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A review of carbonatitic magmatism in the Paraná-Angola-Namibia (PAN) system

Piero Comin-Chiaramonti [1], Celso de Barros Gomes [2], Aldo Cundari [3], Francesca Castorina [4]
and Paolo Censi [5]*

[1] Dipartimento di Scienze della Terra, Università degli Studi di Trieste, Via Weiss, 8, 37124 Trieste, Italy
[2] Instituto de Geociências, São Paulo University, USP, Brazil
[3] Geotrack International, Melbourne, Australia.
[4] Dipartimento di Scienze della Terra, Università degli Studi di Roma, "La Sapienza", P.le A. Moro, 5, 00185 Roma, Italy.
[5] Dipartimento di Scienze Geologiche, Università degli Studi di Palermo, Palermo, Italy.

Abstract. — Mesozoic to Cenozoic allkaline-carbonatitic complexes from southern Brazil, Angola and Nambia occur along main tectonic lineaments. In general, the alkaline-carbonatite complexes show intrusive/subintrusive, subcircular or oval shaped structures and are indicative of high upwelling energy. Processes of liquid immiscibility from trachytic-phonolitic liquids, starting from parental alkaline mafic magmas are believed to have generated carbonatitic liquids, as suggested by field relationships and geochemical characteristics.

Ca-, Mg- and Fe-carbonatites are widespread even in the same complex. The occurrences comprise three main chronogroups, i.e. 1) Early Cretaceous (Eastern Paraguay; Brazil, Ponta Grossa Arch and Anitápolis; Angola and Namibia); 2) Late Cretaceous (Brazil, Ponta Grossa Arch, Lages and Alto Paranaíba; Namibia); 3) Paleogene, Brazil and Namibia. Two principal types of associated alkaline rocks are represented, i.e. plagioleucitites l.s. (Eastern Paraguay; Brazil: Ponta Grossa Arch; Angola and Namibia) and kamafugites l.s. (Brazil: Alto Paranaíba and Lages; Namibia). Significant variations in O-C isotope compositions are found in primary carbonates, the variations being mainly due to isotope exchange between carbonates and H_2O-CO_2-rich hydrothermal fluids, whereas magmatic processes, i.e. fractional crystallization or liquid immiscibility, probably affect the $\delta^{18}O$ and $\delta^{13}C$ values by not more than 2δ‰. The isotope exchange model implies that the most significant isotopic variations took place in a hydrothermal environment, e.g. in the range 400-80°C, involving fluids with CO_2/H_2O ratio ranging from 0.8 to 1. Sr-Nd-Pb isotope systematics highlight heterogeneous mixtures between HIMU and EMI mantle components, similar to the associated alkaline rocks and the flood tholeiites of the Paraná-Angola-Etendeka (Namibia) system. This is also consistent with Re-Os systematics on selected mafic samples from the Alto Paranaíba alkaline-carbonatite province.The data relative to the noble gases suggest that the source(s) are similar to other mantle derived magmas (e.g. HIMU and MORB) and that the carbon of carbonatites is unlikely to be subduction-related carbon, and support a C-O fractionation model starting from mantle-derived sources. In spite of the strong variation shown by C-O isotopes, Sr-Nd-Pb-Os isotopic systematics could be related to an isotopically enriched source where the chemical heterogeneities reflect a depleted mantle "metasomatized" by small-volume melts and fluids rich in incompatible elements. These fluids are expected to have promoted crystallization in the mantle of K-rich phases that gave rise to a veined network variously enriched in LILE and LREE (cf. Foley, 1992b). The newly formed veins

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* Corresponding author, E-mail: censi@unipa.it

(enriched component) and peridotite matrix (depleted component) underwent a different isotopic evolution with time as reflected by the carbonatitic rocks. These conclusions may be extended to the whole Paraná-Angola-Etendeka system, where isotopically distinct parent magmas were generated following two main enrichment events of the subcontinental lithospheric mantle at 2.0-1.4 and 1.0-0.5 Ga, respectively, as also supported by Re-Os systematics. The mantle sources preserved the isotopic heterogeneities over a long time, suggesting a non-convective lithospheric mantle beneath different cratons or intercratonic regions. Overall the data indicate that the alkaline-carbonatitic magmatism originated from a significant, but small scale heterogeneous subcontinental mantle. In this scenario, the Tristan da Cunha, Walvis Ridge-Rio Grande Rise and Vitória-Trindade hotspot tracks might reflect the accomodation of stresses in the lithosphere during rifting, rather than continuous magmatic activity induced by mantle plumes beneath the moving lithosphere.

RIASSUNTO. — Complessi alcalino-carbonatitici sono diffusi lungo lineamenti tettonici presenti nel Brasile meridionale, in Angola e in Namibia. In generale, tali complessi, intrusivi/subintrusivi, evidenziano strutture subcircolari od ovali e sono indicativi di una elevata energia di “risalita”. Le carbonatiti sono ritenute originate da processi di immiscibilità, a partire da liquidi trachitico-fonolitici, come evidenziato dalle relazioni di campagna e dalle risultanze geochimiche. I complessi alcalino carbonatitici comprendono almeno tre cronogruppi principali, dove Ca-, Mg- e Fe-carbonatiti sono diffuse persino nell’ambito dello stesso complesso: 1) Cretacico Inferiore (Paraguay Orientale; Brasile, Arco di Ponta Grossa e Anitápolis; Angola e Namibia); 2) Cretacico Superiore (Brasile, Arco di Ponta Grossa, Lages e Alto Paranaíba; Namibia); 3) Paleogene (Brasile e Namibia). I litotipi alcalini associati sono rappresentati essenzialmente da plagioleucititi l.s. (Paraguay Orientale; Brasile: Arco di Ponta Grossa; Angola e Namibia) e kamafugiti l.s. (Brasile: Alto Paranaíba e Lages; Namibia). In termini di composizione isotopiche O-C, sono state notate significative variazioni per quanto riguarda i carbonati “primari”, dovute principalmente a scambi isotopici tra i carbonati e fluidi idrotermali ricchi in H_2O-CO_2, mentre i processi magmatici (cristallizzazione frazionata e immiscibilità tra liquidi) probabilmente non comportano variazioni per più del 2‰ in termini di $\delta^{18}O$ and $\delta^{13}C$. Nei modelli, le più consistenti variazioni isotopiche appaiono consistenti con un ambiente idrotermale, a temperature tra 400 e 80°C, e fluidi con rapporto CO_2/H_2O tra 0.8 e 1. La sistematica isotopica Sr-Nd-Pb evidenzia nelle carbonatiti mixing eterogenei tra componenti di mantello tipo HIMU e EMI, simili a quelli delle rocce alcaline associate e persino a quelli delle tholeiiti stratoidi del sistema Paraná-Angola-Namibia. Da notare la consistenza della suddetta sistematica isotopica anche con il sistema Re-Os, come da determinazioni effettuate su campioni femici selezionati, soprattutto provenienti dalla provincia alcalina-carbonatitica dell’Alto Paranaíba. I dati relativi ai gas nobili suggeriscono sorgenti simili ad altri derivati mantellici (HIMU e MORB), che il carbonio delle carbonatiti non può porsi in relazione a processi subduttivi e supportano modelli di frazionamento C-O a partire da sorgenti derivanti dal mantello. Nonostante le grandi variazioni isotopiche in termini di O-C, la sistematica isotopica relativa a Sr-Nd-Pb-Os appare consistente con sorgenti isotopicamente arricchite, dove le eterogeneità geochimiche riflettono un mantello impoverito, “metasomatizzato” da piccoli volumi di liquidi e da fluidi ricchi in elementi incompatibili. Tali fluidi dovettero promuovere, in porzioni di mantello, fasi ricche in potassio, dando luogo a una rete di venature variamente arricchite in LILE e REE. Tali vene (componente arricchito) e la matrice peridotitica (componente impoverito) subirono una differente evoluzione isotopica nel tempo, di cui le carbonatiti riflettono l’impronta. Queste considerazioni si possono considerare generali per l’intero sistema Paraná-Angola-Namibia, dove distinti magmi genitori furono generati a partire da due eventi principali di arricchimento, a 2,0-1,4 e 1,0-0,5 Ga, rispettivamente, suggerendo un mantello litosferico non-convettivo sotto i differenti cratoni o regioni intercratoniche, in cui le le eterogeneità isotopiche vengono conservate per lunghi intervalli temporali. Nel complesso i dati indicano che il magmatismo alcalino-carbonatitico ha avuto origine dal mantello subcontinentale significativamente eterogeneo a piccola scala. In questo quadro, le cosiddette tracce hotspot di Tristan da Cunha, Walvis Ridge-Rio Grande Rise e Vitória-Trindade possono riflettere l’adattamento di tensioni litosferiche durante il rifting, piuttosto che attività magmatica continua indotta da mantle plumes sotto la litosfera mobile.

KEY WORDS: *Carbonatites, Paraná-Angola-Namibia system, geochemistry, stable and radiogenic isotopes, lithospheric mantle, geodynamic implications.*

INTRODUCTION

The Paraná Basin is part of the Paraná-Angola-Namibia (Etendeka) Province (PAN; cf. PAEP of Comin-Chiaramonti *et al.*, 1999), characterized by Early Cretaceous flood tholeiites and dyke swarms (129-133 Ma; Piccirillo and Melfi, 1988; Renne *et al.*, 1997; Ernesto *et al.*, 1999, 2002, and therein references) associated with alkaline and alkaline-carbonatite complexes of Early Cretaceous to Paleogene age (Gomes *et al.*, 1990; Reid *et al.*, 1990; Morbidelli *et al.*, 1995; Le Roex and Lanyon, 1998; Alberti *et al.*, 1999). The emplacement of the PAN alkaline and alkaline-carbonatitic complexes occurred mainly along tectonic lineaments active at least since Early Mesozoic, and up to present day, as indicated by the distribution of the earthquakes in southern Brazil (Berrocal and Fernandes, 1996).

Carbonatites, i.e. igneous rocks which contain >50% carbonates, range in age from the late Archean to the present. Almost all carbonatites are restricted to continental areas, although in a few cases, such as Cabo Verde, they are believed to be oceanic. The criteria by which a carbonate-rich rock is considered to be a true carbonatite are difficult to apply with confidence. Although not conclusive, the following evidences are the strongest clues, especially when they are found together (Barker, 1996): 1) field evidences, e.g. subcircular or suboval or ring structures of alkaline complexes with carbonatite body occupying the inner part; 2) association with melilite- or nepheline-bearing rocks; 3) calcite with >1 wt% SrO; 4) presence of perovskite, pyrochlore, F-REE-carbonates and apatite with high silica content (e.g. >2 wt%); 5) enrichment in Sr, Ba, Nb, U, Th and rare-earth elements (with high LREE *vs.* HREE fractionation) and depletion of other elements (e.g. K, Rb, Zr, Hf and Ti) relative to mantle and continental crust (Woolley and Kempe, 1989); 6) ^{87}Sr/^{86}Sr initial ratios similar to those of the associated silicate alkaline rocks (cf. Castorina *et al.*, 1997); 7) stable isotopes (O-C) in the "primary carbonatitic box" (Taylor *et al.*, 1967; Keller and Hoefs, 1995) or following well distinct isotopic fractionation trends (Speziale *et al.*, 1997).

Taking into consideration the above criteria, this paper will summarize field and geological evidences and geochemical characteristics in terms of major elements, incompatible elements (IE), rare earth elements (REE), O-C and Sr-Nd-Pb isotopical data of well known alkaline-carbonatitic complexes and occurrences in and around the Paraná Basin in southern Brazil, in particular, and in the PAN, in general. Additional data on noble gases, i.e. He, Ne, Ar, Kr and Xe (Sasada *et al.*, 1997) and on the Re/Os system (Carlson *et al.*, 1996; Bizzi and Araújo, 2005) are also reported.

GENERAL OUTLINES

Alkaline and alkaline-carbonatitic complexes from the Paraná-Angola-Namibia system (PAN) belong to three main chronogroups: Early Cretaceous, Late Cretaceous and Paleogene (Fig. 1). Notably, the first chronogroup roughly corresponds to the emplacement of the tholeiitic flood basalts of the Serra Geral Formation (Brazil; Piccirillo and Melfi, 1988) and of the Etendeka Group volcanic rocks (Namibia, Ewart *et al.*, 1998).

Early Cretaceous alkaline and alkaline-carbonatite complexes from southern Brazil and Paraguay are found mainly along the 1) Uruguay lineament (Anitápolis and Sapucai, at the eastermost and westernmost side of the Paraná Basin, respectively); 2) Piquirí lineament (Eastern Paraguay: Cerros Chiriguelo and Sarambí); 3) Ponta Grossa Arch (e.g. Barra do Itapirapuã Jacupiranga, Juquiá) and 4) Serra do Mar, at the northern fringe of the Ponta Grossa Arch (e.g. Itanhaém). Regarding tholeiitic flood basalts of the PAN system, these occurrences are pre-tholeiitic (e.g. Cerros Chiriguelo and Sarambí; 138-139 Ma), syn-tholeiitic (e.g. Anitápolis, Jacupiranga, Juquiá; 130-133 Ma), and post-tholeiitic (e.g. Sapucai, 128 Ma; Ipanema, 124 Ma; Barra do Itapirapuã, 115 Ma; cf. Comin-Chiaramonti *et al.*, 1997a, b, 1999, 2007; Ruberti *et al.*, 2002, 2005). In Angola, the alkaline-carbonatitic complexes (138-130 Ma; cf. Lapido-Loureiro, 1973; Issa Filho *et al.*, 1991; Coltorti *et al.*, 1993; Alberti *et al.*, 1999) occur mainly at the Moçâmedes Arch (e.g. Sulima, Bailundo, Longonjo, Coola, Tchivira-Bonga) and at the Khumib region (e.g. Virilundo). In northwestern Namibia (137-124 Ma, cf. Milner *et al.*, 1995; Le Roex and Lanyon, 1998), they are widespread chiefly along the inland of the Damara

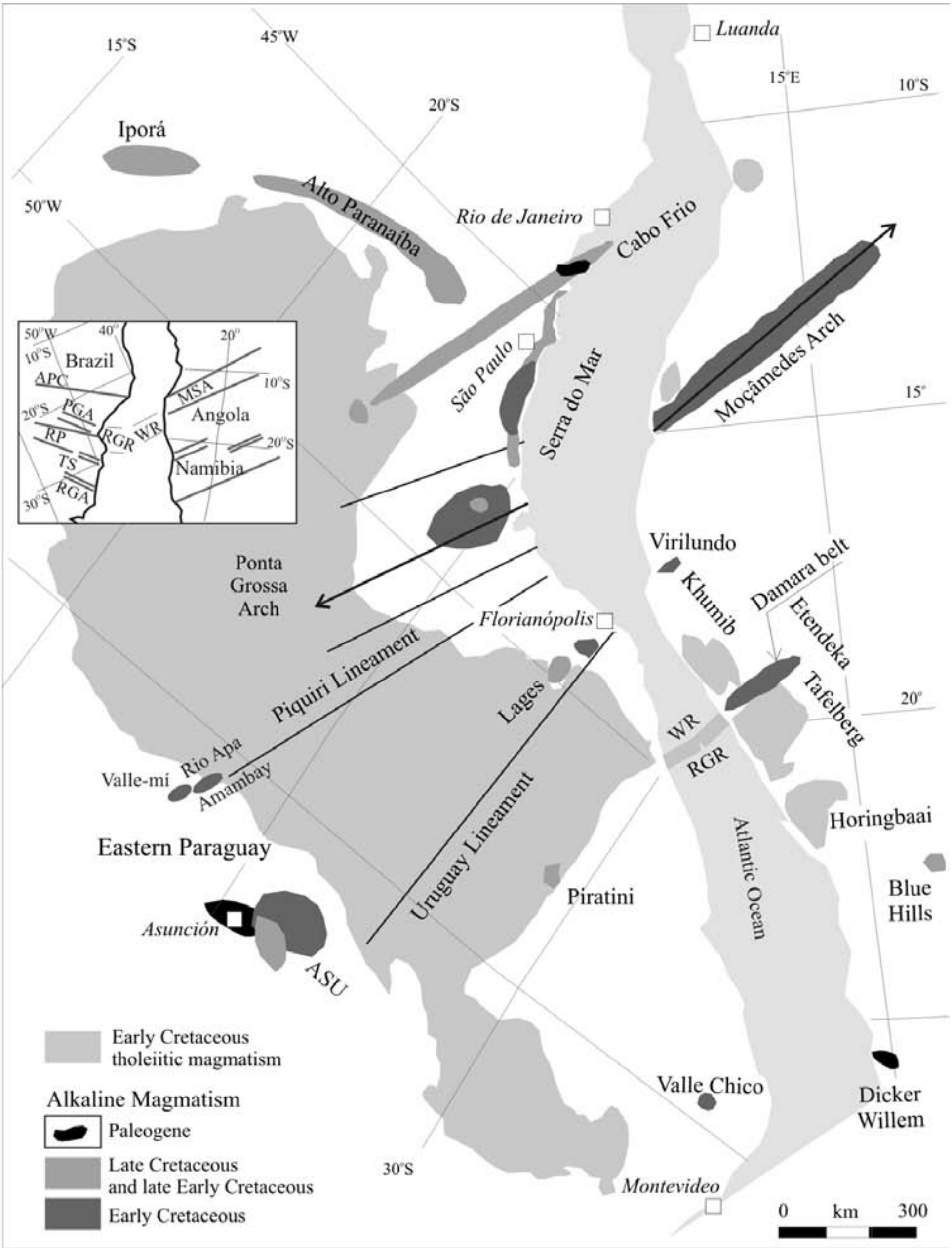


Fig. 1 – Distribution of the magmatism in the Paraná-Angola-Namibia Province (South American and African plates, Western Gondwana, at about 110 Ma; modified after Comin-Chiaramonti *et al*., 1997a, 1999) and location of the main alkaline-carbonatitic occurrences. Abbreviations: RGR, Rio Grande Rise; WR, Walvis Ridge. Inset: main lineaments across Africa and Brazil, corresponding to the main lineaments of the alkaline complexes. APC, Araguaia-Paranaíba-Cabo Frio; PGA, Ponta Grossa Arch; RP, Rio Piquirí; TS, Torres syncline; RGA, Rio Grande Arch; MSA, Moçamedes Arch; RGR, Rio Grande rise; WR, Walvis ridge (after Comin-Chiaramonti *et al*., 1991).

belt (Osongombo, Kalkfeld, Ondurakorume, Okorusu).

Late Cretaceous alkaline-carbonatite complexes from southern Brazil are concentrated along the 1) Iporá-Alto Paranaíba lineament (e.g. Iporá: Morro do Engenho, Caiapó, Santo António da Barra; Alto Paranaíba: Catalão I-II, Salitre, Serra Negra, Araxá, Tapira and São Gotardo), 2) Ponta Grossa Arch (e.g. Mato Preto), 3) Taiúva-Cabo Frio lineament and 4) Uruguay lineament (Lages). In Namibia, Late Cretaceous carbonatite plugs and dykes (Blue Hills, 72-79 Ma, related to the Gross Brukkaros volcanic field) were described by Kurszlaukis and Lorenz (1997) and Kurszlaukis *et al*. (1999).

Paleogene alkaline complexes of Brazil (mainly 64-45 Ma) are distributed along the Taiúva-Cabo Frio lineament (Serra do Mar igneous province; cf. Thompson *et al*., 1998); in Paraguay, Paleogene melanephelinites are reported by Comin-Chiaramonti *et al.* (1991). An Eocene alkaline-carbonatite complex (Dicker Willem carbonatite, 49 Ma) has been described by Cooper and Reid (1998) in southwestern Namibia.

The carbonatites from South America (Figs 2 and 2a) are rarely effusive (e.g. Sapucai and Santo António da Barra), as well as the associated extrusive rocks are rarely preserved. The scarcity of volcanic rocks is probably due to the intense erosion that was responsible for their removal. Hegarty *et al*. (1996) suggested a kilometer-scale uplift and erosion that started at 80-90 Ma. Often the pediplane is characterized by extensive soil and laterites, where the drainage led to the formation of thick soils (up to 200-300 m) originated from weathering of cumulate (ultramafic) rocks and dissolution of carbonates from carbonatites (cf. Fig. 2, Catalão I, and Danni *et al*., 1991). As a result, large supergenic and residual deposits of apatite, pyrochlore, vermiculite, anatase, and REE carbonates and phosphates have been formed.

The general features of the alkaline-carbonatitic complexes in and around the PAN are summarized in Table 1. Intrusive-subintrusive rock-types are usually characterized by well defined circular or oval shaped forms where the carbonatites lie roughly in the center of the intrusions (Fig. 2). In particular, the circular form of the Cerro Chiriguelo complex is of special interest (cf. Fig. 2-1) because the enclosing country rocks are stretched in less than three kilometers and range from an inner ring of Precambrian basement to an outer one of Paleozoic to Jurassic sediments. Overall the structure points to the high energy of emplacement of the complex, especially if we consider the serpentinite blocks present at the contact between the complex and the Precambrian basement as mantle remnants. If this is the case, the ascent of the carbonatitic magma from a depth of ≈ 70-75 km to the surface occurred in less of than 10 hours (cf. Comin-Chiaramonti *et al*., 1991).

The subcircular field configuration has been frequently used for the identification of the complexes by aerophotography (cf. Censi *et al*., 1989). Sometimes the carbonatites display a remarkable complexity, and multiple, distinct carbonatitic events may be recognized by a network-of multiple intrusions (e.g. Table 2, Barra do Itapirapuã; Ruberti *et al*., 2002, 2005). Dykes crosscutting the alkaline complex (e.g. Anitápolis) and plugs or diatremes (e.g. Lages, Brazil, and Brukkaros, Namibia; Comin-Chiaramonti *et al*., 2002a, and Kurszlaukis and Lorenz, 1997, respectively) are also noticeable.

