interaction with carbohydrothermal fluids were also recognized in various occurrences. However, some carbonatites do not present a clear genetic association with silicate rocks, which suggests the possibility of a primary mantle origin for the carbonatites. For the generation of alkaline-carbonatite magmatism, a heterogeneous phlogopite-bearing carbonate-metasomatized mantle source is assigned to different domains of the Brazilian Platform.

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