MAJOR ELEMENT CHEMISTRY

The Brazilian carbonatites vary from calciocarbonatites to magnesiocarbonatites and ferrocarbonatites (Fig. 3), but these three rock-types are rarely associated in the same complex (e.g. Araxá, Barra do Itapirapuã and Mato Preto; Comin-Chiaramonti *et al*., 2002b, Ruberti *et al*., 2002). The Angolan carbonatites (Alberti *et al*., 1999) show a compositional range wider than that of the Brazilian analogues in each complex, roughly corresponding to the distribution of the whole population (Fig. 3a). The Namibian carbonatites (Milner and Le Roex, 1996; Le Roex and Lanyon, 1998; Kurszlaukis *et al*., 1999; Bühn and Trumbull, 2003) are represented by Fe-carbonatites and scarce Ca-carbonatites (Early Cretaceous) and by Mg-carbonatites (Late Cretaceous). Molar ratio CaO/(CaO+MgO+FeO_t+MnO) of Ca-, Mg- and Fe-carbonatites (DI) is negatively correlated with (MgO+FeO_t+MnO) wt% due to the Ca-Mg-Fe substitutions. Some other correlations are significant: SiO_2 versus Al_2O_3 (r = +0.90) and Na_2O+K_2O (r = +0.96), whereas in the rocks with SiO_2<9 wt%, P_2O_5 is negatively correlated with

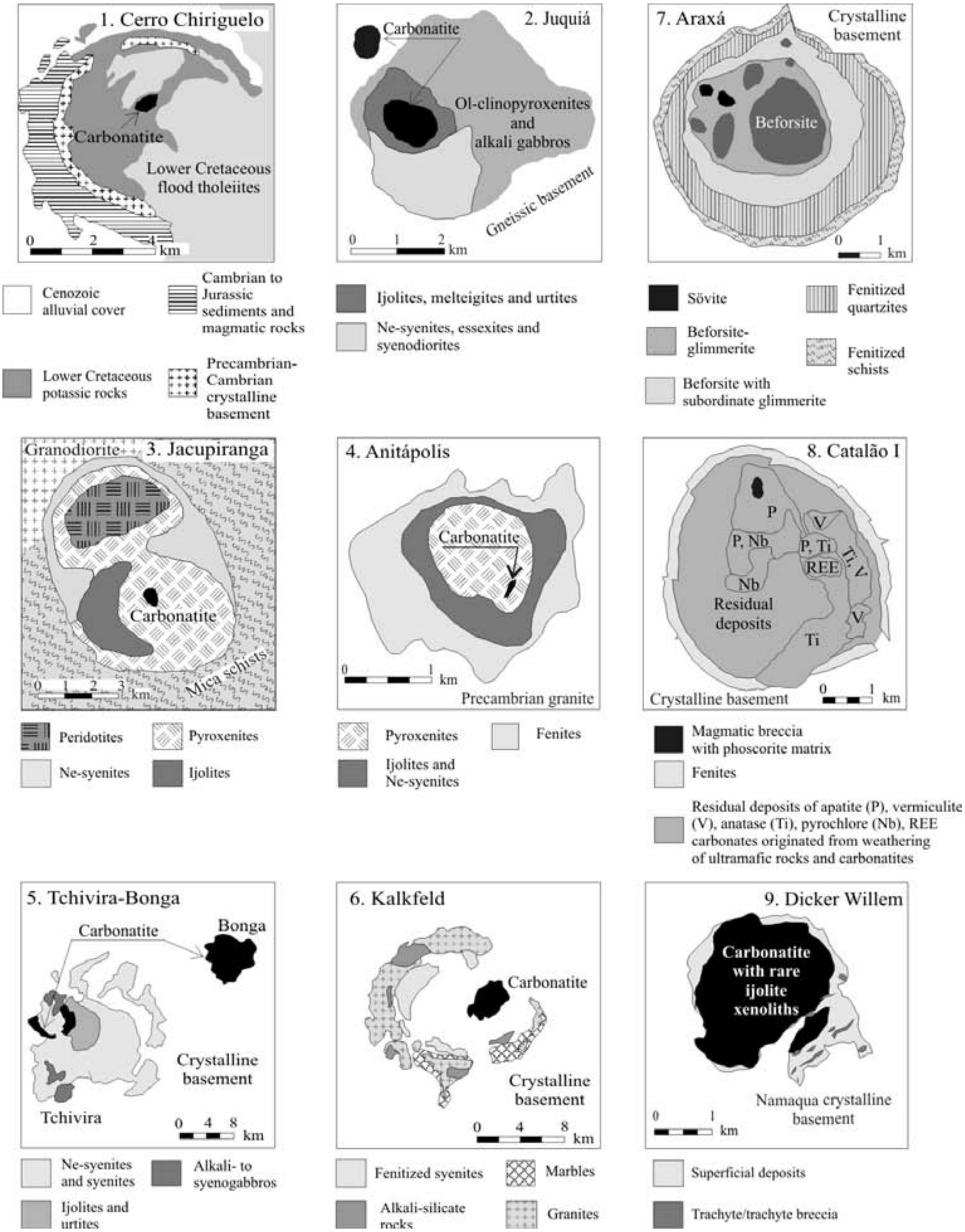


Fig. 2 – Examples of the ring structure characteristic of many alkaline-carbonatitic complexes from the Paraná-Angola-Namibia system (after Lapido-Loureiro, 1973; Issa Filho *et al.*, 1984; Censi *et al.*, 1989; Danni *et al.*, 1991; Beccaluva *et al.*, 1992; Huang *et al.*, 1995; Bühn and Rankin, 1999; Cooper and Reid, 2000; Comin-Chiaramonti *et al.*, 2002a). *Early Cretaceous*: 1, 2, 3, 4: Pre- and syn-tholeiitic complexes from South America: 1, Eastern Paraguay; 2 and 3, Ponta Grossa Arch, Brazil; 4, Santa Catarina State, Brazil; Pre-tholeiitic and syn-tholeiitic complexes: 5, Moçamedes Arch, Angola; 6, Damaraland, Namibia; *Late Cretaceous*: 7 and 8, Alto Paranaíba, Brazil; Paleogene: 9, southwestern Namibia. The carbonatites are indicated by dark fields.

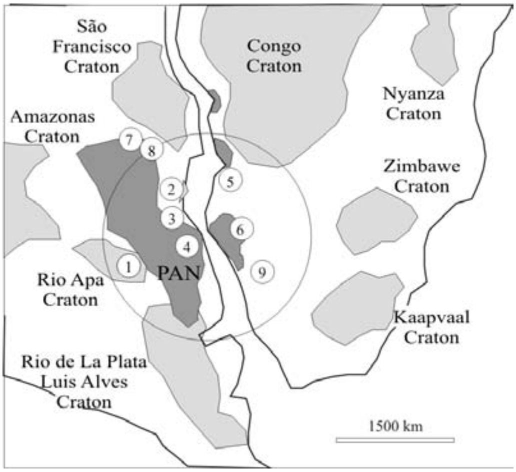


Fig. 2A – Location of the alkaline-carbonatitic complexes in the Paraná-Angola-Namibia system and the postulated location of the Tristan plume head. References (1 to 9 numbers) as in Table 1.

LOI (assumed to represent CO_2; r =-0.98), in good agreement with the modal content of alkali feldspar and apatite, respectively (Gomes *et al.*, 1996; Castorina *et al.*, 1996, 1997; Alberti *et al.*, 1999). On the whole, the data point to multi-stage carbonatite processes in the assemblages with changes of the rock-forming minerals (Table 2; cf. Sokolov, 2002).

The Early Cretaceous carbonatites from Brazil and Angola are usually associated with a potassic magmatism that shows, following Foley's classification (1992a), "plagioleucititic" composition (Gomes *et al.*, 1996; Alberti *et al.*, 1999). It is mainly represented by evolved rock-types (trachyphonolite-phonolite and intrusive equivalents). In Namibia, they are related to lamprophyric rocks, both of potassic and sodic affinities (Le Roex and Lanyon, 1998). On the other hand, in Brazil, the Late Cretaceous carbonatites are characterized by kamafugitic-kimberlitic associations (Traversa *et al.*, 1994, 1996; Gibson *et al.*, 1995a,b; Brod *et al.*, 2005). Less evolved (gabbro-basalt clans) and cumulatic assemblages (e.g. dunite, clinopyroxenite, phoscorite) are common to both Early and Late Cretaceous complexes. The Eocene Dicker Willem carbonatite (Southwestern Namibia) is associated with alkaline (sodic) rocks (melanite ijolite; Cooper and Reid, 1998).

In general, the silicate-rock-types at the contact with the carbonatite bodies are syenitic-trachytic/phonolitic (l.s.) in composition. Experimental data (e.g. Kjarsgaard and Hamilton, 1988; Kjasgaard *et al.*, 1995) show that carbonatitic liquids in equilibrium with trachytic/phonolitic magmas contain high alkali contents, whereas all the investigated carbonatites display very low alkali content. This evidence points to an exsolving carbonatite melt from parental basic magmas or to a more complex evolution of alkali-rich carbonated melts exsolved from evolved magmas, with loss of alkalies during depressurization, hydrothermal stages and volatile transfer (cf. Castorina *et al.*, 1996; Speziale *et al.*, 1997).

In Brazil, the carbonatite occurrences are believed to be originated by processes of liquid immiscibility (Beccaluva *et al.*, 1992; Castorina *et al.*, 1996). In particular, at Juquiá, a parental basanitic magma fractionated under virtually closed system conditions, with the development of an inner zone side-wall cumulates of olivine clinopyroxenite to nepheline syenite, progressively enriched in trapped liquid. At a more advanced fractionation stage, an immiscible carbonatitic liquid was exsolved from a CO_2-rich mafic nepheline syenite magma, resulting in the formation of carbonatite liquid which crystallized as Mg-carbonatite at the core of the intrusion. Continuous crystal fractionation of the silicatic magma gave rise to ijolite-melteigite-urtite cumulates. Primary carbonates occur as large interstitial crystals or form "ocelli" in some nepheline syenites. The "ocelli", where clinopyroxene and alkali feldspar can be present, are frequent in the more evolved rock-types and are in general surrounded by biotite/phlogopite shells, indicating a local increasing of fluid activity (Beccaluva *et al.*, 1992). In conclusion, the Juquiá model of Beccaluva *et al.* (1992) may represent a suitable picture for the examined carbonatites, where the various stages are: 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) derivation of the least differentiated maphic nepheline syenite from the essexitic magma through subtraction of syenodioritic assemblages and 3) exsolution of a carbonate liquid from a CO_2-enriched magma (cf. Fig. 4).

TABLE 1

General features of the alkaline-carbonatitic complexes from the Paraná-Angola-Etendeka system. Age: in parenthesis 2σ; Ne = nepheline. Data sources, in order of quotation in the Table: (1) Castorina *et al. (1997); (2)* Comin-Chiaramonti and Gomes *(1996); (3)* Comin-Chiaramonti *et al. (1999); (4)* Lapido-Loureiro *(1973); (5)* Coltorti *et al. (1993); (6)* Alberti *et al. (1999); (7)* Issa Filho *et al. (1991); (8)* Prins *(1981); (9)* Bühn and Rankin *(1999); (10)* Comin-Chiaramonti *et al. (2002a); (11)* Morbidelli *et al. (1995); (12)* Beccaluva *et al. (1992); (13)* Gomes *et al. (1990); (14)* Le Roex and Lanyon *(1998); (15)* Ruberti *et al. (2002, 2005); (16)* Comin-Chiaramonti and Gomes *(2005); (17)* Milner *et al. (1995); (18)* Meyer *et al. (1994); (19)* Traversa *et al. (2001); (20)* Traversa *et al. (1996); (21)* Comin-Chiaramonti *et al. (2002b); (22)* Reid *et al. (1990); (23)* Kurszlaukis and Lorenz *(1997); (24)* Kurszlaukis *et al. (1999); (25)* Cooper and Reid *(2000)*

EARLY CRETACEOUS

	Age, Ma	Region	Main rock associations	Form	References
Pre-tholeiitic					
PARAGUAY					
Rio Apa	138 (1)	Northern Paraguay	Basanite, Phonotephrite, Phonolite, Carbonatitic K-basanite dykes	Globular Ca-carbonate patches in dykes	(1)
Cerro Chiriguelo	138 (3)	Northern Paraguay	Tephrite, Trachyte, Phonolite, Silicocarbonatite, Ca-Carbonatite	Circular	(2)
Cerro Sarambí	139 (1)	Northern Paraguay	Pyroxenite, Glimmerite, Trachyte, Silicocarbonatite, Ca-Carbonatite	Subcircular	(1), (3)
ANGOLA					
Tchivira-Bonga	135 (1)	Southwestern Moçamedes Arch	Alkaline gabbro, Ijolite, Urtite, Melteigite, Nepheline syenite, Syenite, Ca- and Mg-Carbonatite	Subcircular	(4), (5), (6)
Monte Verde	137 (?)	Moçamedes Arch	Nepheline syenite, Ca-Carbonatite	Semiring	(4), (6), (7)
Sulima	137 (?)	Moçamedes Arch	Syenite, Ca-Carbonatite	Ring	(4),(7)
NAMIBIA					
Kalkfeld	137 (2)	NW Namibia, Damaraland	Nepheline syenite; Syenite, Ca- to Fe-Carbonatite	Subcircular	(6), (9)
Syn-tholeiitic					
BRAZIL					
Anitápolis	131 (1)	Santa Catarina	Pyroxenite, Glimmerite, Ijolite, Ne-syenite, Syenite, Tinguaite, Ca-Carbonatite	Subcircular	(10)
Jacupiranga	130 (1)	São Paulo, Ponta Grossa Arch	Dunite, Pyroxenite, Ijolite, Alkali gabbro, Syenogabbro, Syenodiorite, Syenite, Nepheline syenite, Carbonatite, Basanite, Phonolite	Oval	(11)
Juquiá	132 (2)	São Paulo, Ponta Grossa Arch	Pyroxenite, Alkali gabbro, Ijolite, Essexite, Nepheline syenite, Melteigite, Ankaratrite, Phonotephrite, Phonolite Mg-, Ca-Carbonatite	Suboval	(12)
Itanhaém	133 (5)	São Paulo, Serra do Mar	Tinguaite, Carbonatite	Dyke	(13)
ANGOLA					
Longonjo	130 (2)	Moçamedes Arch	Ca-, Mg-, Fe-Carbonatite	Semiring	(4), (6), (7)
Coola	130 (2)	Moçamedes Arch	K-Ijolite, Nepheline syenite Mg-, Ca-Carbonatite	Semiring	(4), (6), (7)
Bailundo	129 (2)	Moçamedes Arch	Syenite, Ca-Carbonatite	Semiring	(4), (6), (7)
Virilundo	129 (?)	SW Angola, Khumib	Ca-carbonatite	Circular	(4), (6), (7)
NAMIBIA					
Osongombo	129?	Damaraland	Mg-, Fe-Carbonatite	Plugs	(14)
Ondurakorume	129?	Damaraland	Nepheline syenite, Syenite, Mg-(REE), Ca-Carbonatite	Plugs	(14)

Post-tholeiitic					
PARAGUAY					
Central Province	126 (2)	Eastern Paraguay	K-tephrite to phonolite, K-alkaline basalt to trachyte, K-theralite, alkali gabbro, syenogabbro, essexite, (Mg-, Ca-carbonatite	Lava flows	(2)
BRAZIL					
Barra do Itapirapuã	115 (10)	Ponta Grossa Arch	Syenite, Ca-Mg-Fe-carbonatite	Stockwork	(15)
Itapirapuã	109 (7)	Ponta Grossa Arch	Melteigite, tinguaite, Ne-syenite, melteigite, carbonatite	Irregular, elongated intrusion	(11), (13), (16)
Ipanema	125 (10)	Ponta Grossa Arch	Pyroxenite, glimmerite, syenite, shonkinite, Ca-carbonatite	Circular	(13), (16)
NAMIBIA					
Okorusu	125 (7)	Damaraland	Foyaite, urtite, syenite, melanephelinite, nephelinite, Ca-carbonatite	Plugs	(17)
LATE CRETACEOUS					
BRAZIL	Age, Ma	Region	Main rock associations	Form	References
Araxá	88 (10)	Alto Paranaíba	Pyroxenite, Glimmerite, Phoscorite, Ca-Mg-Fe-Carbonatite	Circular	(11), (13), (18), (19)
Tapira	79 (9)	Alto Paranaíba	Dunite, Pyroxenite, Phoscorite, Uncompahgrite, Syenite, Trachyte, Ca-Mg-Fe-Carbonatite	Oval	(13), (18), (19)
Lages	76 (4)	Santa Cataina, Magmatic field	Ol-melilitite, Nephelinite, Melteigite, Nepheline syenite, Trachyte, Phonolite, Ca-Fe-Carbonatite	Sheet-like intrusions, dykes, sills, stocks and plugs	(13), (16), (20),(21)
NAMIBIA					
Blue Hills	77 (2)	Gross Brukkaros Volcanic Field	Mica-olivine-carbonate picrite,monticellite picrite, Mg-carbonatite	Diatremes and dykes	(22), (23),(24)
PALEOGENE					
NAMIBIA					
Dicker Willem	49 (3)	Southwestern Namibia	Ijolite, Ca-Carbonatite	Circular	(22), (25)

TABLE 2

Generalized evolution of carbonatite mineral compositions by overlapping stages of the carbonatite processes in PAN (cf. also Sokolov*, 2002). Data source:* Rodrigues *and* Lima *(1984),* Censi *et al. (1989),* Walter *et al. (1995),* Speziale *et al. (1997),* Andrade *(1998),* Comin-Chiaramonti *et al. (2002a, b),* Ruberti *et al. (2002)*

	Main major minerals	Main accessory 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	Baddeleyte (Zr), pyrochlore-I (Nb), hatchettoloite (Nb, Ta, U, Th), zirkelite (Zr, Nb)
III STAGE	Calcite, dolomite (Fe-dolomite), tetrapherriphlogopite, apatite III, magnetite, sphene	Pyrochlore (Nb, Th, U), burbankite (Sr, Ba, REE)
IV STAGE	Dolomite (Fe-dolomite), ankerite, siderite, magnesite, fluorite rodochrosite, K-feldspar, quartz	Pyrochlore (U, Th, Nb), bastnäsite (REE), parisite (REE), ancylite (Sr, REE), synkisite (REE), strontianite (Sr), celestine (Sr)

A similar process is also applicable to the genesis of the carbonatites from Eastern Paraguay (Castorina *et al*., 1996). Jacupiranga carbonatites show a more complex scenario (Fig. 4).

The evolution line (alkali gabbro to syenogabbro to nepheline syenite) is linked to the removal of large amounts of cumulatic material, mainly olivine and clinopyroxene, as indicated by the abundance of pyroxenitic and dunitic rocks in the field (cf. Fig. 2-3). 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 (Morbidelli *et al*., 1986).

MINOR AND TRACE ELEMENT CHEMISTRY

As a rule, there are very large variations in the normalized values (Figs. 5a, b) from one carbonatite complex to another for any given incompatible element. The scattering of the incompatible elements (IE) for the different carbonatites reflects to some extent the variable distribution and concentration of mineral phases such as phosphates (e.g. apatite and monazite: REE), oxides (e.g. pyrochlore: Nb, REE, Th, U; calzirtite: Ti, Zr; zirconolite: Ti, Zr, Nb; loparite: REE, Ti, Nb), REE-carbonates and fluorocarbonates (e.g. ancylite, bastnaesite, burbankite, parisite).

Model experiments with natural and artificial mixtures show that carbonatite melts might be enriched in K, P, Sr, Ba, U, Th and REE, as well as in F and Cl (Kjarsgaard *et al*., 1995, and therein references). F in silicate-carbonate systems positively influences the entry of Nb (Ta, U, Th, REE) into the carbonate fraction. Transfer of IE and REE is supported by experimental results on Nb and LREE solubility in synthetic carbonate liquids (cf. Jones *et al*., 1995). According to Jago and Gittings (1993), calciocarbonatite liquids are able to dissolve 5-7.5 wt% of Nb_2O_5 at 950-

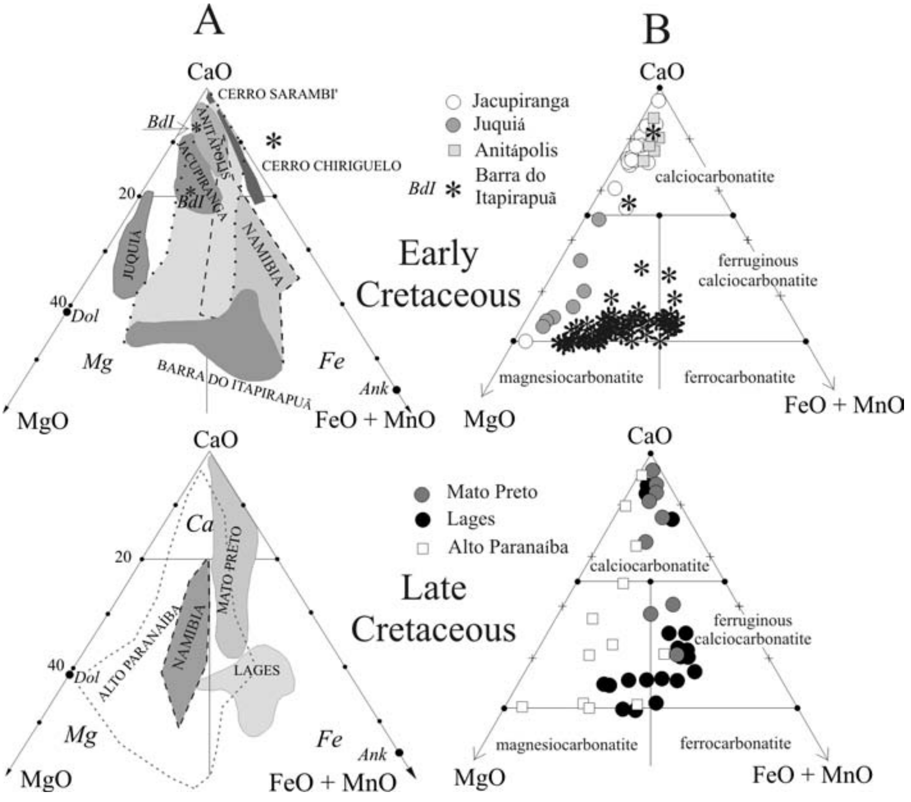


Fig. 3 – A: Fields relative to the classification of the carbonatitic associations (after Woolley and Kempe, 1989) in the various complexes and regions from the PAN. Abbreviations: Dol, dolomite; Ank, ankerite. B: Diagrams for classifying Brazilian carbonatites (molar proportions) after Gittins and Harmer (1997). Data source, Brazil: Morbidelli *et al.* (1986), Censi *et al.* (1989), Beccaluva *et al.* (1992), Meyer *et al.* (1994), Huang *et al.* (1995), Toyoda *et al.* (1995), Ruberti *et al.* (2002), Comin-Chiaramonti *et al.* (2002a, 2002b) and unpublished data; Angola: Alberti *et al.* (1999) and references therein ; Namibia: Milner and Le Roex (1996), Le Roex and Lanyon (1998), Kurszlaukis *et al.* (1999), Bühn and Trumbull (2003).

600°C. Crystallization of these liquids at first promotes the precipitation of a perovskite-type phase and then of pyrochlore together with calcite. Phase relationships in the section calcite-REE hydroxide (Jones and Wyllie, 1983) 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%: bastnaesite may crystallize together with calcite from magmatic carbonate liquids with temperature falling from liquidus (650-625°C) to eutectic (about 540°C) and under definite relations of carbon dioxide, water and fluorine.

On the other hand, REE-carbonates, fluorocarbonates and oxides, which are the products of low temperature (mainly hydrothermal) environment, represent to some extent the fenitizing fluids enriched in IE with respect to the primary carbonates (cf. Castorina *et al*., 1997). For example, four distinct generations of carbonatite dykes are present in the Barra do Itapirapuã complex, two of which clearly displaying overprint of hydrothermal alteration (Andrade *et al*., 1999a; Ruberti *et al*., 2002).

Overall the PAN carbonatites cover the wide variation field of Andersen (1987), in terms of La *vs.* La/Yb relationships. The carbonate fractions of carbonatites display La/Yb ratios and La content 2-3

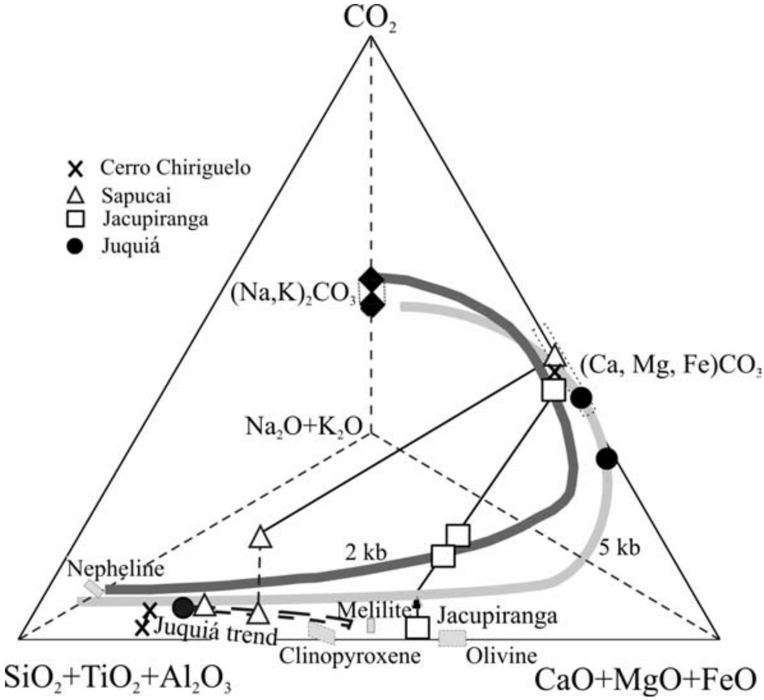


Fig. 4 – Quaternary diagram showing residual liquid trends (after Kjarsgaard and Hamilton, 1989). Data source in Castorina *et al.* (1996). The curves labelled 2 kb and 5 kb are theoretical isobaric-polythermal solvi.

times higher than those of the corresponding rocks. On the other hand, the carbonate fractions from the associated silicate rocks show both higher La and La/Yb than those of the corresponding silicate fractions (Castorina *et al.*, 1997; Alberti *et al.*, 1999). As an example, Fig. 6 illustrates the La/Yb relationships for basanite-tephrite and phonolite-trachyte suites and associated primary carbonates from Eastern Paraguay. If the differentiation of the CO_2-bearing parental magma is relatively restricted (i.e. basanite to phonotephrite), the exsolved carbonatitic melt is relatively small and crystallizes forming groundmass patches or “ocelli”. On the other hand, if the evolution from basic melts leads to phonolite or trachyte, the latter magmas may exsolve carbonatite melts having high La and La/Yb relative to the parental fluid-rich mafic magmas. The mixing curves between parental magma(s) and carbonatites (Fig. 6) provide an estimation of the CO_2-rich melt fraction(s). Considering that the primary carbonates (up to 15-20 wt%) of the silicate rocks represent late crystallized phases, and that the carbonatites may represent the carbonatitic liquid exsolved from the trachytic/phonolitic magma, the total carbonatitic magma appears to be higher than 30-35 wt% of the carbonate content in the parental silicate melt. Then, if the basanite of Fig. 6 is assumed as the parental magma of a carbonatite, the evolution may be shown in terms of two main steps: 1) basanite to trachyphonolite differentiation leading to derivative rock-types by crystal fractionation and concentration of CO_2-rich fluids, and 2) exsolution of about 20 wt% carbonatitic liquids from the differentiated phonolitic magma (cf. inset of Fig. 6).

The fact that both the parental magmas and the associated carbonatites plot within the “carbonatite field” (Andersen, 1987) suggests that the parental magmas are characterized by high CaO/Al_2O_3, La/Yb and Ti/Eu (cf. Dalton and Wood, 1993; Rudnik *et al.*, 1993).

The CaO/Al_2O_3 *vs.* La/Yb and Ti/Eu diagrams, respectively (Fig. 7), show that primitive rocks

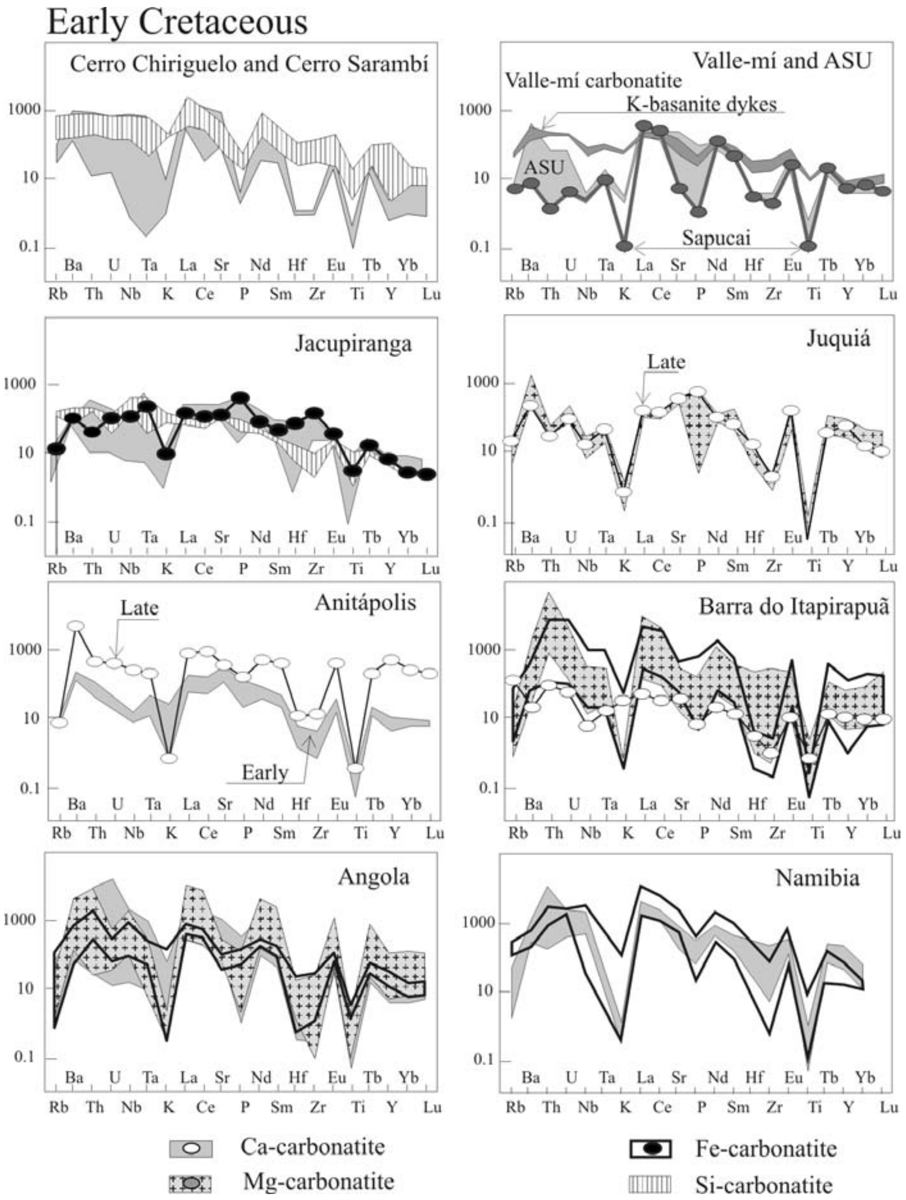


Fig. 5A – Incompatible elements normalized to primitive mantle concentrations (Sun and McDonough, 1989) for carbonatite rock-types from the PAN, Early Cretaceous. Data sources: Eastern Paraguay (Cerro Chiriguelo, Cerro Sarambí, Valle-mí and ASU), Comin-Chiaramonti *et al.* (1995) and unpublished data, Comin-Chiaramonti and Gomes (1996), Castorina *et al.* (1996, 1997), Antonini *et al.* (2005); Brazil, Jacupiranga: Morbidelli *et al.* (1986), Nelson *et al.* (1988), Toyoda *et al.* (1995), Huang *et al.* (1995), Castorina *et al.* (1996); Juquiá: Beccaluva *et al.* (1992), Castorina *et al.* (1996); Anitápolis, Comin-Chiaramonti *et al.* (2002a); Barra do Itapirapuã, Ruberti *et al.* (2002); Alto Paranaíba: Toyoda *et al.* (1995), Meyer *et al.* (1994), Traversa *et al.* (2001), Comin-Chiaramonti and Censi unpublished data; Mato Preto, Comin-Chiaramonti *et al.* (2002b); Lages, Traversa *et al.* (1994, 1996), Comin-Chiaramonti *et al.* (2002a); Angola, Alberti *et al.* (1999); Namibia, Damaraland: Le Roex and Lanyon (1998); Blue Hills: Kurszlaukis *et al.* (1999); Dicker Willem Eocene complex: Cooper and Reid (1998).

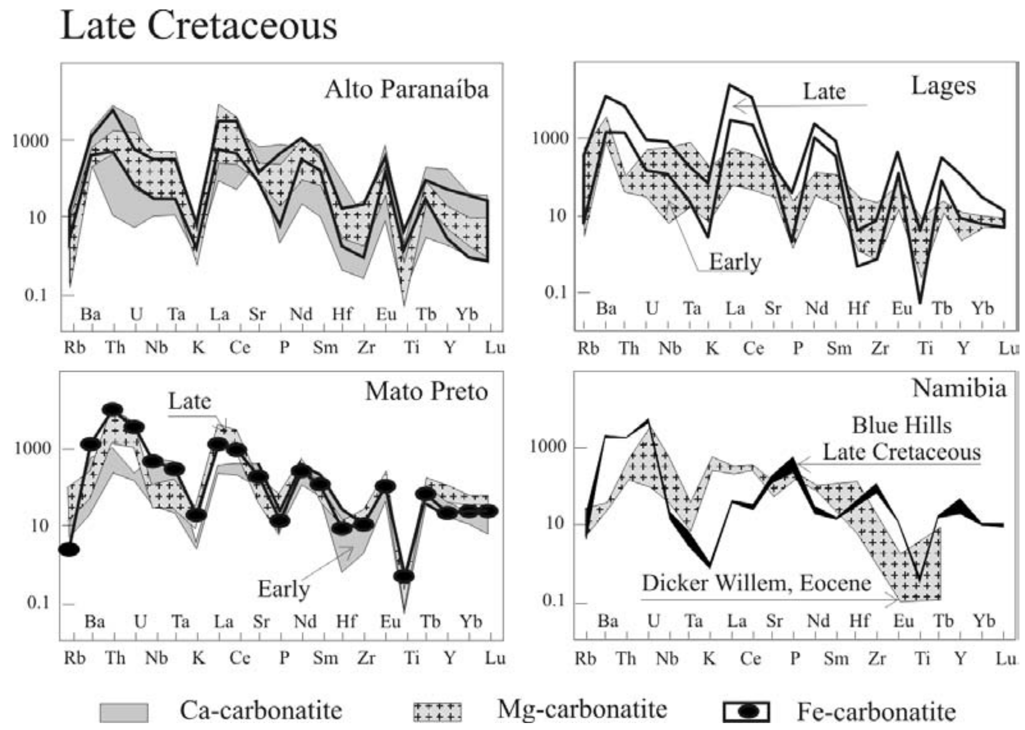


Fig. 5B – Incompatible elements normalized to the primitive mantle concentrations (Sun and McDonough, 1989) for carbonatite rock-types from the PAN, Late Cretaceous and Paleogene. Data sources: Alto Paranaíba, Gomes and Comin-Chiaramonti (2005); Lages, Scheibe and Formoso (1982), Scheibe *et al*. (2005); Mato Preto, Comin-Chiaramonti *et al*. (2002b); Namibia: Blue Hills, Bühn and Trumbull (2003); Dicker Willem, Cooper and Reid (1998, 2000).

belonging to carbonatite-free and carbonatite-bearing complexes plot into distinct fields (cf. Castorina *et al*., 1997; Morbidelli *et al*., 2000).

It is remarkable that the K-basanites from the Valle-mí and Cerro Chiriguelo occurrences (cf. Figs. 1 and 2) have higher CaO/Al_2O_3 ratios than those from central Eastern Paraguay (ASU, Asunción Province of Comin-Chiaramonti *et al*., 1997a, b) and, therefore, may reflect mantle regions that underwent significant carbonatitic metasomatism. The initial stages of differentiation of the CO_2-rich K-basanites are characterized by a silicate fraction that prevails on the carbonatitic component (cf. kamafugitic rock-types from Alto Paranaíba, APIP of Gibson *et al*., 1995a,b), which, instead, is prominent on the last stages of differentiation.

The REE display remarkable scatters even in any single complex, particularly for samples belonging to different stages of crystallization, i.e. from magmatic, to late-magmatic and to hydrothermal conditions. Scatters may be due, at least in part, to the presence of main accessory minerals such as apatite, REE fluorocarbonates, fluorite and barite. REE fluorocarbonates are relatively abundant in the late Fe-carbonatites. Apart from well distinct anomalies, e.g. Eu (Cerro Chiriguelo) and Sm (ASU) negative spikes, some different types of REE distributions may be distinguished (Fig. 8):

1) Patterns with a strong increase from Lu to La, as indicated for the Cerro Chiriguelo, Jacupiranga (Mg-carbonatites), Alto Paranaíba (Mg-carbonatites), Mato Preto and Lages (both early and late carbonatites), and Angolan and Namibian complexes. It should be noted that the Cerro Chiriguelo patterns, for both Ca- and Si-carbonatites, parallel that of the coexisting apatite (note also Eu negative spike); the Mato Preto and Lages behaviours appear to be controlled by the coexisting fluorite and by late carbonatite veins,

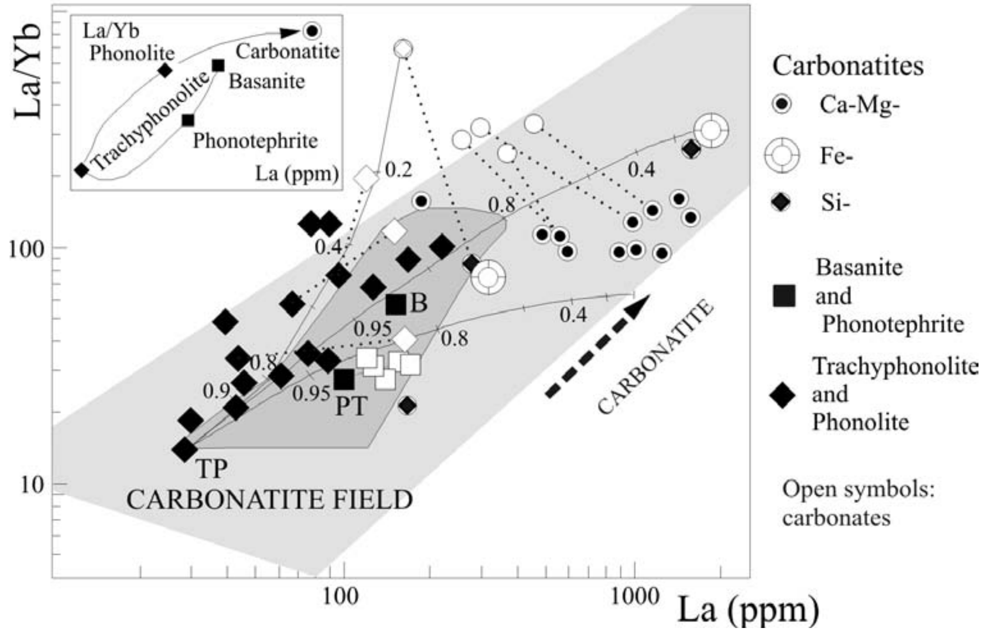


Fig. 6 – La *vs.* La/Yb ratios for silicate rocks, carbonatites and carbonates from Eastern Paraguay (after Castorina *et al*., 1997, modified). B, basanite; PT, phonotephrite; TP, trachyphonolite. Carbonatite field from Andersen (1987). The dark-gray field represents the melts with unexsolved carbonate liquids. The labelled curves represent mixing lines between silicate and carbonatitic liquids, from which it can be inferred that the exsolution of an immiscible carbonatitic mass occurs for contents ≥ 20% of carbonate equivalent dissolved in the parent silicate liquid. Tie dotted lines join the silicate fractions with the carbonates. Inset: evolutionary path, as determined for Rio Apa dykes.

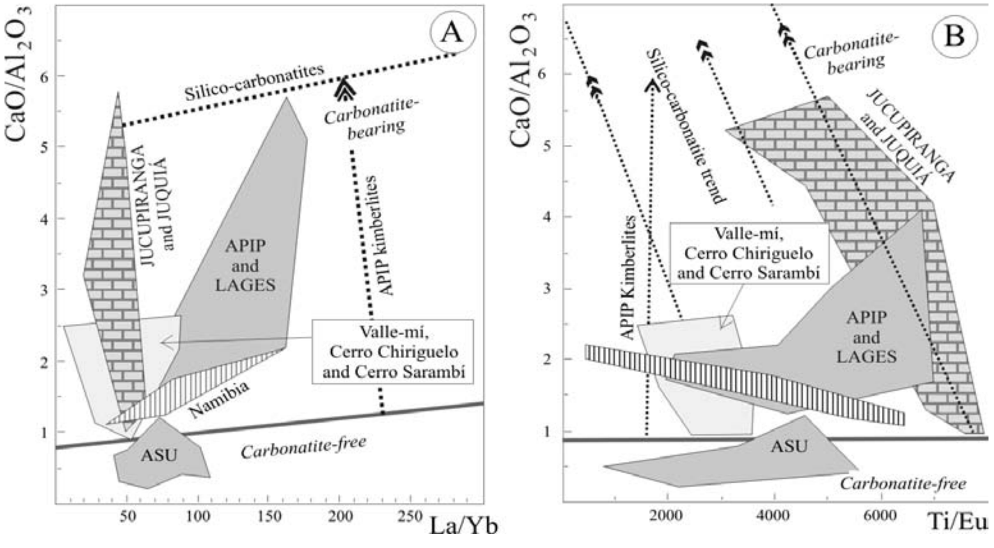


Fig. 7 – CaO/Al$_2$O$_3$ *vs.* La/Yb (A) and CaO/Al$_2$O$_3$ *vs.* Ti/Eu (B) diagrams for carbonatite-free and carbonatite-bearing alkaline

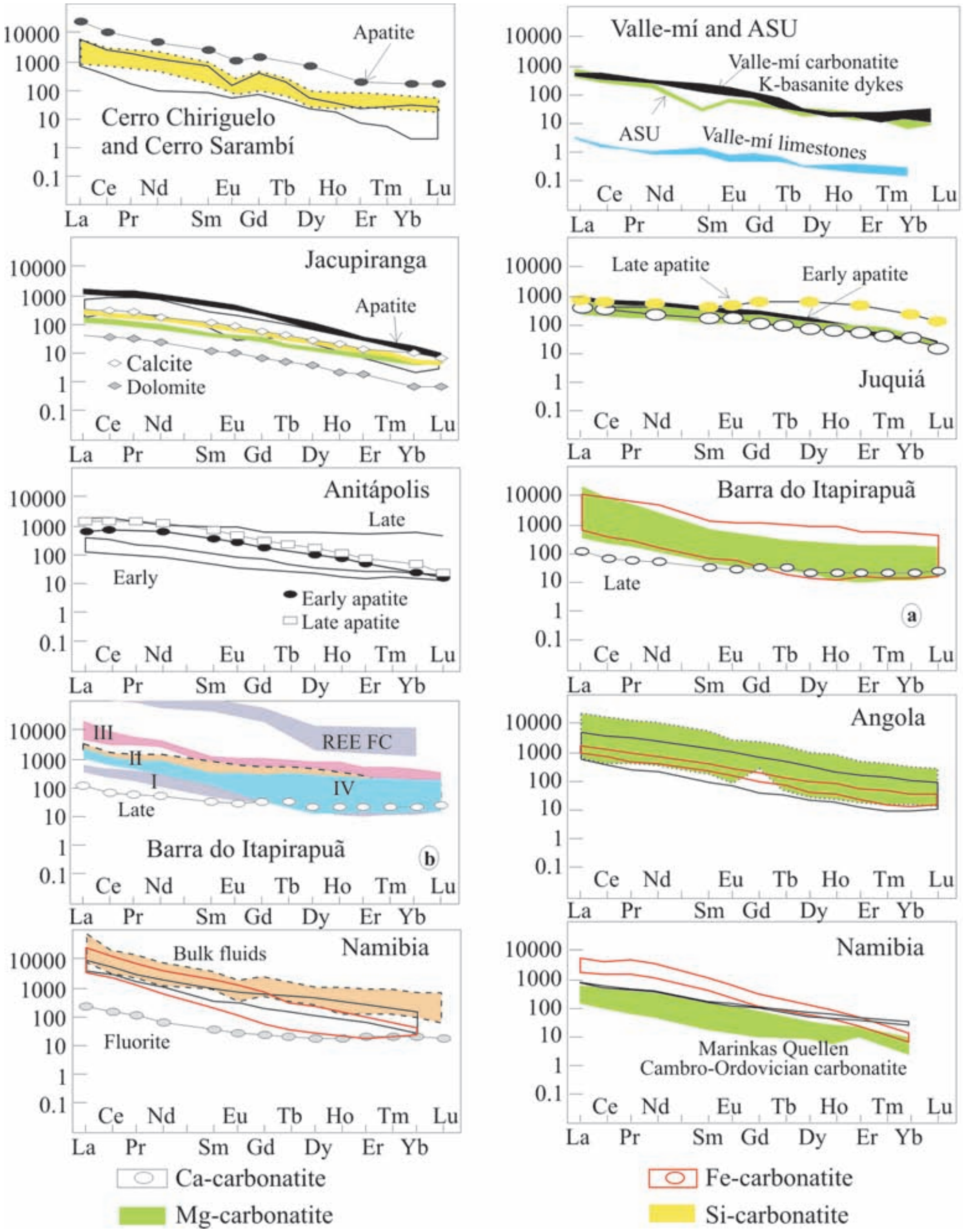


Fig. 8.A.– Early Cretaceous: Chondrite-normalized (Boynton, 1984) REE distribution for the various complexes from the PAN and for some associated minerals. Data source as in Fig. 5 and Walter *et al.* (1995), Andrade (1998), Hornig-Kjarsgaard (1998), Smithies and Marsh (1998), Bühn *et al*. (2002). The Barra do Itapirapuã complex was subdivided into two diagrams: **a**, representing the whole population of the three main carbonatite-types, i.e. calcio-, magnesio- and ferrocarbonatites; **b**, showing the different types of carbonatite dykes (oldest, I, to youngest, IV). For comparison the patterns of the Cambro-Ordovician carbonatitic complex of Marinkas Quellen (Namibia; Smithies and Marsh, 1998) are also reported.

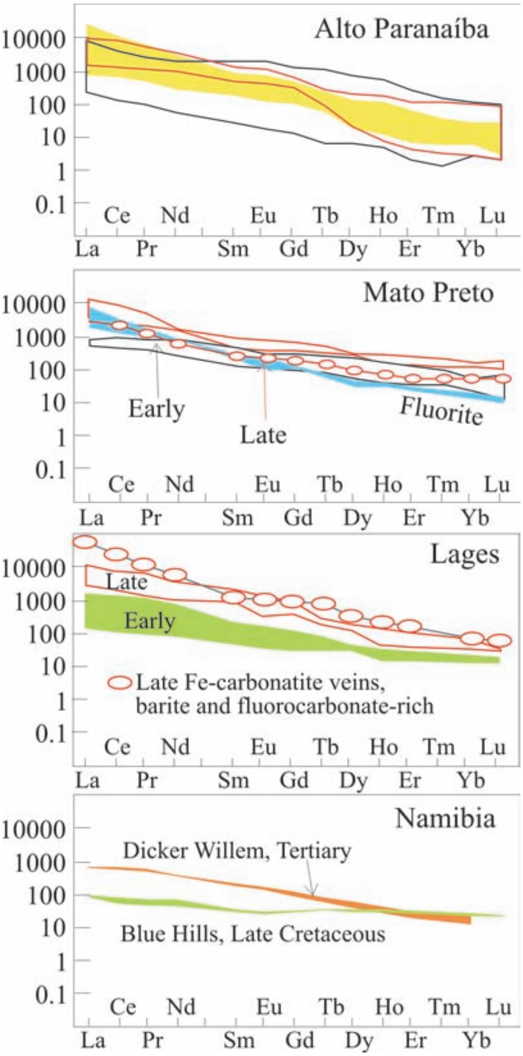


Fig. 8.B.– Upper Cretaceous and Paleogene: REE chondritic normalization of carbonatites (see Fig. 8A).

barite and fluorocarbonate-rich; the Namibian carbonatites display patterns driven by their bulk fluids (cf. Bühn *et al*., 2002).

2) Flat LREE, or patterns with a relative weakly decrease from La to Lu, as shown in the Jacupiranga (Ca-carbonatites), Juquiá (Mg- and Ca-calciocarbonatites), Anitápolis, Barra do Itapirapuã (late Ca-carbonatites) and Blue Hills complexes. In these occurrences the distribution seems to be related to the apatite composition (early-crystallized, apatite I; late-crystallized, apatite II).

3) Concave patterns with HREE plateau, and a steady increase from Dy to LREE, are found in the Valle-mí and Barra do Itapirapuã occurrences. In the latter, showing four distinct generations of carbonatitic dykes, the most "hydrothermally altered" dykes (field III of Fig. 8b; cf. Andrade *et al*., 1999a, b) contain the highest LREE concentrations as due to the presence of REE fluorocarbonates (Andrade, 1998).

Notably, the Valle-mí dykes cutting a Cambro-Ordovician carbonatic platform are REE enriched by a factor 1000 relative to the sedimentary carbonates (Valle-mí limestones of Fig. 8).

Concluding, the different behaviours of the early-crystallized carbonatites, that are believed to be "primary" carbonatitic liquids (Fig. 8), would reflect the chemical signatures of their parental melts (cf. primary Ca-carbonatites and Mg-carbonatites of the Jacupiranga and Juquiá complexes, respectively), as also outlined by Hornig-Kjasgaard (1998). The presence of late-crystallized Fe-carbonatites, variably enriched in fluorocarbonates, points to hydrothermal processes.

O-C ISOTOPES

The oxygen and carbon isotopes provide important informations about the evolution of a CO$_2$-rich magma, both in terms of "magmatic processes" (including partial melting, fractional crystallization and liquid immiscibility) and of "fluid processes" (interaction between rocks and fluids at different temperatures, including low-temperature weathering).

Carbonatite complexes display large compositional ranges of oxygen and carbon isotopes of the carbonate phases (Taylor *et al*., 1967; Pineau *et al*., 1973; Deines, 1989; Nelson *et al*., 1988; Censi *et al*., 1989; Santos and Clayton, 1995). In the PAN carbonatites, the δ^{18}O values cover a wide interval from about 5 to 25‰ *vs*. V-SMOW notation (Deines, 1989), but about 50% of the analyses fall into a narrow field between 6 and 10‰ . The variation of δ^{13}C is more restricted, i.e. 91% of δ^{13}C values fall in the range between -2‰ and -8‰ *vs*.

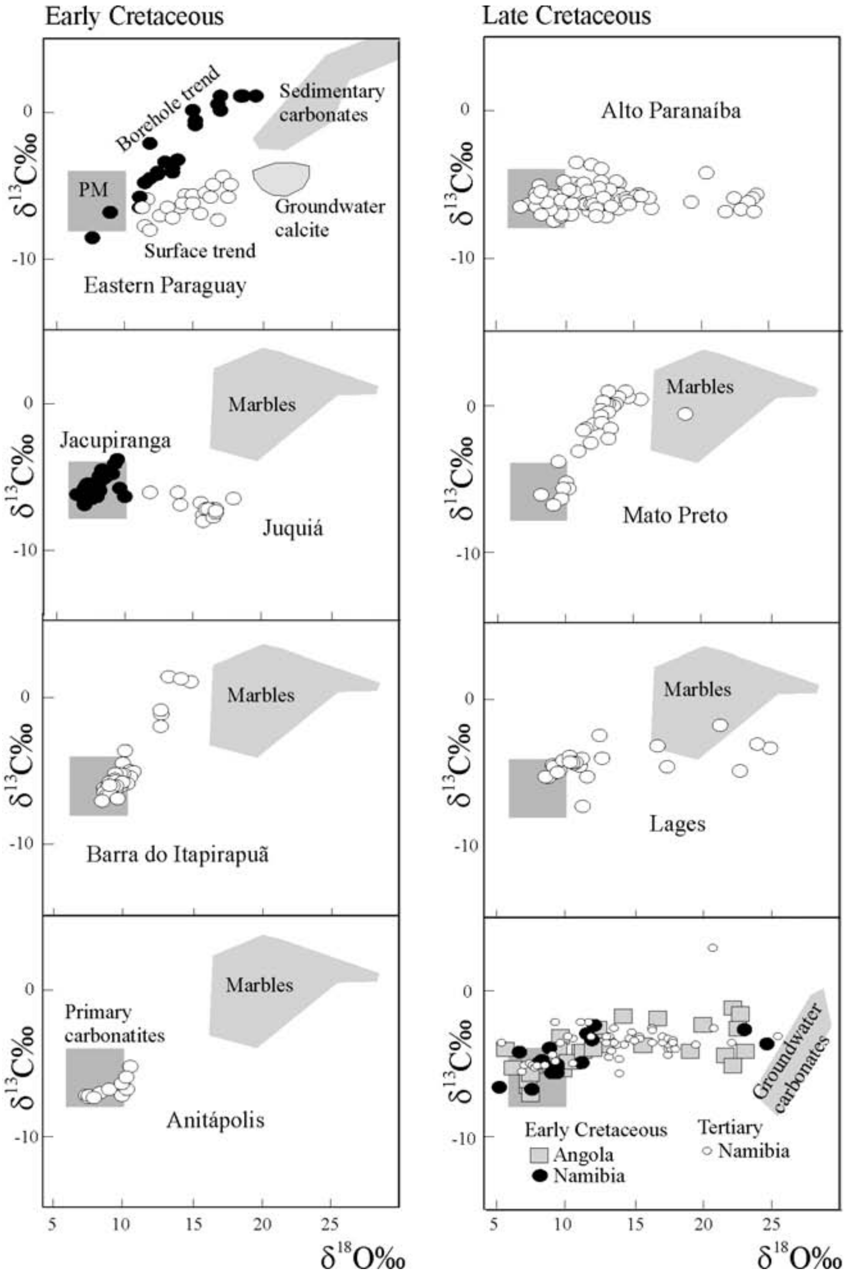


Fig. 9. – Plot of δ^{18}O‰ (V-SMOW) and δ^{13}C‰ (PDB-1) for the carbonatites from the PAN. For comparison the fields relative to sedimentary carbonates, groundwater calcite and marbles are also shown. Data sources: Scheibe and Formoso (1982), Censi *et al.* (1989), Robaina *et al.* (1991), Reid and Cooper (1992), Castorina *et al.* (1994, 1997), Huang *et al.* (1995), Santos and Clayton (1995), Walter *et al.* (1995), Horstmann and Verwoerd (1997), Speziale *et al.* (1997), Mello and Bettencourt (1998), Le Roex and Lanyon (1998), Alberti *et al.* (1999), Comin-Chiaramonti *et al.* (2002a, b and unpublished data), Ruberti *et al.* (2002). PC: "primary carbonatite box" (Taylor *et al.*, 1967; Keller and Hoefs, 1995; see text).

PDB-1 notation (Deines, 1989). Ranges of δ^{18}O and δ^{13}C between 6 and 10‰ and between -4 and -8‰, respectively, may reflect primary carbonatites (cf. Taylor *et al.*, 1967; Keller and Hoefs, 1995). Different emplacement levels (i.e. deep-seated, up to near surface, or near-surface environments; Deines and Gold, 1973), and superimposed primary and secondary processes are believed to play a role in the isotopic variations. These may be related to 1) isotopic compositional differences in the source, 2) fractionation processes during the magmatic evolution, 3) loss of fluids during pressure reduction at the time of emplacement, 4) crustal contamination, 5) post-magmatic and deuteric-groundwater processes. Most of the largest variations in heavy oxygen from carbonatites could be explained by the interaction with hydrothermal fluids, whereas the variations in heavy carbon may be associated with both primary (i.e. isotopic composition of parental magma) and secondary (i.e. hydrothermal re-equilibration) processes (Taylor *et al.*, 1967; Pineau *et al.*, 1973; Deines, 1989). Determining to what extent the oxygen and carbon isotopic variations in carbonatites are primary or secondary has important implications for evaluating the geochemical characteristics of the source regions. For example, the carbonatite complexes may be useful for deciphering the nature of the subcontinental mantle (cf. Castorina *et al.*, 1994, 1997).

In order to address some of these problems, this chapter developes a model of isotopic O-C fractionation relative to the PAN carbonatites substantially starting from three main considerations: 1) the carbonatitic complexes from the PAN are some of the the best known in the worldwide literature from the geological, petrological and geochemical point of view (Scheibe and Formoso, 1982; Nelson *et al.*, 1988; Morikiyo *et al.*, 1990; Bizzi *et al.*, 1994; Castorina *et al.*, 1994; 1997; Meyer *et al.*, 1994; Huang *et al.*, 1995; Santos and Clayton, 1995; Toyoda *et al.*, 1995; Walter *et al.*, 1995; Le Roex and Lanyon, 1998; Alberti *et al.*, 1999; Ruberti *et al.*, 2002; Comin-Chiaramonti *et al.*, 2002a, b);

2) over 500 O-C isotopic data and a large number of radiogenic isotope data are available for these occurrences (quoted references and unpublished data);

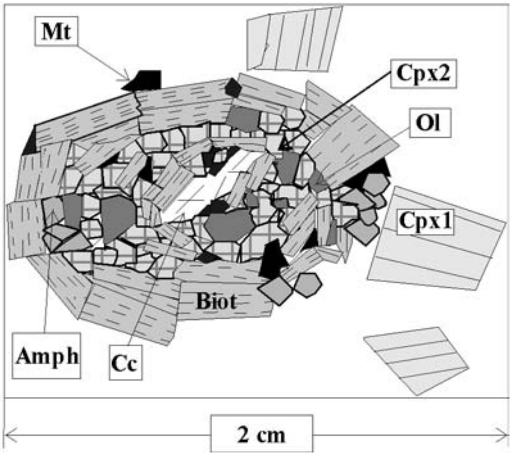


Fig. 10 – Sketch of an ocellus in ijolite from the Cerro Santa Elena alkaline complex (Early Cretaceous, Central Eastern Paraguay). Cpx1, clinopyroxene phenocrysts; Cpx2, clinopyroxene from ocelli; Mt, magnetite; Biot, biotite; Amph, amphibole; Cc, carbonate. Groundmass (white field), leucite + nepheline + alkali feldspar.

3) the interpretation of the isotopic data is controversial as to the role of primary processes versus crustal contamination.

δ^{18}O‰ (V-SMOW) and δ^{13}C‰ (PDB-1) data for the PAN carbonates in carbonatites display typical values of primary carbonatites, along with a number of samples with higher δ^{18}O and δ^{13}C values. Enrichments in heavy isotopes are interpreted in terms of heterogeneity in the mantle source (Nelson *et al.*, 1988), or contamination by host rocks (Santos and Clayton, 1995), or magmatic *vs.* hydrothermal evolution of the carbonatite at shallow level (Censi *et al.*, 1989; Castorina *et al.*, 1997; Speziale *et al.*, 1997). δ^{18}O and δ^{13}C for sedimentary carbonates and groundwater calcite are in the range 20 to 30‰ and 20 to 24‰, and -4 to +5‰ and -6 to -4‰, respectively. It should be noted that the marbles from southern Brazil show δ^{18}O and δ^{13}C ranges from 16 to 23‰ and from -4 to +3‰, respectively (Fig. 9).

Two main isotopic C-O variations for the Brazilian carbonatites are delineated: 1) a trend characterized by a shifting towards positive values for δ^{18}O and δ^{13}C increase (Jacupiranga, Barra do Itapirapuã, Anitápolis, Mato Preto and Lages), and 2) a trend of heavy oxygen increase at about constant δ^{13}C (Juquiá, Alto Paranaíba). The Angola and Namibia carbonatites display characteristics similar to the former trend up to $\delta^{18}O$ =15‰ and $\delta^{13}C$ =2‰. The trend 1) appears to be an extension of the Jacupiranga carbonatite, which is believed to have a primary signature (cf. Huang *et al*., 1995). Also in Eastern Paraguay two main linear trends are apparent, in this case the first being defined by carbonatitic samples and primary carbonate of silicate rocks from bore-holes (Castorina *et al*., 1997), while the latter represents carbonatitic specimens sampled near to or at the topographic surface, or carbonatitic lava flows. The two trends intercept at $\delta^{18}O$ = 7.5‰ and $\delta^{13}C$ = -8.5‰, similar to the values obtained for primary carbonate phases of an ijolite from Cañada (Central Paraguay Province), i.e. $\delta^{18}O$ = 6.9‰ and $\delta^{13}C$ = -8.5‰, respectively.

Additional data from silicates, oxides and carbonates associated in "ocelli" from the Cerro East of Santa Elena and Cerro Cañada (Fig. 10; Comin-Chiaramonti and Gomes, 2005 and unpuplished data) or silicate-oxide-carbonate phases in Jacupiranga carbonatite and apatite-calcite pairs in Jacupiranga and Juquiá carbonatites, respectively (Comin-Chiaramonti *et al*., 2005; Haynes *et al*., 2003), are reported in Table 3 along with calculated temperatures of isotopic equilibration.

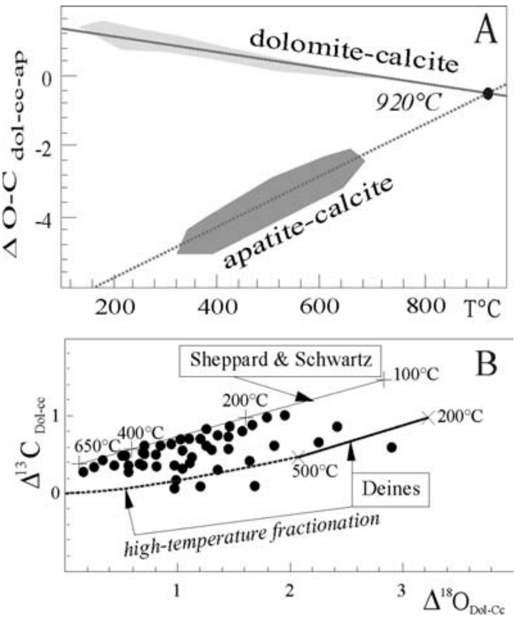


Fig. 11 – PAN carbonatites. **A**: Plots $\Delta^{18}O_{apatite\text{-}calcite}$ and $\Delta^{18}O\text{-}C_{dolomite\text{-}calcite}$ *vs*. temperatures (°C), according to Alberti *et al*., (1999). **B**: $\Delta^{18}O_{dolomite\text{-}calcite}$ *vs*. $\Delta^{13}C_{dolomite\text{-}calcite}$, for coexisting calcite – Fe-dolomite pairs. Equilibration lines, metamorphic and magmatic-hydrothermal, are from Sheppard and Schwartz (1970), Deines (1989) and Jenkin *et al*. (1991), respectively.

Isotope thermometry

The crystallization history of the carbonatites would involve sequential nucleation of calcite, apatite, oxides and silicates over an interval between the liquidus and solidus temperatures. Isotopic compositions for relatively slow diffusing silicates and oxides as clinopyroxene and magnetite would be established over the temperature interval of crystallization of these minerals. Relatively quickly diffusing phases as biotite and apatite may experience subsolidus exchange with carbonate phases below the crystallization temperatures. Notably, the oxygen isotopic fractionation between immiscible melts is unknown from direct experiments, but thought to be close to the fractionation between, for example, pyroxene and calcite. Thus, considering the "ocelli" of Fig. 10 (assumed as a closed microsystem) and the results of Table 3, liquidus and solidus temperatures may fall between 1200 and 800°C, respectively, and the lowest temperatures may be attributed to the cooling following the crystallization (cf. Haynes *et al*., 2003, for a discussion). Moreover, oxygen isotopes of the dolomite-calcite and apatite-calcite pairs are positively correlated and define two distinct temperature trends intercepting at about 920°C (Fig. 11a). It should be noted that this temperature is consistent with the range (i.e. 850-950°C) estimated for the exsolution of carbonatitic liquids from trachyphonolitic magmas by Comin-Chiaramonti *et al*. (1992, 1995), Castorina *et al*. (1994, 1996) and Halama *et al*. (2005). The differences in isotopic composition between the two coexisting carbonates, as well as the relationships that should be expected if coexisting carbonates were formed in isotopic equilibrium (Sheppard and Schwartz, 1970: metamorphic equilibrium; Gittings, 1979; Deines, 1989: fractionation processes at about 700°C), are shown in Fig. 11b. The data are not consistent with an isotopic equilibrium at magmatic temperatures between Fe-dolomite/ankerite and calcite, although a roughly

TABLE 3

Measured isotope compositions of silicates, oxides, apatite and calcite in some alkaline and alkaline-carbonatitic occurrences in the Brazilian platform (δ‰ notation: a, unpublished data; b, Comin-Chiaramonti *and* Gomes, *1996, 2005; c,* Haynes *et al., 2003). Abbreviations: Cpx, clinopyroxene; Ol, olivine; Mt, magnetite; Amph, amphibole; Biot, biotite; Cc, calcite; Ap, apatite. Calculated isotopic temperatures based on fractionation of oxygen isotopes in mineral pairs according to the general equation* $1000\ln\alpha = A(10^6T^{-2}) + B$*, where A and B are coefficients of the equation and T is the absolute temperature (cf.* Faure, *1986). Refs: (1)* Bottinga *and* Javoy *(1975); (2)* Matthews *et al. (1983); (3)* Chiba *et al. (1989); (4)* Fortier *and* Giletti *(1991); (5)* Fortier *and* Luttge *(1995)*

CERRO EAST of S. ELENA Ijolite	$\delta^{18}O$‰ (V-SMOW)	$\delta^{13}C$‰ (PDB-1)		A	B	Ref.	T°C
Clinopyroxene[a]	4.85		Cpx-Ol	1.24	0	1	852
Olivine[a]	3.87		Cpx-Mt	4.03	0	2	808
Magnetite[a]	1.40		Cpx-Amph	0.478	-0.30	2	746
Amphibole[a]	4.69		Cc-Cpx	2.37	0	3	908
Biotite[a]	4.62		Cc-Mt	5.91	0	3	798
Calcite[a]	6.55	-8.90	Average				822±61
			Biot-Amph	2.33	+0.60	1	799
			Cc-Biot	1.84	0	4	703
			Biot-Cpx	-0.57	+0.60	1	556
			Biot-Mt	-0.092	+0.30	2	510
			Average				642±133
CAÑADA							
Ijolite							
Clinopyroxene[b]	5.20		Cpx-Ol	1.24	0	1	1202
Olivine[b]	4.63		Cc-Cpx	2.37	0	3	908
Biotite[b]	5.54		Biot-Cpx	-0.57	+0.60	1	1208
Calcite[b]	6.90	-8.50	Cc-Biot	1.84	0	4	890
			Average				1052±180
JACUPIRANGA							
Carbonatite							
Clinopyroxene[a]	4.20		Cpx-Mt				858-890
Magnetite[c]	1.05		Cc-Mt	5.91	0	3	675-706
Magnetite[c]	1.23		Cc-Biot	1.84	0	4	436-458
Biotite[c]	3.96		Biot-Cpx	-0.57	+0.60	1	551
Calcite[c]	7.40	-6.58	Cc-Cpx	2.37	0	3	560-588
Calcite[c]	7.62	-6.68	Range				440-890
JUQUIA’							
Carbonatite							
Apatite[b]	14.11±1.87	-6.60 ± 0.39	Cc-Ap	1.60	0	5	863
Calcite[b]	15.35±2.34	-6.87 ± 0.81					

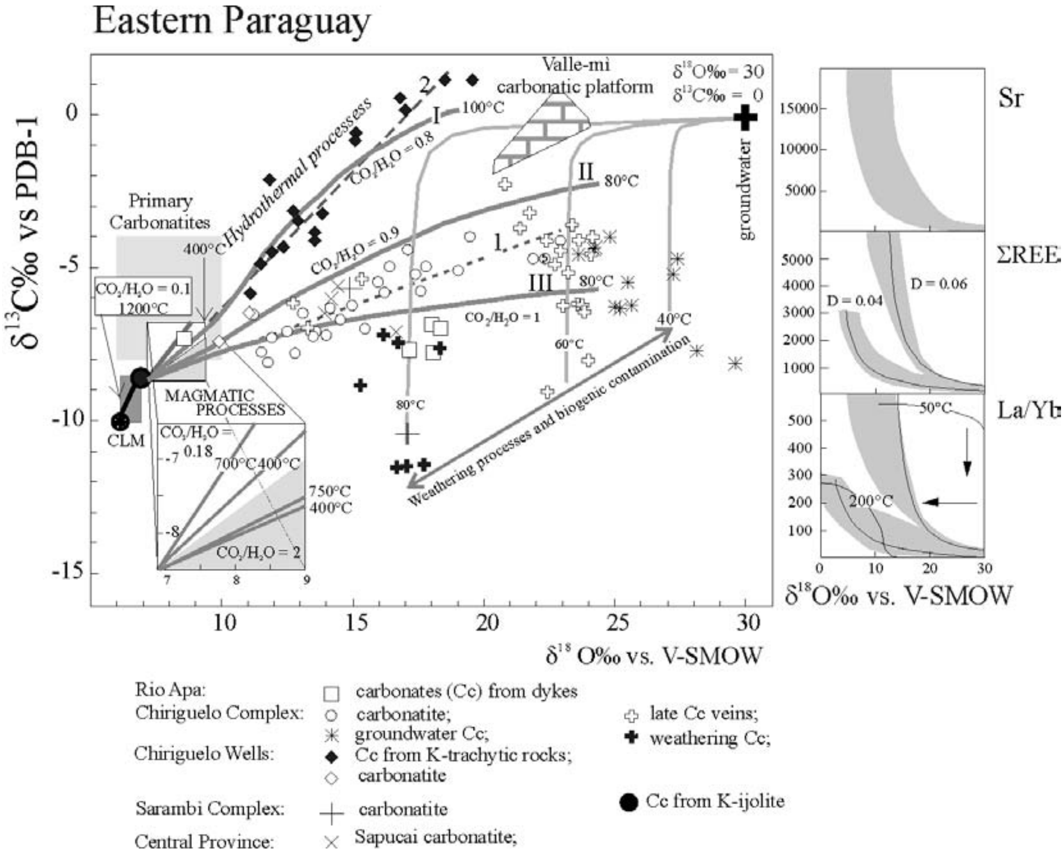


Fig. 12 – Plot of $\delta^{18}O$ *vs.* $\delta^{13}C$ for carbonates from Eastern Paraguay (Early Cretaceous, cf. Table 1) and evolution of the O-C isotope compositions. Magmatic conditions: 1200-400°C; hydrothermal environment: I up to 100°C, II and III up to 80°C (cf. Castorina *et al.*, 1997, and references therein; Comin-Chiaramonti *et al.*, 2005); low temperature conditions: biogenic component with pH ~ 5 and temperature = 40-80°C. Arbitrary starting compositions of groundwater: $\delta^{13}C$ = 30‰, $\delta^{18}O$ = 0 (cf. Taylor, 1978 and Usdowski, 1982). CLM: continental lithospheric mantle (Kyser, 1990). 1 and 2: regression lines from field and borehole samples, respectively. Primary carbonatites after Taylor *et al*. (1967) and Keller and Hoefs (1995). Data source for Valle-mí carbonate platform: Castorina *et al*. (1996). Inset: calculated paths of $\delta^{18}O$ *vs.* Sr, ΣREE (ppm) and La/Yb ratio in neo-carbonates (following fluid-rock interaction in a hydrothermal environment, after Castorina *et al.*, 1997) compared with the analytical results (grey fields). $D = Cwf/C^{(cc)}$ (see text). The temperature range is 200-50°C and the

equilibrium between the variables is apparent. This is suggestive of metasomatic changes at low temperatures, trending to hydrothermal conditions.

For the carbonatites from Eastern Paraguay, Castorina *et al*. (1997) and Speziale *et al*. (1997) developed a model in terms of C-O isotopic fractionation of carbonates for "magmatic differentiation processes" (i.e. liquid immiscibility and fractional crystallization), and "fluid processes" (i.e. interaction between rocks and fluids at different hydrothermal temperatures and CO_2/H_2O ratios). Based on the model, about 30% of the analyzed samples plot in the box of "magmatic processes" (i.e. temperatures in the range 900-400°C, $\delta^{18}O$ 5.5-9‰), while the other samples follow trends related to "fluid processes" (i.e. temperatures in the range 400-100°C) at CO_2/H_2O ratios roughly between 0.8 and 2 (Fig. 12).

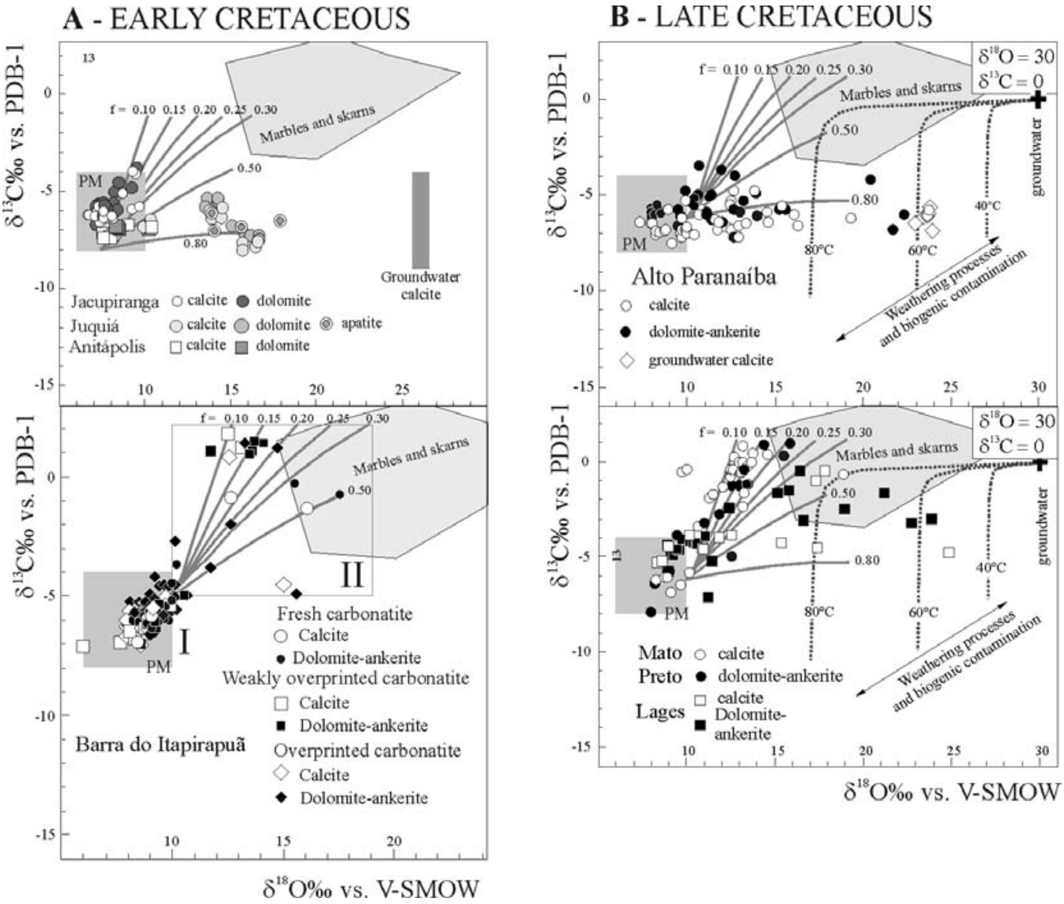


Fig. 13 – Plot of δ^{18}O *vs.* δ^{13}C for the carbonatite samples from Early Cretaceous (A: Jacupiranga, Juquiá, Anitápolis; Barra do Itapirapuã) and Late Cretaceous complexes (B: Alto Paranaíba, Mato Preto and Lages), compared with the results from the proposed model (f = [(A-b)/A] ; I, magmatic evolution; II, fluid-related hydrothermal recrystallization; see text). Data for Meso- and Neoproterozoic marbles and skarns after Mello and Bettencourt (1998); groundwater calcite, after Alcover *et*

The O-C isotopic variations out of the primary carbonatite box, the differences in isotopic composition between coexisting calcite and dolomite/ankerite, the petrographical and geochemical characteristics of the investigated carbonatites, as well as the relationships which would be expected if coexisting carbonates were formed in isotopic equilibrium (Sheppard and Schwarz, 1970: metamorphic equilibrium; Deines, 1989: fractionation processes at about 700°C), show that in general the data are not consistent with the existence of isotopic equilibrium at magmatic temperatures between coexisting Fe-dolomite/Mg-ankerite and calcite. This fact might indicate metasomatic changes at low temperatures, not far from hydrothermal conditions (i.e. ≤375°C at P=1 atm). Sub-solidus groundwater interaction might be an explanation for δ^{18}O values of carbonates higher than 12‰. The known carbonate-H_2O oxygen fractionation values (Deines, 1989) and the typically negative δ^{18}O values for meteoric groundwaters (Hoefs, 1987) require that any interaction with groundwater must have occurred at low temperatures (<250°C; Deines 1989; Speziale *et al.*, 1997). Alteration of Fe-dolomite/ Mg-ankerite by groundwater could be related to the low temperature hydrothermal cycle (112-150°C; Roedder, 1973) responsible for the formation of the fluorite deposits, as e.g. at Mato Preto and Barra do Itapirapuã where carbonatite emplacement and fluorite deposition are closely related (cf. Santos *et al.*, 1996). On the whole, the data support the hypothesis that isotopic re-equilibrations have occurred both during a magmatic stage, the subsequent hydrothermal stage, low-temperature and interaction with groundwaters, as inferred also by Andrade (1998), Bühn and Rankin (1999) and Bühn *et al.* (2002).

Magmatic processes

Assuming the K-ijolite from Cañada [Table 1; mg# = $Mg/(Mg+Fe^{2+})$ = 0.68; Comin-Chiaramonti and Gomes, 1996] as representative of an O-C near primary, mantle-derived melt (intercumulus calcite: $\delta^{18}O$ = 6.9‰ and $\delta^{13}C$ = -8.5‰, $\Delta^{18}O$ = 0.7, $\Delta^{13}C$ = 1.5; cf. Kyser, 1990), and that fractional crystallization+liquid immiscibility were responsible for variations not higher than 2‰ both for $\delta^{18}O$ and $\delta^{13}C$ (cf. Santos and Clayton, 1995), the expected values for $\delta^{18}O$ and $\delta^{13}C$ should not exceed 9‰ and -6.5‰, respectively.

The magmatic paths may be related to two evolutionary steps, i.e. a) partial melting of subcontinental lithospheric mantle $\delta^{18}O$ = 6.9‰ and $\delta^{13}C$ = -10‰; Kyser, 1990) and differentiation of the primary magmas to the values of the K-ijolite with CO_2/H_2O ratio ≈ 0.1, and b) evolution with a CO_2/H_2O≈0.2 (shallow intrusion), and with a CO_2/H_2O ≈ 2.0 (surface conditions), respectively (cf. Fig. 12).

Magmatic evolution

Hypothesis:

A) crystallization of the carbonatitic liquid under nearly closed-system conditions, in the temperature interval from 700°C to about 400°C (cf. Kuellmer *et al.*, 1966; Wyllie, 1989, and therein references), according to the reaction:

$CO_2+H_2O \rightarrow CO_3^{2-} + 2H^+$

The initial isotopic composition is assumed to have been $\delta^{18}O$ = 8.0‰ and $\delta^{13}C$ = -7.5‰;

B) only CO_2 and H_2O are the oxygen carriers, and CO_2 is the carbon carrier too;

C) mass balance equations for oxygen and carbon are:

[1] $2\mathbf{A}\delta^{18}O(CO_2)_i + \mathbf{B}\delta^{18}O(H_2O)_i = 2\mathbf{a}\delta^{18}O(CO_2) + 3\mathbf{b}\delta^{18}O(cc) + \mathbf{c}\delta^{18}O(H_2O)$ and:

[2] $\mathbf{A}\delta^{13}C(CO_2)_i = \mathbf{a}\delta^{13}C(CO_2) + \mathbf{b}\delta^{13}C(cc)$

where **a**, **b**, **c** are CO_2, CO_3^{2-} and H_2O molar concentrations in the fluid-mineral system at time "t". **A** and **B** are the initial CO_2 and H_2O molar concentrations, respectively, in the magmatic fluid at "i" before crystallization of the carbonate (cc) (i.e., fixed **A**, from CO_2/H_2O initial molar ratio, **B** is defined). From the equations the concentration values of the various components can be defined at each time "t" as **b=A-a** and **c=B-b**. It follows that the $\delta^{18}O$‰ and $\delta^{13}C$ compositions of the carbonate can be written in terms of **a**, **b** and **c**, as well as of the fractionation factors $\Delta^{18}O(CO_2\text{-}cc)$, $\Delta^{18}O(cc\text{-}H_2O)$ and $\Delta^{13}C(CO_2\text{-}cc)$ (O'Neil *et al.*, 1969; Bottinga and Javois, 1975), according to the equations:

[3] $\delta^{18}O(cc)=[2\mathbf{A}\delta^{18}O(CO_2)_i + \mathbf{B}\delta^{18}O(H_2O)_i - 2\mathbf{a}\Delta^{18}O(CO_2\text{-}cc)+\mathbf{c}\Delta^{18}O(cc\text{-}H_2O)] / [3\mathbf{b}+2\mathbf{a}+\mathbf{c}]$

[4] $\delta^{13}C(cc) =[\mathbf{A}\delta^{13}C(CO_2)_i -(\mathbf{A}\text{-}\mathbf{b})\Delta\ ^{13}C(CO^{13}\text{-}cc)] / \mathbf{A}$

Fluid-related hydrothermal recrystallization

After the crystallization of primary carbonates, recrystallization occurs by interactions with hydrothermal fluids at T <400°C. According to Zheng and Hoefs (1993), isotopic effects can be described by the equations:

[5] $\delta^{18}O(cc)= [\delta\ ^{18}O(H_2O)_i +\Delta^{18}O(cc\text{-}H_2O)] - \{[(\delta^{18}O(H_2O)_i +\Delta^{18}O(cc\text{-}H_2O)) - \delta\ ^{18}O(cc)_i]$
$\exp[-W/R(O)]\}$

[6] $\delta^{13}C(cc) = [\delta^{13}C(HCO_3)_i + \Delta^{13}C(cc\text{-}HCO_3)] -$

$- \{[(\delta^{13}C(HCO_3)_i + \Delta^{13}C(cc\text{-}HCO_3) - \delta^{13}C(cc)_i]$
$\exp[-W/R(C)\ \chi(HCO_3)]\}$

with $\delta^{18}O$ and $\delta^{13}C$, initial isotopic composition of the carbonate; $\delta^{13}C(HCO_3)_i$: initial carbon isotopic composition of HCO_3^- in the fluid; $\chi(HCO_3)$, HCO_3^- molar fraction in the fluid; $W/R(O)$ and $W/R(C)$, rock/water ratios in atom percentages of oxygen and carbon in the fluid and in the rock, and related to the calcite solubility product (Kps) that depends on temperature according to the equation (Jacobson and Langmuir, 1974):

[7] $\log Kps = -13.870 - 3059/T\ °K - 0.04035*T\ °K$

As well as W/R ratios, also HCO_3^- molar fraction in the fluid is a function of the temperature, due to the equilibria $CO_2 + H_2O \times H_2CO_3$ (K_0), $H_2CO_3 \times H^+ + HCO_3^-$ (K_1), $HCO_3^- \times H^+ + CO_3^{2-}$ (K_2) and related equilibrium constants:

[8] $\log K_0 = -14.0184 + 2385.73/T\ °K + 0.0152642*T\ °K$ (Harned and Davis, 1943)

[9] $\log K_1 = 14.8435 + 3404.71/T\ °K - 0.032786*T\ °K$ (Harned and Davis, 1943)

[10] $\log K_2 = 6.498 - 2902.39/T\ °K - 0.02379*T\ °K$ (Harned and Sholes, 1941)

where the carbon speciation depends on the temperature and the pH. The initial $\delta^{13}C(HCO_3^-)_i$ can be calculated from the isotopic fractionation factors relative to $\Delta^{13}C(CO_2 - HCO_3^-)$ (Ohmoto and Rye, 1979), for various $\delta^{13}C$ values calculated for CO_2 in the fluid.

In hydrothermal environments, the rock/water (R/W) interaction modifies also the trace element content. Following Nabelek (1987):

$[R/W(O)]^{-1} = 1/D\ \{\ln[Cw_i - C(cc)_i\, D)/(Cw_i - C(cc)_f D)]\}$,

where Cw_i, $C(cc)_i$ and $C(cc)_f$ are the concentrations of a trace element in the fluid (w) and in the carbonate (cc), at the beginning (i) and at the end (f) of the interaction, respectively.

D $[Cw_f / C(cc)_f]$ is the ratio between a trace element in the fluid (w_f) and in the carbonate (cc_f) at the end of the interaction. From calculated rock/fluid ratios (Castorina *et al.*, 1997; Speziale *et al.*, 1997), and for fixed Cw_i, $C(cc)_i$ and $C(cc)_f$ values, the variation of a trace element and $\delta^{18}O$ is calculated by the above equation. According to Nabelek's (1987) model, the highest concentration of trace elements like Sr and REE are associated with temperatures higher than 200°C.

The variation paths of $\delta^{18}O$ *vs.* Sr, ΣREE contents (ppm) and La/Yb ratio are represented in the inset of Fig. 12. In the model Cw_i is > $C(cc)_i$, i.e. "fenitizing" fluid enriched in incompatible elements with respect to the primary carbonates, according to the enrichment of halogens in the fluid and Sr, REE, and other elements as halogen-complexes (Wood, 1990; Bau, 1991; Rubin *et al.*, 1993; Bühn *et al.*, 2002). In hydrothermal environments, the speciation of halogen-, hydroxide- and carbonate-complexes is a pH function in the fluid (Haas *et al.*, 1995). According to the interaction model of fluid-carbonatite, the pH range compatible with the system will depend on the CO_2/H_2O ratio of the fluid, varying from 8.4-6.5 at 350°C to 5.3-3.4 at 50°C, respectively. It seems conceivable that a variable speciation in the hydrothermal fluid will start with REE strongly linked to hydroxides, and will stop with F-Cl-REE complexes at the end of the hydrothermal process (cf. Haas *et al.*, 1995).

Concluding, the magmatic paths may be related to two main evolutionary steps, i.e. (a) partial melting of subcontinental mantle ($\delta^{18}O = 6.9$ and $\delta^{13}C = -10$) and differentiation of the primary magmas to the values $\delta^{18}O = 7.5$ and $\delta^{13}C = -8.5$ with CO_2/H_2O ratio ≈ 0.1, and (b) evolution with $CO_2/H_2O \approx 0.2$ (shallow intrusion), and with $CO_2/H_2O \approx 2.0$ ("surface" conditions), respectively (Fig. 12). After the crystallization of primary carbonates, the residual fluids may migrate and fenitize the country rocks, as well as the previously crystallized carbonates. The variations of O-C isotopes of neo-carbonates, due to the interaction between fluid and primary carbonates, will follow paths which depend on temperature and rock/water ratio (Zheng and Hoefs, 1993). In Fig. 12 the variation paths relative to the O-C isotopic compositions during hydrothermal water-rock interaction are shown for a temperature range 400-100°C (curve I, $CO_2/H_2O = 0.8$), and 400-80°C (curves II and III, $CO_2/H_2O = 0.9$ and 1, respectively). Note that the low temperature carbonates plot between curves II and III, or below III. The lowest values of $\delta^{13}C$ (enrichment in ^{12}C) may be related to hydrolysis of biogenic CO_2. In this case, if the pH of the solutions is determined by humic acids, the ratio $[HCO_3^-]/[Ca^{++}]$ is a temperature function (Taylor, 1978; Usdowski, 1982). The major contribution of biogenic components, at temperatures between 40 and 80°C and for pH ≈ 5, is also shown in Fig. 12. The model may be extended to the all PAN occurrences (Fig. 13; Comin-Chiaramonti and Gomes, 2005).

Summary of the O-C results

The O-C isotope compositions of the carbonatites from the PAN appear in general to be in agreement essentially with a magmatic origin from hypercrytical fluids with $CO_2/H_2O \approx 0.2$-0.6 molar ratios and temperatures ranging from ≈800 to 400°C (i.e. orthomagmatic *vs.* pegmatitic-pneumatolititic environment; cf. Wyllie, 1989). However, significant variations in O-C isotope compositions are noticed in primary carbonates of alkaline rock-types and associated carbonatites and are mainly due to isotope exchange between carbonates and H_2O-CO_2 rich fluids; magmatic processes, i.e. fractional crystallization or liquid immiscibility, probably affect the $\delta^{18}O$ and $\delta^{13}C$ values by not more than 2‰. The isotope exchange model implies that the main isotopic variations occurred at low temperatures, in a hydrothermal environment, e.g. in the range 400-80°C, involving fluids with a CO_2/H_2O ratio ranging from 0.8 to 1.

Two main paths of $\delta^{18}O$ and $\delta^{13}C$ fractionation appear to have been generated by the emplacement levels (cf. Fig. 12). Weathering and groundwater fluids are locally important, as well as meteoric water, which yielded samples strongly enriched in light carbon due to contamination by a biogenic component.

The addition of carbonates from the country rocks to fresh and even to overprinted carbonatites, as suggested by Santos and Clayton (1995) (e.g. Açunguí Group: $\delta^{18}O = 25.0$ to 24.4‰ and $\delta^{13}C = 3.5$ to -8.6‰), appears to be unnecessary to explain the considerable enrichment in both heavy oxygen and carbon of some samples. This interpretation is also supported by the initial $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ isotope ratios of the carbonatites that mantain the same values of the associated alkaline rocks (see below).

SR-ND-PB ISOTOPES

Previously published data on the PAN magmatic rocks (tholeiitic, alkaline and carbonatitic samples) are diagrammatically summarized in the Figs. 14 to 16. Isotopic ratios included for comparison are those from the Brazilian offshore islands (Fodor *et al*., 1998) and of rock-types from Tristan da Cunha (Le Roex, 1985; Le Roex *et al*., 1990) and Trindade islands (Marques *et al*., 1999b; Siebel *et al*., 2000). DMM, HIMU, EMI and EMII are approximations of mantle end-members as in Bell and Tilton (2001), taken after Hart *et al*. (1986, 1992).

In particular, Tristan da Cunha and Trindade islands are believed to be mantle plumes related to the genesis of the Early Cretaceous tholeiitic and alkaline and Late Cretaceous alkaline magmatism from the PAN, respectively (e.g. O'Connor and Duncan, 1990; Müller *et al*., 1993; Gibson *et al*., 1995b, 1997, 1999; Van Decar *et al*., 1995; Milner and Le Roex, 1996; Thompson *et al*., 1998). It is worthy noting that Ernesto *et al*. (2002) provided petrological, geochemical and geophysical data that do not support a genesis of the Early Cretaceous Paraná magmatism closely related to the Tristan da Cunha plume.

Sr-Nd isotopes

The carbonatites from the PAN usually show the same isotopic $^{87}Sr/^{86}Sr$ (Sr_i) and $^{143}Nd/^{144}Nd$ (Nd_i) initial ratios of the associated alkaline rocks, even in the late stages of fluid-rock re-equilibration (i.e.

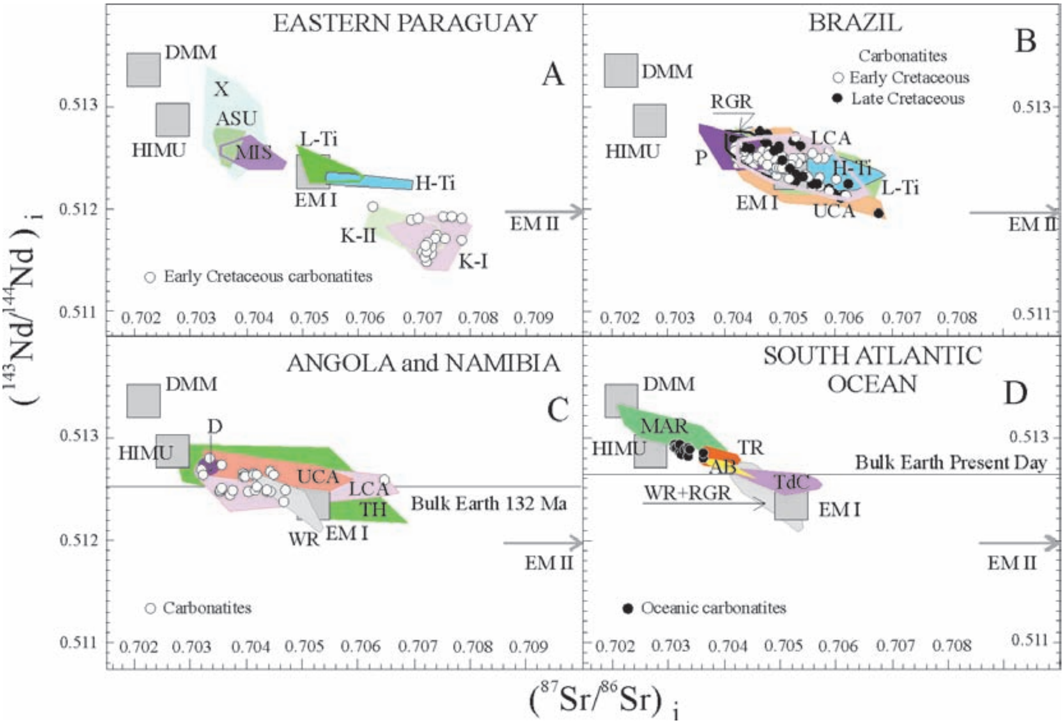


Fig. 14 – Initial ^{87}Sr/^{86}Sr (Sr$_i$) *vs.* initial ^{144}Nd/^{143}Nd (Nd$_i$) correlation diagrams. The represented basalts and andesi-basalts have MgO ≥ 4 wt% and Sr$_i$ ≤ 0.7065, i.e. those believed to be poorly crustally contaminated or uncontaminated (cf. Piccirillo and Melfi, 1988). **A**, **Paraguay**; *Early Cretaceous*: K-I and K- II, potassic alkaline complexes, pre- and post-tholeiites, respectively; H-Ti and L-Ti, high- and low-Ti tholeiitic basalts and andesi-basalts, respectively; *late Early Cretaceous*: MIS, sodic alkaline magmatism from Misiones Province; *Paleocene*: ASU, sodic alkaline magmatism from Asunción and X, associated mantle xenoliths. Data sources: Comin-Chiaramonti *et al.* (1991, 1995, 1996, 1997, 2001), Comin-Chiaramonti and Gomes (1996, 2005), Castorina *et al.* (1997), Marques *et al.* (1999a). **B**, **Brazil**: H-Ti, L-Ti and LCA, *Early Cretaceous* high- and low-Ti flood tholeiites and alkaline complexes, respectively; UCA and RGR, *Late Cretaceous* alkaline complexes and Rio Grande Rise rock-types; P, *Paleocene* alkaline complexes from Serra do Mar. Data sources: *Early Cretaceous*: Garda *et al.* (1995), Huang *et al.* (1995), Toyoda *et al.* (1995), Walter *et al.* (1995), Andrade *et al.* (1999a), Gibson *et al.* (1999), Marques *et al.* (1999a), Comin-Chiaramonti *et al.* (2002a, b), Ruberti *et al.* (2002); *Late Cretaceous*: Gamboa and Rabinowitz (1984), Bellieni *et al.* (1990), Bizzi *et al.* (1994, 1995), Meyer *et al.* (1994), Gibson *et al.* (1995, 1997, 1999), Toyoda *et al.* (1995), Carlson *et al.* (1996), Thompson *et al.* (1998); *Paleocene*: Thompson *et al.* (1998), Bennio *et al.* (2002). **C**, **Angola and Namibia**: TH and LCA, tholeiitic basalts and andesi-basalts, and alkaline complexes, *Early Cretaceous*; UCA, *Late Cretaceous* alkaline rock-types; WR, Walvis Ridge rock-types; D, Eocene Dicker Willem alkaline-carbonatitic complex. Data sources: Richardson *et al.* (1982), Milner and Le Roex (1996), Cooper and Reid (1998), Ewart *et al.* (1998), Le Roex and Lanyon (1998), Smithies and Marsh (1998), Gibson *et al.* (1999), Alberti *et al.* (1999), Harris *et al.* (1999), Kurzslaukis *et al.* (1999); Ewart *et al.* (2004). D, Atlantic Ocean: WR+RGR, *Walvis Ridge*, (Richardson *et al.*, 1982) and *Rio Grande Rise* (Gamboa and Rabinowitz, 1984); *Mid Atlantic Ridge* (MAR), Hamelin *et al.* (1984), Ito *et al.* (1987), Fontignie and Shilling (1997); *Tristan da Cunha* (*Inaccessible and Gough*), TdC, Le Roex (1985), Le Roex *et al.* (1990); *Trindade*, TR, Marques *et al.*, (1999b), Siebel *et al.* (2000); *Abrolhos*, Fodor *et al.* (1989). DMM, HIMU, EMI and EMII are approximations

hydrothermal environment), as shown by Castorina *et al.* (1997) and Speziale *et al.* (1997).

In *Eastern Paraguay*, at the westermost fringe of the PAN, typical specimens from the Early Cretaceous K-alkaline rocks (both pre- and post-Early Cretaceous tholeiitic magmatism) and associated carbonatites yielded Sr$_i$ and Nd$_i$ within the ranges 0.70612-0.70754 and 0.51154-0.51184, respectively (Fig. 14a). These are distinct from the values obtained for the Late Early Cretaceous to Paleocene Na-alkaline rocks, i.e: Sr_i = 0.70362-70524 and Nd_i = 0.51225-0.51277. In Fig. 14a, the carbonatites and associated K-alkaline rocks show higher Sr_i and lower Nd_i values compared to the Low Nd array of Hart *et al.* (1986); (cf. Comin-Chiaramonti *et al.*, 1995, 1997a), whereas the Na-alkaline rocks and associated mantle xenoliths (Comin-Chiaramonti *et al.*, 2001) approach the Bulk Earth (BE) values, varying from the depleted quadrant to the enriched one. The Paraguayan flood tholeiites, both low- and high-Ti variants, are intermediate between the K- and the Na-alkaline rocks. On the whole, a trend between HIMU and the potassic rocks is apparent ("Paraguay array" of Comin-Chiaramonti *et al.*, 1995).

In *Brazil* (Fig. 14b), the Early Cretaceous carbonatites have Sr_i between 0.70425 and 70595 and Nd_i between 0.51213 and 0.51280 (mean Sr_i = 0.70527±0.00034 and mean Nd_i = 0.51224±0.00011; Comin-Chiaramonti *et al.*, 1999). The Sr_i and Nd_i values of the Early Cretaceous Brazilian rocks are higher and lower, respectively, than those of the coeval rocks, both sodic and potassic, from Namibia (mean Sr_i = 0.70398±0.00046 and Nd_i = 0.51248±0.00002). The alkaline complexes from Uruguay (not shown in Fig. 14b), interpreted as crustally contaminated by Kirkstein *et al.* (2000), are distinct in having Sr_i 0.70560-0.70893 and Nd_i 0.51166-0.51195.

Late Cretaceous alkaline-carbonatitic complexes yielded the following Sri and Ndi mean values, respectively: Alto Paranaíba (APIP), Sr_i = 0.70527±0.00036 and Nd_i = 0.51224±0.00006 (Bizzi *et al.*, 1994; Gibson *et al.*, 1995a,b, and therein references); 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.* 2002b). It should be noted that the alkaline-carbonatite magmatism trends to the Sr_i and Nd_i field delineated by the Late Cretaceous tholeiites from Walvis Ridge and Rio Grande Rise (Richardson *et al.*, 1982; Gamboa and Rabinowitz, 1984).

In *Angola* and *Namibia*, at the easternmost fringe of the PAN, Sr_i and Nd_i values for most Early Cretaceous Angolan carbonatites (Fig. 14c) vary between 0.70321 and 0.70466, and between 0.51273 and 0.51237, respectively, showing on the whole depleted characteristics relative to BE (Alberti *et al.*, 1999). On the other hand, the Early Cretaceous carbonatites from Namibia have a similar Sr_i range (0.70351-0.70466), but almost constant Nd_i (0.51250 to 0.51244; Milner and Le Roex, 1996, and Le Roex and Lanyon, 1998). Mixing models (not shown) between the parental magmas and crustal components imply unrealistic (up to 50%) contaminant fractions (Alberti *et al.*, 1999). According to Bell and Blenkinsop (1989), Sr_i and Nd_i values from the Angola-Namibia carbonatites may result from either mixing between depleted and enriched mantle components, or from ancient mantle reservoirs.

The Angola-Namibia occurrences, as well as the East Africa Early Cretaceous carbonatites, show similar Sr_i and Nd_i values, whereas the Paleogene East Africa and Namibia analogues generally have lower Sr_i and higher Nd_i values (0.70307-0.70367 and 0.51268-0.51283, respectively; East Africa: Bell and Tilton, 2001; Namibia: Cooper and Reid, 1998). Additionally, the Cambro-Ordovician carbonatitic samples from Namibia (Marinkas Quellen: Smithies and Marsh, 1998) display Sr_i values similar to those of the Paleogene carbonatites of the country (0.70285-0.70415), but their Nd_i ratios are significatively lower than the other carbonatitic specimens (0.51218-0.51228). Notably, the Early Cretaceous Namibia flood tholeiites (Ewart *et al.*, 1998, 2004, and therein references) have Sr_i and Nd_i values mainly between 0.70419 and 0.70550 and 0.51237 and 0.51277, respectively.

Alkaline rocks, carbonatites and tholeiites from the Atlantic Ocean Islands and Mid Atlantic Ridge (MAR) define a linear array between DMM and EMI mantle components (Fig. 14d).

The alkaline and alkaline-carbonatite complexes from the PAN appear to follow a well defined array involving depleted and enriched mantle components. Both the Early and Late Cretaceous Brazilian alkaline-carbonatite complexes vary from close to the BE to the enriched quadrant, fitting the fields of the uncontaminated low-Ti and high-Ti tholeiites from Paraná-Angola-Namibia (Etendeka) Province (Comin-Chiaramonti *et al.*, 1997a, b, 1999; Castorina *et al.*, 1997; Speziale *et al.*, 1997;). The isotopically Sr-enriched rocks (e.g.

Eastern Paraguay alkaline-carbonatite complexes) are not easily explained by crustal contamination, since this requires high percentages of crustal components in a mixing process (up to 90%; cf. Comin-Chiaramonti *et al*., 1997a). On the contrary, we stress that oxygen isotope data suggest a primary, mantle-derived origin for silicate phases (cf. Comin-Chiaramonti *et al*., 1997a): whole-rock $\delta^{18}O$ data for the potassic rocks yielded +5.45 to +5.91‰ (V-SMOW), which are consistent with the values for its mineral constituents, clinopyroxene (+4.85 to +5.20‰) and biotite (+3.96 to +5.54‰) and the expected mantle values (cf. Table 3).

On the whole, the Na-rocks, close to the BE, and the K-rocks, typically high in radiogenic Sr worldwide, represent the range of virtually uncontaminated source magmas from the PAN. In summary, the data support the view that the carbonatites from Angola, mainly ranging in composition from a depleted component to the BE, and the carbonatites and alkaline rocks from Eastern Paraguay, represent the end-members of virtually uncontaminated source magmas from subcontinental mantle segments variously affected by "metasomatic l.s." processes (Comin-Chiaramonti *et al*., 1997a, 1999; Alberti *et al*., 1999).

Nd-Model Ages

Studies of the initial $^{143}Nd/^{144}Nd$ ratios from Precambrian terrains suggest that the mantle which supplied continental crust (as in the PAN; cf. Comin-Chiaramonti *et al*., 1999) has evolved since earliest time with Sm/Nd ratios higher than that of CHUR (chondritic uniform reservoir; cf. Faure, 1986; DePaolo, 1988). For this reason, model ages (TDM) for the continental crust are usually calculated with reference to the depleted mantle (DM: $^{143}Nd/^{144}Nd = 0.513151$, $^{147}Sm/^{144}Nd = 0.2188$) reservoir rather than CHUR (chondritic uniform reservoir; cf. DePaolo, 1988). The isotopic and/or temporal overlapping of different igneous rocks (i.e. high- and low-Ti tholeiites, K- and Na-alkaline rocks and carbonatites) cannot be accidental and points to sampling of ancient reservoirs formed at the same time from the same subcontinental upper mantle (SCUM). Whatever the implication, i.e. heterogeneity induced by recicled crust in the mantle (Menzies, 1990; Weaver, 1991) or occurrence of variably veined material in the SCUM (Meen *et al*., 1989), or both, it is clear that magma genesis involved ancient lithospheric mantle reset at well defined isotopic ranges.

Although the Nd model ages have little real meaning because do not reflect the true ages of the sources, being a function of the Sm/Nd fractionation during the melting and magma differentiation (cf. Arndt and Goldstein, 1987), however, the PAN magmatic rocks may provide a notional estimate of the time when a main metasomatic event may have occurred, as a function of the different geochemical behaviours in the different sectors of the PAN.

Utilizing the TDM(Nd) model ages on the whole Paraná-Angola-Namibia (Etendeka) system (cf. Comin-Chiaramonti and Gomes, 2005; Gastal *et al*., 2005), in general: 1) the PAN H-Ti flood tholeiites and dykes mainly range from 0.8 to 2.4 Ga; 2) the L-Ti flood tholeiites span between 0.8 and 2.7 Ga; 3) the pre-tholeiitic potassic rocks and

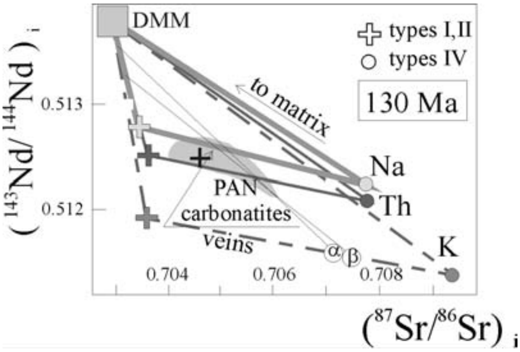


Fig. 15 – Calculated SCUM isotopic composition at 1.8 Ga ago, projected to 130 Ma. Parental melts with various Rb/Sr and Sm/Nd ratios are assumed for K , Na (potassic and sodic rocks from Paraguay, respectively; Comin-Chiaramonti *et al*., 1997a) and Th (PAN tholeiitic basalts; Piccirillo and Melfi, 1988). It is noted that the compositions of metasomatites formed from a single metasomatizing melt vary with the evolution of the melt. Consequently, the veins will define a trend of shallow slope, and mixing curves between vein and matrix will define an array towards the matrix (cf. α and β regression lines). Model DMM: Rb = 0, Sr = 0.133, Sm = 0.314, Nd = 0.628; present day Bulk Earth: $^{87}Sr/^{86}Sr = 0.70475$, $^{87}Rb/^{86}Sr = 0.0816$, $^{143}Nd/^{144}Nd = 0.512638$, $^{147}Sm/^{143}Nd = 0.1967$; $(Rb/Sr)_{diopside}:(Rb/Sr)_{melt} \approx 0.125$, $(Sm/Nd)_{diopside}:(Sm/Nd)_{melt} \approx 1.5$; K: Rb/Sr = 0.0957, Sm/Nd = 0.1344; Na: Rb/Sr = 0.0732, Sm/Nd = 0.2295; Th: Rb/Sr = 0.0733, Sm/Nd = 0.2082.

associated mainly range from 0.8 to 2.5 Ga; 4) Early Cretaceous syn- and post-tholeiitic alkaline and carbonatitic magmatism mainly range from 0.6 and 0.9 Ga; 5) Late Cretaceous alkaline rocks and carbonatites range between 0.6 and 0.9 Ga (cf. Alberti *et al.*, 1999; Comin-Chiaramonti and Gomes, 2005).

If the comparison is made between Eastern Paraguay (the westernmost side of the PAN) and the Angola-Namibia (easternmost side of the PAN) (Comin-Chiaramonti *et al.*, 2004; Comin-Chiaramonti and Gomes, 2005), the following are notable:

TDM of pre-tholeiitic K-alkaline rocks from Eastern Paraguay display two main peaks at 1.1 (Valle-mí, Apa Block) and at 1.4 Ga (Amambay), respectively. The post-tholeiitic K-alkaline complexes and dykes from ASU show a mean TDM of 1.7 Ga (Comin-Chiaramonti *et al.*, 1995). The high-Ti tholeiitic basalts have TDM ranging from 0.9 to 1.4 Ga. On the other hand, the low-Ti tholeiites exhibit model ages varying from 0.7 to 2.8 Ga, with TDM increasing from North to South and from West to East. Finally, the Na-alkaline rocks display TDM mean values of 0.6 Ga (Na-ASU, Paleocene) and 1.0 Ga (Misiones, Late Early Cretaceous), respectively (Comin-Chiaramonti *et al.*, 2007).

The Angolan carbonatites yielded TDM of 0.53±0.07 (0.41-0.61: Coola, Longonjo, Sulima and Bailundo) and of 0.88±0.15 Ga for Tchivira Bonga. The youngest model ages are similar to those of the Early Cretaceous alkaline outcrops from NW Namibia (i.e. 0.7±0.2; Milner and Le Roex, 1996, and Le Roex and Lanyon, 1998) and of the Brazilian Mato Preto carbonatite (Ponta Grossa Arch: 0.58±0.08; Ruberti *et al.*, 2005). The Tchivira Bonga carbonatites are instead similar to those of the Early Cretaceous carbonatites of Barra do Itapirapuã and Jacupiranga (Ponta Grossa Arch) and northwestern Namibia (0.7±0.2 Ga). The latter model ages virtually coincide with those of the Marinka Quellen complex (0.68±0.02 Ga) of Early Cambrian age (550 Ma; Smithies and Marsh, 1998).

Thus, the range of model ages in the PAN (cf. Fig. 9 of Alberti *et al.*, 1999) implies that the corresponding Paleozoic, Cretaceous and Paleogene magmas derived from subcontinental lithospheric mantle modified by metasomatic l.s. processes (asthenospheric components?) since Neoarchean to Neoproterozoic times (Comin-Chiaramonti *et al.*, 1997a, b, 1999, 2004, 2007).

It should be noted that: 1) the isotopic overlapping of different igneous rocks (i.e. tholeiites, alkalines and carbonatites) cannot be accidental and points to sampling of ancient reservoirs formed at the same time from the same subcontinental upper mantle; 2) whatever the implication, i.e. heterogeneity induced by recycled crust in the mantle (Menzies, 1990; Weaver, 1991) or occurrence of variably veined material in the subcontinental upper mantle, or both, Pb isotope data (see below) indicate a mantle source of ca. 1.8 Ga for the Paraná high-Ti tholeiites. Since much of the crust in southern Brazil appears to have been formed at ca. 2 Ga ago (Hawkesworth *et al.*, 1986), it follows that magma genesis involved ancient lithospheric mantle reset at well defined isotopic ranges. A veined lithospheric mantle (amphibole/phlogopite-carbonate-lherzolite and amphibole-lherzolite+CO_2-fluid type III and IV veins of Meen *et al.*, 1989) of Proterozoic age may well account for the magmatism of the PAN (Fig. 15).

Pb isotopes

The available data for the alkaline-carbonatite complexes and tholeiites from the Paraná-Angola-Namibia system (PAN) are illustrated in Figs. 16 and 17. These graphs show patterns compatible with mixing processes mainly involving HIMU and EMI end-members, and subordinaterly DMM and EMI, as well crustal l.s. components (e.g. EMII). It should be noted that all the rock-types lie, on the whole, well to the right of the 132 Ma geochron of Ewart *et al.* (2004), excepting for the post-tholeiitic K-rocks from Eastern Paraguay that plot close to the 132 Ma geochron. Moreover, the tholeiitic flood basalts from Eastern Paraguay and from Angola-Namibia, at the westernmost and easternmost sides of the PAN, respectively, delineate well distinct fields (Fig. 17).

MAR and OIB define trends between the DMM and HIMU mantle components. In comparison, the PAN carbonatites plot close to the EMI/DMM-HIMU mixing lines for both Pb-Sr and Pb-Nd (cf. Comin-Chiaramonti and Gomes, 2005). This observation seems to confirm the advantages in using carbonatite over silicate rocks, as indicators

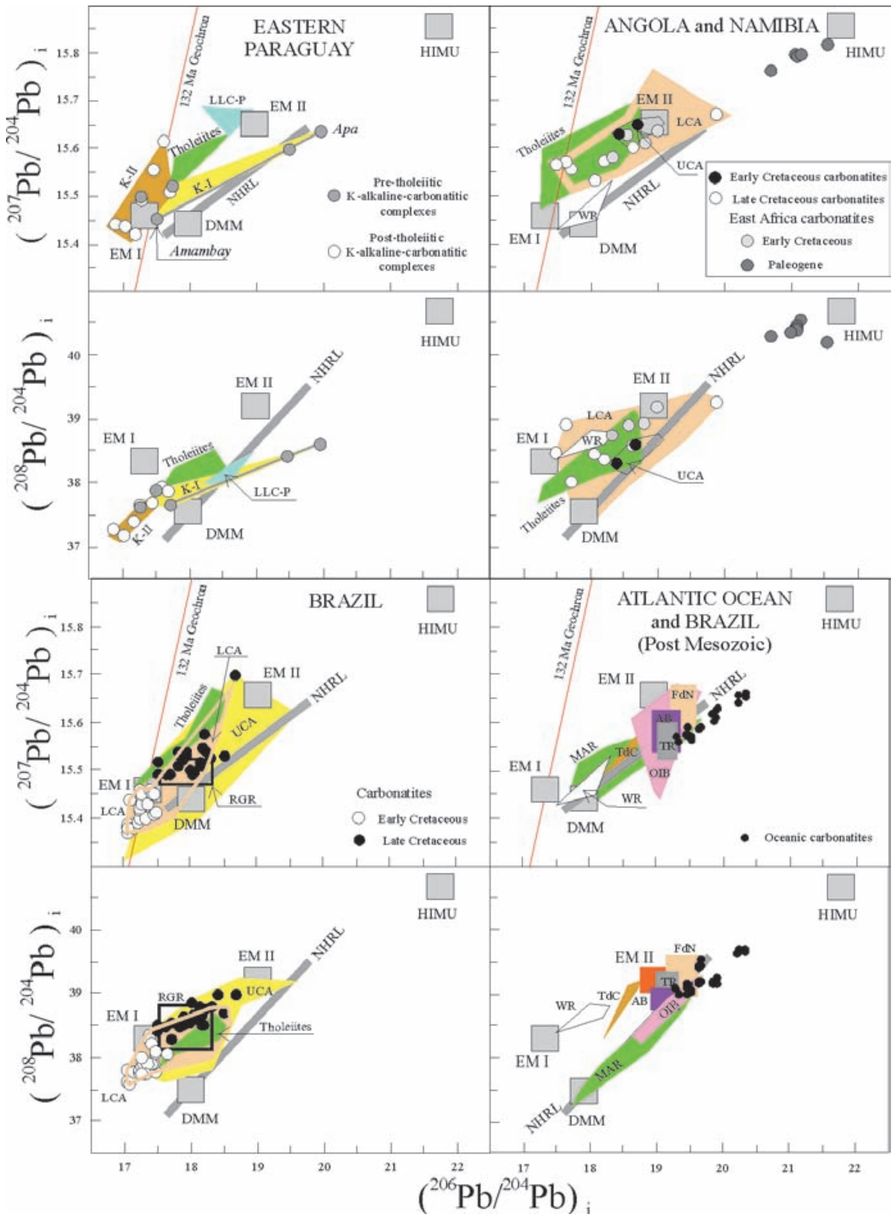
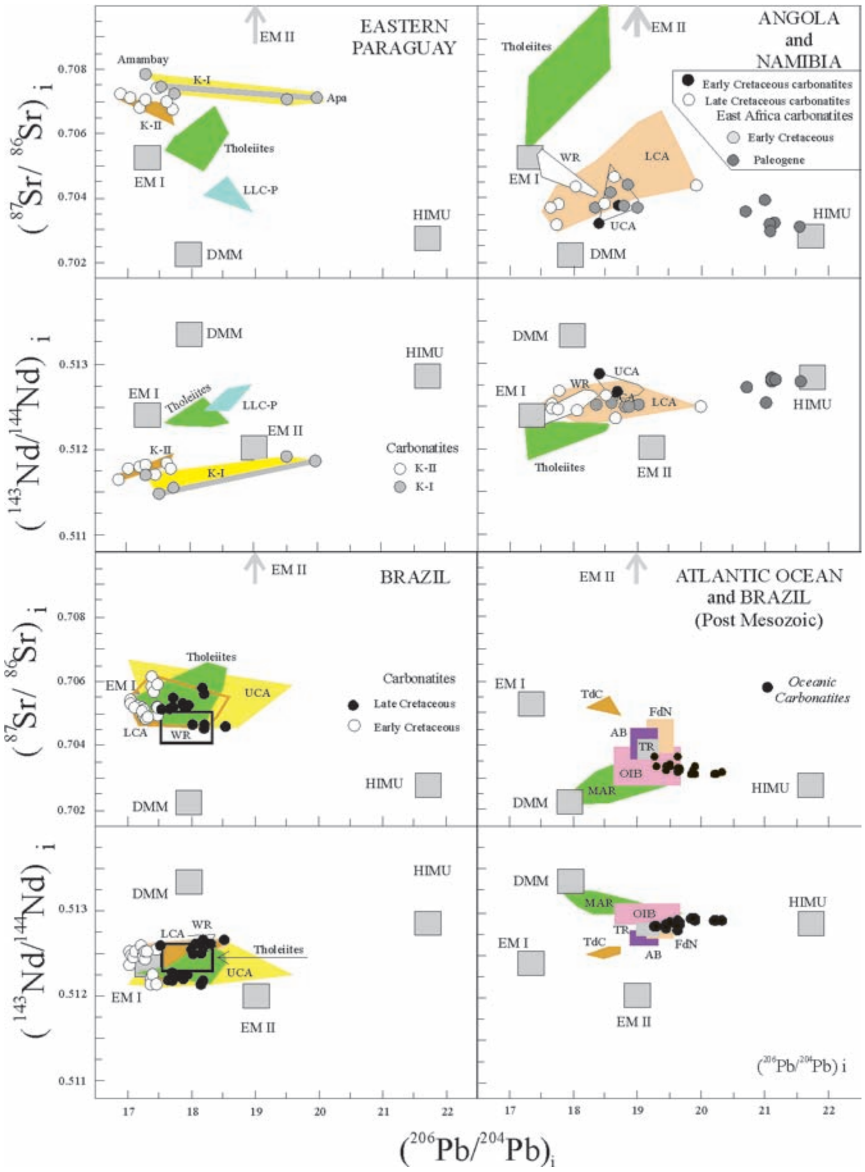


Fig. 16 – $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ *vs.* $^{206}Pb/^{204}Pb$ (initial ratios) for rock-types from the PAN. **Eastern Paraguay**: K-I and K-II potassic alkaline magmatism, pre- and post tholeiitic magmatism (Early Cretaceous), respectively; LLC-P, late Early Cretaceous and Paleocene magmatism; **Angola and Namibia**: LCA and UCA, Lower and Late Cretaceous alkaline magmatism, respectively; WR, Walvis Ridge; **Brazil**: LCA and UCA, Lower and Late Cretaceous alkaline magmatism, respectively; RGR, Rio Grande Rise; **Atlantic Ocean and Brazil**: MAR, median Atlantic Ridge; OIB, ocean island basalts; AB, Abrolhos islands; FdN, Fernando de Noronha (Gerlach *et al.*, 1987); TdC, Tristan da Cunha island (plus Inaccessible and Gough); TR, Trindade island; oceanic carbonatites, Hoernle *et al*. (2002). Other data sources, as in Fig. 14. NHRL (North



of mantle sources, because of their rapid ascent to the surface conditions, and buffering against crustal assimilation due to their high Sr, Nd and Pb concentrations in the liquids.

The results indicate that any model proposed for the evolution of the HIMU and EMI end-members must be consistent with the following constraints: 1) HIMU and EMI are not restricted to the oceanic environment; 2) end-members are variously associated in space as a function of the various protoliths; 3) mantle regions with HIMU and EMI isotope characteristics are capable of generating melts that may lead to the formation of a wide variety of silicate rocks, including melts enriched in CO_2 (cf. Bell, 1998); 4) Na-alkaline rock-types are systematically grouped together in fields well distinct in comparison with the K-alkaline fields in Paraguay, but falling in the fields of K-alkaline-carbonatite fields of the Angola-Namibia; 5) even the Na-alkaline rock-types from the Central Rift of sub-Andean system (Late Cretaceous; cf. Lucassen *et al*., 2002) fit the Triassic to Neogene analogues from Eastern Paraguay (cf. Comin-Chiaramonti *et al*., 2007).

Le Roex and Lanyon (1998), Thompson *et al*. (1998) and Ewart *et al*. (2004) postulated that the Early Cretaceous alkaline-carbonatitic and tholeiitic magmatism from northwestern Namibia and the Late Cretaceous alkaline and alkaline-carbonatitic magmatism from Alto Paranaíba-Serra do Mar (southern Brazil) would reflect the variable contributions of the asthenospheric mantle components related to the Tristan da Cunha and Trindade plumes, respectively. On the contrary, Comin-Chiaramonti *et al*. (1997a, 1999, 2004), Castorina *et al*. (1997), Alberti *et al*. (1999) suggested that the alkaline and alkaline-carbonatitic magmatism in the PAN originated from lithospheric mantle sources without appreciable participation of plume-derived materials. On the basis of geochemical and geophysical data, Ernesto *et al*. (2000, 2002) proposed that the genesis of the PAN tholeiites mainly reflects melting of heterogeneous subcontinental mantle reservoirs, and that the geochemical and isotopic signatures of the Walvis Ridge and Rio Grande Rise basalts may be explained by contamination through detached continental lithospheric mantle left behind during the continental break-up processes.

The Early Cretaceous alkaline magmatism from the PAN appears to be related with heterogeneous mantle sources spanning from time-integrated HIMU and enriched mantle components (Figs. 16 and 17). According to Tatsumi (2000), for example, relatively low $^{206}Pb/^{204}Pb$ and high $^{207}Pb/^{204}Pb$ compositions could be related to delamination of pyroxenite restites formed by anatexis of the initial basaltic crust in Archean-Proterozoic times. The PAN alkaline magmatism mimics, in terms of isotopic compositions, the coeval flood tholeiites. We stress that, in general, the enriched isotopic signatures of the Early Cretaceous alkaline magmatism decreases from West (Paraguay) to East (Brazil, SE-continental margin, and Angola and Namibia). A similar decreasing isotopic shift is also indicated for the age of the magmatism in Paraguay and Brazil, i.e. Early-Late Cretaceous to Paleogene. These results suggest that the PAN magmatism is related to both large- and small-scale heterogeneous mantle sources. Also it should be noted that the isotopic signature of the Trindade and Abrolhos islands (Figs. 16 and 17) is consistent with that of the alkaline-carbonatitic magmatism of Early Cretaceous age from Angola and Namibia, but quite different from that (EMI signature) of the Late Cretaceous-Paleocene analogues from the Alto Paranaíba (APIP), Ponta Grossa Arch, and Cabo Frio-Taiúva-Serra do Mar areas (Comin-Chiaramonti and Gomes, 2005). According to Thompson *et al*. (1998), the APIP would be the inland surface expression of the "dogleg" track left by the Trindade plume. However, in terms of Sr-Nd-Pb isotopes, the contribution, if any, of the asthenospheric components related to the that plume is difficult to account for.

Hawkesworth *et al*. (1986) interpreted the Etendeka (Namibia) high-TiO_2 (HTZ) basalts as resulting from melting of a Proterozoic lithospheric mantle, which, in the case of the Walvis Ridge (WR2 basalts, cf. Richardson *et al*., 1982), was floating inside the oceanic asthenosphere during the opening of the South Atlantic. Alternatively, the elemental and isotopic signature of the HTZ basalts could be related to contamination of oceanic mantle by ancient subcontinental lithospheric mantle. In summary, the isotopic signature of the Early and Late Cretaceous alkaline-carbonatite complexes from the PAN reflects ancient heterogeneities preserved in the subcontinental lithospheric mantle.

On the whole, all the data are consistent with a thermally-eroded metasomatic SCLM and/or delaminated lithospheric materials stored for long time, for example, towards the transition zone or deeper mantle in Archean-Proterozoic times. The important role of the Tristan plume claimed by Ewart *et al*. (2004) is not apparent. Therefore, we support Ernesto *et al*. (1999, 2002), that the hypothesis of asthenospheric plumes for the PAN magmatism is not compelling, except that it may represent a thermal perturbation, and as supported also by fluidodinamic of the Earth, where solid core, fluid core and mantle have three well different inertial momenta.

NOBLE GASES

The elemental and isotopic compositions of noble gas (i.e. He, Ne, Ar, Kr and Xe) trapped in mantle-derived samples, such in basalts erupted at mid-oceanic ridges (MORBs) and intraplate settings (e.g. Hawaii, Réunion, Samoa, Kerguelen), have provided unique and important constraints relating to the evolution of the Earth atmosphere. However, in contrast to the relatively abundant data obtained from samples derived from the suboceanic mantle, results from samples from the subcontinental environment are scarce. In particular, very few worldwide carbonatites were analyzed for noble gases. This section reports the main results and conclusions of Sasada *et al*. (1997). Regarding the PAN, only two calciocarbonatites were analyzed for forsterite and apatite, Jacupiranga (Early Cretaceous, 130 Ma; forsterite and apatite) and Tapira (Late Cretaceous, 79 Ma; apatite), respectively. Apatite data, obtained by stepwise heating of separated mineral (Table 4), are compared with those from other mantle-derived materials and with the Precambrian Borden Lake carbonatite from Canada (Tilton and Kwon, 1990), with an attempt to place geochemical constraints in the source regions.

Argon

The measured ^{38}Ar/^{36}Ar in the apatites fall near the atmospheric values of 0.1880, where the ^{40}Ar/^{36}Ar are highly variable from Tapira, near the field representing the Polynesian region, believed to represent an HIMU source (Hanyu *et al*., 1999), to about 6000 (Jacupiranga), and trending to a MORB source (Fig. 18a).

Xenon

Xenon isotope results (Fig. 18b) are indistinguishable from Hawayan and Australian mantle xenoliths (Rocholl *et al*., 1996, and Matsumoto *et al*., 1998, respectively). However, a sample from Jacupiranga, and above all an apatite from Borden Lake carbonatite, have high ^{134}Xe/^{130}Xe, believed to be related with the continental crust evolution (Staudacher and Allègre, 1982; Pepin, 1991).

Comparison between Xenon and Argon isotopes

Important features are the presence of excess ^{129}Xe relative to the air, and that the highest ^{129}Xe/^{130}Xe ratios (i.e. > 6.8) are comparable to other mantle-derived materials, such as MORBs and diamonds. However, the apatites from carbonatites display ^{40}Ar/^{39}Ar ratios lower than those from MORBs for similar ^{129}Xe/^{130}Xe ratios. Hence, the relatively low ^{40}Ar/^{39}Ar ratios in carbonatites (≈ 6000) suggest that the source for carbonatites is less degassed than the MORB source. Two mixing curves are shown in Fig. 18c, between A (air or sea water) and M components (M assumed as end- member for the MORB source; cf. popping rock 2ΠD43 of Staudacher *et al*., 1989), relative to R values of 1.7 and 16, respectively (cf. legend of Fig. 18a). An important observation is that the apatite samples from Jacupiranga and Borden Lake have similar Ar and Xe signatures, suggesting similar sources for the volatile elements (carbon and the noble gases). This is surprising, given that their Sr and Nd isotopic signatures reflect enriched (Jacupiranga) and depleted sources (Borden Lake; cf. Tilton and Kwon, 1990), respectively.

Krypton

Sasada *et al*. (1997) show that the samples have an excess of $^{131\text{-}136}$Xe and suggest that this excess is essentially of ^{238}U-fissiogenic origin. For all the samples displaying excess $^{131\text{-}136}$Xe, there is also an excess of ^{86}Kr, particularly for the apatite from Borden Lake. The same authors calculated the amount of in situ produced fissiogenic ^{136}Xe and ^{86}Kr in the apatite specimens comparing these values with the determined excess ^{136}Xe and ^{86}Kr: assuming that ^{130}Xe and ^{82}Kr have no fissiogenic components, the results show that only 50-80% of the observed excess ^{136}Xe and ^{86}Kr may be derived by an in situ fission of ^{238}U. The remaining excess is perhaps due to the implantation of fissiogenic Xe and Kr from relatively U-rich phases present in the carbonatite (e.g. pyrochlore).

Neon

The isotope composition of Ne is very different from that of the atmosphere with very low $(^{20}\text{Ne}/^{22}\text{Ne})_{\text{apatite}}/(^{20}\text{Ne}/^{22}\text{Ne})_{\text{air}}$ ratios (Fig. 18d), i.e. (total gas released) 0.51 to 0.43 (Tapira and Jacupiranga)

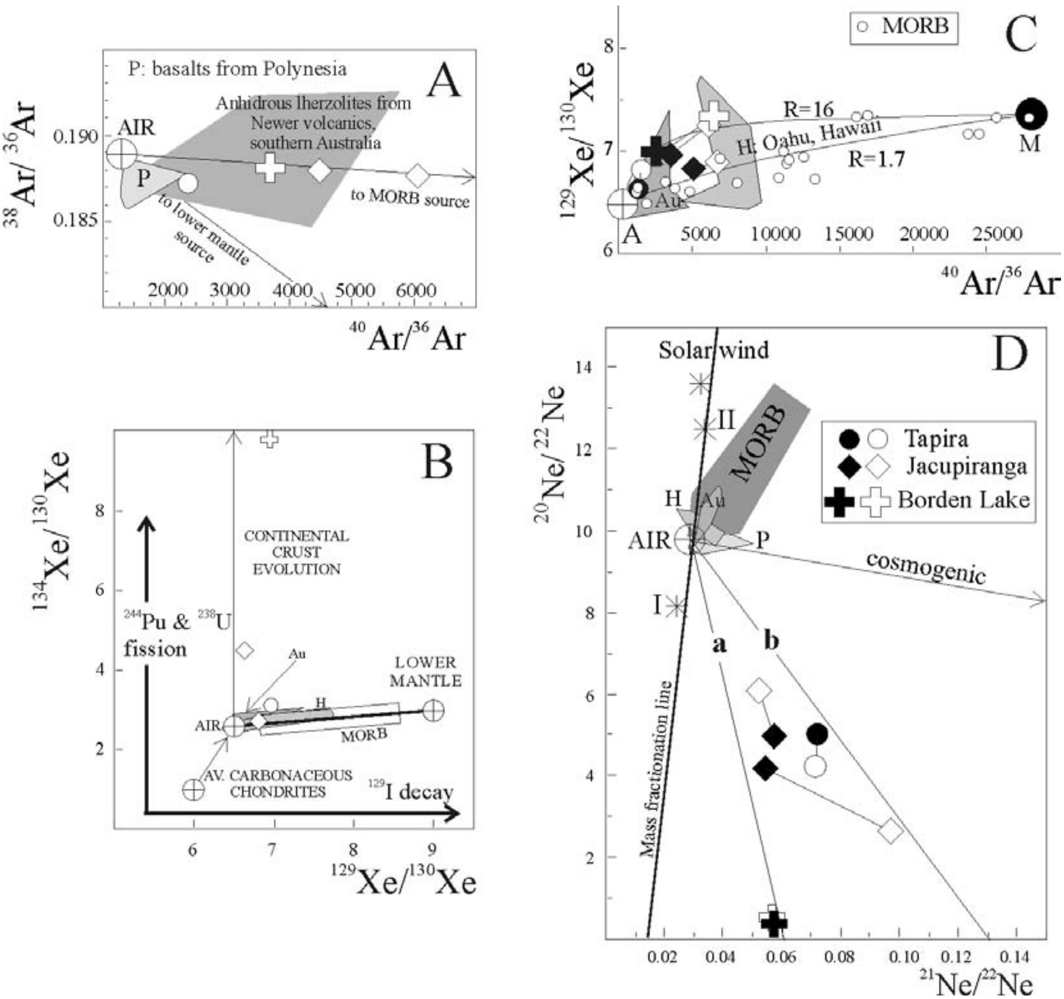


Fig.18 – A. $^{40}Ar/^{36}Ar$ *vs.* $^{38}Ar/^{36}Ar$ diagram. P, field representing basalts from Polynesian region (Hanyu *et al*., 1999). Lower mantle and MORB trends are inferred from Pepin, 1998 and Tolstikhin *et al*., 2002. B. $^{129}Xe/^{130}Xe$ *vs.* $^{134}Xe/^{130}Xe$. Au, field of the anhydrous lherzolites from the Newer volcanics, southern Australia (Matsumoto *et al*., 1998); H, field representing mantle xenoliths from Oahu, Hawaii (Rocholl *et al*., 1996). For the other trends, cf. Staudacher and Allègre, 1982 and Pepin, 1991. C. $^{40}Ar/^{36}Ar$ *vs.* $^{129}Xe/^{130}Xe$ plot for apatites from the Jacupiranga (130 Ma) and Tapira (79 Ma) Brazilian carbonatites. Full and open symbols, total and high temperatute (≥ 1700°C) gas released, respectively. Au, field of the anhydrous lherzolites from the Newer volcanics, southern Australia (Matsumoto *et al*., 1998). For comparison the data from the Precambrian Borden Lake carbonatite (Canada) and MORBs are shown (data sources: Sasada *et al*. , 1997 and references therein). Two mixing lines betwee M (assumed as MORB source with $^{40}Ar/^{36}Ar = 28000$ and $^{129}Xe/^{130}Xe = 7.35$) and A (air or air-saturated water, $^{40}Ar/^{36}Ar = 296$, $^{129}Xe/^{130}Xe = 6.48$) are shown for R=1.7 and R=16. The R parameter, relative to the $^{130}Xe/^{36}Ar$ ratio, is defined by:

$$R = (^{130}Xe/^{36}Ar)_M/(^{129}Xe/^{36}Ar)_{Air} = F(^{130}Xe)_{M/F}(^{130}Xe)_{Air}$$

where $F(^{130}Xe)_i$ is a fractionation factor (Ozima and Alexander, 1976), and it is calculated from:

$$F(^{130}Xe)_i = (^{130}Xe/^{36}Ar)_i/(^{129}Xe/^{36}Ar)_{Air}$$

D. Neon three isotope correlation diagram showing the plot of the analyzed samples relative to a mixing line between atmospheric and nucleogenic neon (cf; Kennedy *et al*., 1990). I and II represent the “planetary” neon compositions in some

TABLE 4

Selected isotopic compositions and concentrations of Xe, Ar, Kr, Ne and He in apatite from the Tapira and Jacupiranga carbonatites, (Brazil, Upper and Early Cretaceous, respectively; cf. Table 2) and Borden carbonatites (Canada, Precambrian), as in Sasada *et al. (1997). Errors are 1σ, including errors in mass spectrometry, variations in standard air calibration and 20% variations in hot blanks. Errors in He concentrations are about 10%*

	Jacupiranga 1	Jacupiranga 2	Tapira	Borden Lake		Jacupiranga 1	Jacupiranga 2	Tapira	Borden Lake
^{130}Xe (10^{-13} ccSPT/g)					^{129}Xe/^{130}Xe				
T°C									
600	0.82±0.08					6.580±0.177			
800	0.22±0.02			1.43±0.14		6.746±0.264			7.001±0.183
1200	0.15±0.01			0.65±0.06		6.684±0.246			6.643±0.156
1300		2.87±0.29					6.579±0.075		
1400	0.51±0.05	1.81±0.18	0.46±0.09	0.73±0.07		6.960±0.137	7.020±0.108	6.557±0.227	6.833±0.253
1500		0.35±0.04					7.185±0.267		
1600		0.52±0.06					7.105±0.322		
1700		0.24±0.03					0.876±0.670		
1800	1.42±0.14		0.18±0.04	0.54±0.05		7.236±0.123		6.784±0.299	7.325±0.263
Total	3.12±0.30	5.80±0.58	0.64±0.12	3.35±0.32		6.958±0.080	6.813±0.066	6.621±0.183	6.946±0.108
Air						6.489			
^{132}Xe/^{130}Xe					^{134}Xe/^{130}Xe				
T°C									
600	6.671±0.167					2.632±0.083			
800	6.560±0.247			6.819±0.155		2.683±0.113			2.879±0.072
1200	8.659±0.237			8.327±0.173		5.007±0.220			4.991±0.138
1300		6.582±0.068					2.605±0.049		
1400	7.346±0.119	6.857±0.094	7.017±0.182	15.88 ± 0.56		3.648±0.074	2.806±0.058	3.329±0.160	15.91 ± 0.58
1500		6.837±0.243					2.951±0.128		
1600		6.888±0.305					2.916±0.156		
1700		6.559±0.607					2.638±0.279		
1800	6.910±0.101		10.05±0.40	22.43 ± 0.73		3.019±0.054		7.417±0.368	25.69 ± 0.89
Total	6.977±0.071	6.710±0.060	7.873±0.172	11.60 ± 0.16		3.092±0.038	2.718±0.036	4.484±0.150	9.793±0?151
Air	6.600					2.562			

TABLE 4 — *continued...*

	Jacupiranga 1	Jacupiranga 2	Tapira	Borden Lake		Jacupiranga 1	Jacupiranga 2	Tapira	Borden Lake
$^{136}Xe/^{130}Xe$					$^{38}Ar/^{36}Ar$				
T°C									
600	2.263±0.063					0.188±0.002			
800	2.285±0.102			2.560±0.067		0.188±0.001			0.189±0.001
1200	4.802±0.224			5.087±0.120		0.189±0.005			0.187±0.002
1300		2.219±0.034					0.1882±0.0030		
1400	3.357±0.075	2.412±0.040	3.126±0.127	17.99 ± 0.66		0.187±0.001	0.189±0.011	0.189±0.027	0.187±0.003
1500		2.494±0.090					0.185±0.024		
1600		2.605±0.125					0.185±0.018		
1700									
1800	2.653±0.052	2.263±0.218	8.239±0.355	30.35 ± 1.06		0.188±0.002	0.185±0.045	0.188±0.046	0.187±0.008
Total	2.742±0.035	2.333±0.026	4.571±0.127	10.88 ± 0.17		0.188±0.001	0.188±0.004	0.187±0.024	0.188±0.001
Air	2.177					0.1880			
^{4}He (10^{-10} ccSPT/g)									
T°C									
600	0.95±0.08								
800	4.53±0.35			4.63±0.37					
1200	0.41±0.03			1.05±0.08					
1300		6.22±1.64							
1400	2.08±0.17	1.21±9.32	2.02±0.39	1.17±0.09					
1500		0.73±0.22							
1600		1.27±0.36							
1700									
1800	3.21±0.26	0.47±0.16	1.16±0.31	0.60±0.05					
Total	11.2 ± 0.9	9.90±2.61	3.18±0.57	7.45±0.59					
Air									
^{84}Kr (10^{-12} ccSPT/g)					$^{82}Kr/^{84}Kr$				
T°C									
600	3.38±0.44					0.205±0.004			
800	1.24±0.16			8.41±1.09		0.200±0.008			0.203±0.004
1200	0.62±0.08			4.33±0.56		0.201±0.003			0.204±0.003
1300		14.6 ± 1.3					0.204±0.002		
1400	4.46±0.57	8.89±0.79	4.48±0.55	2.99±0.39		0.202±0.003	0.203±0.002	0.203±0.004	0.206±0.004
1500		1.91±0.17					0.203±0.007		
1600		3.03±0.27					0.200±0.004		
1700		1.23±0.11					0.202±0.008		
1800	8.78±1.13		2.70±0.31	1.74±0.22		0.203±0.003		0.204±0.003	0.198±0.004
Total	18.5 ± 2.4	29.7 ± 2.6	7.54±0.86	17.5 ± 2.3		0.203±0.002	0.203±0.001	0.204±0.003	0.203±0.002
Air					0.2022				

TABLE 4
continued...

	Jacupiranga 1	Jacupiranga 2	Tapira	Borden Lake		Jacupiranga 1	Jacupiranga 2	Tapira	Borden Lake
$^{86}Kr/^{84}Kr$					$^{20}Ne/^{22}Xe$				
T°C									
600	0.305±0.004					10.03 ± 0.41			
800	0.304±0.008			0.307±0.005		2.52 ± 0.13			1.13 ± 0.02
1200	0.316±0.011			0.317±0.005		1.42 ± 0.03			0.142±0.002
1300		0.305±0.003					3.79 ± 0.10		
1400	0.309±0.005	0.307±0.003	0.308±0.005	0.3695±0.0060		6.54 ± 0.09	4.61 ± 0.18	5.27 ± 1.26	0.401±0.005
1500		0.306±0.010					5.57 ± 2.88		
1600		0.302±0.006					5.05 ± 0.91		
1700		0.304±0.013					2.63 ± 2.85		
1800	0.307±0.004		0.317±0.003	0.442±0.008		6.11 ± 0.11		4.21 ± 3.67	0.503±0.007
Total	0.307±0.002	0.305±.0.002	0.311±0.004	0.333±0.003		4.97 ± 0.05	4.18 ± 0.22	5.04 ± 1.28	0.384±0.003
Air	0.3052				9.80				
^{20}Ne (10^{-10} ccSPT/g)					$^{21}Ne/^{22}Xe$				
T°C									
600	0.422±0.047					0.0354±0.0086			
800	0.166±0.019			0.807±0.086		0.0680±0.0064			0.0546±0.0013
1200	0.284±0.031			0.438±0.047		0.0775±0.0028			0.0574±0.0012
1300		2.31 ± 0.25					0.0577±0.0027		
1400	1.55 ± 0.17	1.27± 0.14	1.29 ± 0.33	1.32 ± 0.14		0.463±0.0014	0.0458±0.0027	0.0721±0.0126	0.0581±0.0011
1500		0.431±0.176					0.0524±0.0294		
1600		0.151±0.029					0.0675±0.0157		
1700									
1800	1.51 ± 0.08	0.022±0.023	0.292±0.237	0.626±0.067		0.0523±0.0031	0.0967±0.0700	0.0716±0.0256	0.0567±0.0016
Total	3.93 ± 0.42	4.19 ± 0.48	1.58 ± 0.43	3.20 ± 0.34		0.0573±0.0016	0.0546±0.0031	0.0720±0.0114	0.0573±0.0010
Air					0.0029				

TABLE 4
continued...

	Jacupiranga 1	Jacupiranga 2	Tapira	Borden Lake
^{4}He (10^{-4} ccSPT/g)				
T°C				
600	0.070			
800	0.126			0.393
1200	0.015			0.361
1300		0.226		
1400	0.00007	0.00005	0.370	0.0014
1500		0.000002		
1600		0		
1700		0		
1800	0.000004		0.00002	0.00001
Total	0.213	0.226	0.370	0.775

and 0.04 (Borden Lake), and very high $(^{21}Ne/^{22}Ne)_{apatite}/(^{21}Ne/^{22}Ne)_{air}$ ratios, i.e. 18.8 to 24.8, for both Brazilian and Canadian carbonatites. The data can be explained by the mixing of atmospheric Ne and a component with a very low $^{20}Ne/^{22}Ne$ ratio of about 0 and a variable $^{21}Ne/^{22}Ne$ ratio between 0.06 and 0.13 (**a** and **b** lines of Fig. 18d).

The latter component has a very high excess of $^{21-22}Ne$ relative to air: such a component could have been produced by Wetherill (1954) reactions, i.e. $^{18}O(\alpha,n)^{21}Ne$ and $^{19}F(\alpha,n)^{22}Na(\beta^+)^{22}Ne$. The linear correlation inferred by Hünemohr (1989) between nucleogenic Ne isotopes and O/F ratio can be used to calculate the O/F ratio of the samples: a O/F atomic ratio of 11-29 appears to be reasonable, because such a low ratio is consistent with the high F concentration in the Brazilian carbonatites (cf. Comin-Chiaramonti and Gomes, 2005).

Helium

All the samples show high concentration of ^{4}He (21 to 78 x 10^{-6} ccSTP/g). ^{3}He was not detected in the analyzed apatites; only in an olivine from Jacupiranga $^3He/^4He$ is 2.72±1.12 x 10-6. The ^{4}He abundances can be attributed to the in situ decay of U and Th. Notably, the $^3He/^4He$ ratio from the Jacupiranga olivine is higher than the atmospheric ratio (Sasada *et al.*, 1997), providing evidence for a mantle source with excess ^{3}He.

In summary, the data relative to the noble gases suggest that 1) the apatites from the Tapira and Jacupiranga carbonatites are in the same range of possible mantle derived sources (e.g. HIMU and MORB; 2) sources are enriched in F; 3) the source of carbon of carbonatites is unlikely to be subduction-related carbon, and support the presented C-O fractionation model starting from mantle-derived sources.

NOTES ON THE RE-OS SYSTEM

Rhenium is a refractory metal with two isotopes, ^{185}Re and ^{187}Re, respectively. ^{187}Re (62% of total rhenium) undergoes β decay to ^{187}Os, a platinum group element with seven naturally occurring isotopes. Like Pb, osmium has siderophile-chalcophile affinities, but unlike the U-Pb system, Re and Os display marked fractionation between mantle and crustal systems. On the other hand, rhenium is a moderately incompatible element that is readily partitioned from the mantle into magmatic liquids, whereas osmium is a highly compatible element which is held in the mantle.

Although the carbonatites are not suitable materials for the analysis of platinum group elements, however, many carbonatitic complexes are strictly associated with mafic-ultramafic high-K rocks of kamafugitic and kimberlitic affinity,

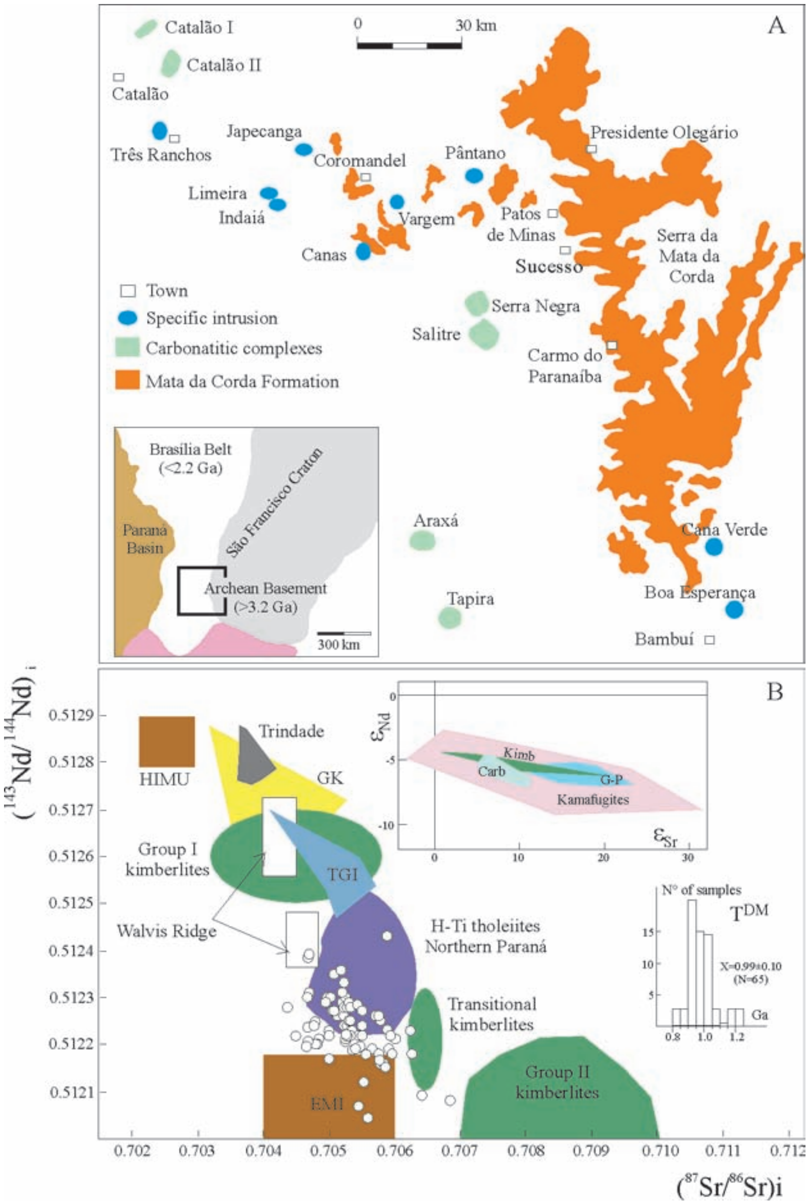


Fig.19 – **A.** Sketch-map showing the main alkaline occurrences in the Alto Paranaíba region (modified after Meyer *et al*., 1994). Inset: schematic structural map representing the main area of the APIP outcrops (cf. Fig. 1).
B. ^{87}Sr/^{86}Sr *vs.* ^{144}Nd/^{143}Nd initial ratios for rock types from Alto Paranaíba. GK, Gibeon kimberlites (Davies *et al*., 2001); TGI, Tristan da Cunha, Inaccessibile and Gough islands (Le Roex, 1985; Le Roex *et al*., 1990). Other data sources: Bellieni *et al*. (1990), Bizzi *et al*. (1993, 1995), Meyer *et al.* (1994), Gibson *et al*. (1995a, b, 1997, 1999), Toyoda *et al*. (1995), Carlson *et al*. (1996); Trindade island, Marques *et al*., (1999b), Siebel *et al.* (2000); kimberlites, Smith (1983), Clark *et al*. (1991). **Insets**: time integrated notations, ε_{Sr} *vs.* ε_{Nd} correlation diagrams; Nd model ages (TDM) for Alto Paranaíba alkaline and carbonatite rocks [TDM values: calculation of model dates relative to a depleted reservoir, ^{143}Nd/^{144}Nd = 0.513114 and ^{147}Sm/^{144}Nd = 0.222; cf. Faure, 1986].

TABLE 5

Rb, Sr, Sm, Nd, Re and Os concentrations and isotopic initial ratios relative to selected samples from the Alto Paranaíba Igneous Province and one sample from Lages (notional ages 85 and 75 Ma, respectively). Data sources, Carlson *et al., 1996;* Bizzi *and* Araujo, *2005 and references therein*

	Limeira		Tres Ranchos		Pantano	Salitre			Santa Rosa	Verdiana	Canas
Kimberlites									Glimmerites		
ppm											
Rb	114	94	48	38	183	124	21.1	132	333	1161	144
Sr	2540	2215	1811	2927	2029	2267	1450	1070	1668	1771	1632
Sm	30.3	42	23.5	43	24.9	25.6	20.0	42.9	22	22	22.2
Nd	224.6	312	208.4	348	195.1	186	116.5	324.8	160	162	165
Pb	11	15	19.5	13	9.2	12	13	13.2	23.2	16.4	17.4
U	4	28	7.1	8	6.4	18	8.2	11.4	4.3	4.8	4.3
Th	23	41	29.6	42	25.4	40	25	30.9	18.2	20.9	20.9
ppb											
Re	0.418	0.315	1.992	0.2173	0.2170	0.3347	0.7192	1.3135	1.101	6.33	2.23
Os	1.612	1.221	1.982	1.2624	0.8080	1.1646	1.9271	1.4295	0.518	0.582	0.609
^{187}Re/^{188}Os	1.334	1.2313	4.845	0.6227	1.2960	1.3344	1.8619	4.4295	10.46	54.14	18.07
initial ratios											
^{87}Sr/^{86}Sr	0.70528	0.70543	0.70493	0.70514	0.70532	0.70540	0.70541	0.70505	0.70564	0.70624	0.70595
^{143}Nd/^{144}Nd	0.51225	0.51222	0.51228	0.151227	0.51225	0.51220	0.51230	0.51223	0.51219	0.51218	0.51218
^{206}Pb/^{204}Pb	17.84	21.48	18.67	18.11	17.84	21.44	17.86	19.35	17.22	17.24	17.24
^{207}Pb/^{204}Pb	15.49	15.66	15.53	15.51	15.47	15.74	15.61	15.58	15.39	15.41	15.40
^{208}Pb/^{204}Pb	38.25	39.73	38.18	38.61	39.21	39.67	38.92	38.40	37.78	37.76	37.81
^{187}Os/^{188}Os	0.113338	0.12679	0.12138	0.11986	0.12618	0.12861	0.11721	0.12456	0.27471	0.30452	0.26677

e.g. in the Rio Verde-Iporá (Goiás), Alto Paranaíba (Minas Gerais and Lages Santa Catarina) areas (Late Cretaceous magmatism; cf. Table 1). In particular, Bizzi *et al*. (1994, 1995), Carslon *et al*. (1996), Araújo *et al*. (2001) and Bizzi and Araújo (2005) provided some Re, Os and platinoids data for rocks from the Alto Paranaíba Igneous Province (APIP, Fig. 19a; cf. also Figs. 1 and 2a), with the aim to develop a petrogenetic model regarding the kamafugitic-kimberlitic magmatism and associated carbonatites. For this purpose, this section present a brief review for the main APIP rock-types, i.e. kimberlites, kamafugites, phlogopite-rich peridotites, glimmerites and associated carbonatites, in order to compare the Sm-Nd-Pb isotope results with the available Re-Os data.

Representative isotope results are listed in Table 5. In terms of initial ratios ^{87}Sr/^{86}Sr *vs.* ^{143}Nd/^{144}Nd (Fig. 19b), the APIP rock-types straddle the field of the high-Ti tholeiites of the Northern Paraná Basin (Early Cretaceous) and are intermediate between the Kimberlites I (and the 72 Ma kimberlites of Gibeon, Namibia; Davies *et al*., 2001) and the Kimberlites II of Smith (1983) and Clark *et al*. (1991).

In general, the high concentrations of the most IE in all the APIP alkaline rocks (Gomes and

Table 5
continued...

	Limeira		Tres Ranchos		Presidente Olegario				Lages
Kamafugites									
ppm									
Rb	176	153	219	294	176	124	106	120	77
Sr	2490	1162	1570	2995	1815	1823	1907	1234	1881
Sm	30.7	20.3	23.0	33.5	29.8	28.1	21.8	16	9.7
Nd	226.1	148.3	177.8	259	231	213	147	117	63
Pb	31.4	13	15	14	17.6	14.8	9.3	7.6	20.3
U	5.3	5.2	5.0	5.0	6.4	5.6	3.3	3.6	6.39
Th	26.1	25	20	21	34.7	27.7	14.6	15.0	18.3
ppb									
Re	0.057	0.3845	0.0438	0.0645	0.131	0.068	0.421	0.061	0.170
Os	0.404	0.7001	0.1229	0.8434	0.353	0.381	1.205	1.760	0.278
^{187}Re/^{188}Os	0.681	2.6487	1.7217	0.3569	1.794	0.855	1.681	0.167	2.996
initial ratios									
^{87}Sr/^{86}Sr	0.70582	0.70506	0.70507	0.70686	0.70591	0.70549	0.70582	0.70524	0.70519
^{143}Nd/^{144}Nd	0.51223	0.51235	0.51225	0.51209	0.51223	0.51227	0.51223	0.51230	0.51236
^{206}Pb/^{204}Pb	18.01	18.28	18.03	17.60	17.79	17.39	18.01	17.39	18.04
^{207}Pb/^{204}Pb	15.55	15.51	15.51	15.51	15.46	15.37	15.55	15.39	15.52
^{208}Pb/^{204}Pb	38.42	38.61	38.63	38.33	37.91	37.76	38.42	37.82	38.30
^{187}Os/^{188}Os	0.15195	0.12679	0.13313	0.12743	0.15440	0.12485	0.11451	0.14217	0.1289

Comin-Chiaramonti, 2005) suggest that the effects of crustal contamination on the Sr-Nd isotopic system were negligible and that the parental magma compositions are more likely attributable to mantle-enriched sources related to variable degrees of metasomatism. The data, time-integrated ε-notations, are widespread mainly in the enriched quadrant, with εSr and εNd extending in the ranges from -4 to 31 and from -2.5 to -9, respectively. The field relative to the kamafugitic rock-types contains all the other lithologies (inset of Fig. 19b), i.e. kimberlites, glimmerites, mica peridotites and carbonatites. The constant behaviour of the Sm/Nd ratio in the APIP rocks (^{147}Sm/^{144}Nd = 0.085±0.009; Comin-Chiaramonti and Gomes, 2005) allows to consider the Nd model age as indicative of the main metasomatic event affecting the lithosphere beneath the Alto Paranaíba region. The model ages (calculation with respect to the depleted mantle, TDM) for the whole APIP population (65 samples; cf. inset of Fig. 19b) fit 0.99±0.10 Ga.

The initial isotopic compositions displayed on ^{206}Pb/^{204}Pb *vs.* ^{207}Pb/^{204}Pb and ^{206}Pb/^{204}Pb *vs.* ^{208}Pb/^{204}Pb diagrams (Fig. 20) define essential linear main arrays that are subparallel to both the Early Cretaceous tholeiites from the Paraná Basin (Marques *et al.*, 1999a) and the Northern Hemisphere Reference Line (NHRL of Hart, 1984). A possible explanation for the Pb isotope behaviour is that the data represent a secondary isochron, giving an apparent age of 2.5 Ga, suggesting an Archean-Proterozoic mantle source, as already pointed out by Hawkesworth *et al.* (1986) for the tholeiites from the Paraná Basin. Alternatively, the observed trends are due to the mixing of different mantle components. Notably, some kimberlites appear approaching the HIMU mantle component.

On the whole, the APIP alkaline rock-types and associated carbonatites plot in the field of the Brazilian Late Cretaceous alkaline-carbonatite complexes. The latter contains the fields of all the magmatic rock-types from the Paraná Basin (i.e. Early Cretaceous flood tholeiites and alkaline-carbonatite complexes; cf. Fig. 14). In particular, the APIP extends from EMI and DMM to EMII mantle components, overlapping the field of the Tristan da Cunha volcanics (Fig. 19). Considering the diagrams ^{206}Pb/^{207}Pb *vs.* ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}

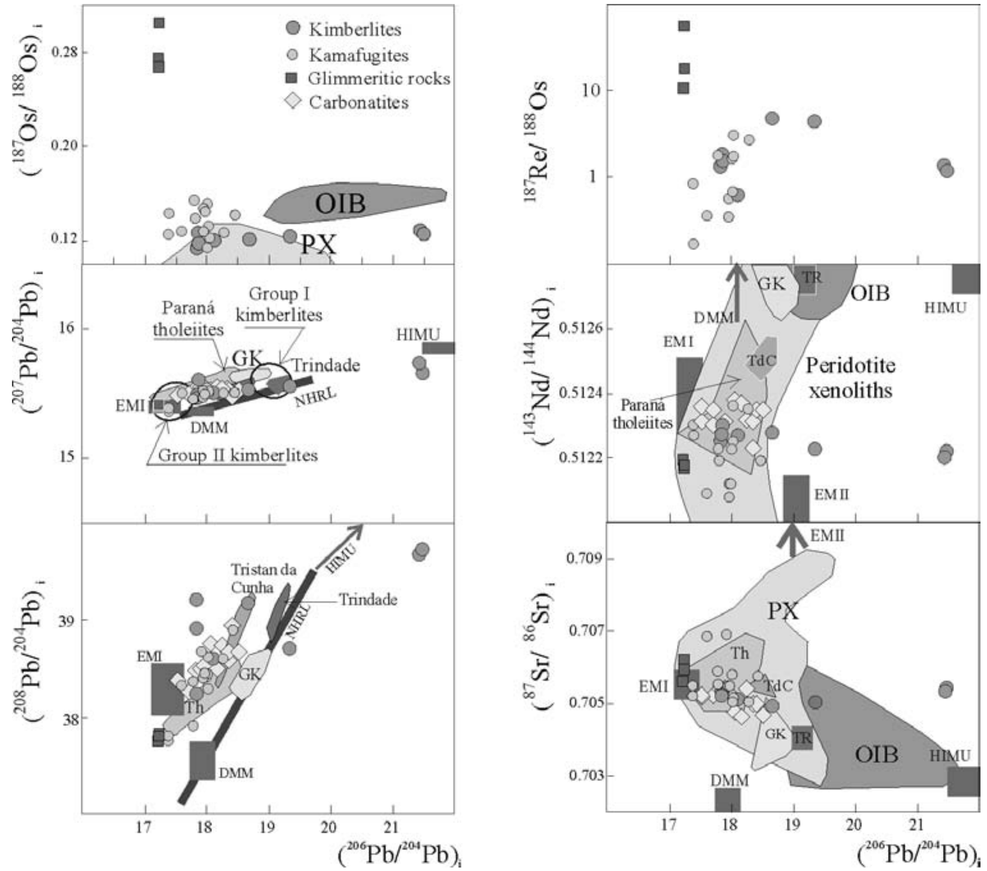


Fig.20 – Sr, Nd, Pb and Os initial ratios and Re isotopic signatures relative to the Alto Paranaíba samples of Table 5. HIMU, DMM EMI and EMII components, as defined by Zindler and Hart (1986) and by Hart and Zindler (1989); Group I and Group II kimberlites, OIB, Ocean island basalts, and peridotite xenoliths, after Smith (1983), Smith *et al.* (1985) and Clark *et al*. (1991); Paraná tholeiites ("uncontaminated" high-Ti tholeiites after Comin-Chiaramonti *et al*., 1997a and references therein); TR, Trindade, after Siebel *et al.* (2000) and Marques *et al.* (1999b); TdC, Tristan da Cunha-Gough-Inaccessible, after Le Roex *et al*. (1990). GK, Gibeon kimberlites, after Davies *et al.* (2001). NHRL: North Hemisphere Reference Line, after Hart (1984).

Nd (initial ratios) of Fig. 20, it should be noted that mostly of the APIP rocks are in the field of the peridotite xenoliths, some kimberlites excepted; the latter show characteristics of less radiogenic Nd with respect, e.g. of the Late Cretaceous kimberlites from Gibeon (Davies *et al*., 2001).

The Re-Os isotope systematics do not allow a clear distinction among the different rock-types. Kimberlites have Re and Os between 0.32 and 1.99 ppb, and 0.81 and 1.98 ppb (av. 0.69±0.64 and 1.43±0.40 ppb, respectively). On the other hand, ^{187}Os/^{188}Os initial ratios vary in a restrict range, i.e. from 0.11 to 0.13 (av. 0.122±0.005). Kamafugites show Re and Os from 0.06 to 0.38 ppb and from 0.12 to 1.76 ppb (av. 0.156±0.140 and 0.672±0.526 ppb, respectively) and have ^{187}Os/^{188}Os initial ratios ranging from 0.11 to 0.15 (av. 0.134±0.013). Well distinct are the glimmerites that contain the highest ^{187}Os/^{188}Os and ^{187}Re/^{188}Os ratios (cf. Fig. 20).

TRD (Os) model ages range between 1.39 and 1.64 Ga, thus setting a minimum Re age of the source region protolith (Bizzi and Araújo, 2005), showing an older event with respect to the APIP Nd model age (1.0±0.1). Notably, these model ages are in the same range of the Paraguay alkaline-carbonatite rocks (1.1-1.7 Ga). The cluster of isotopic data seems point to old lithospheric sources.

Arguments in favour of lithospheric sources for the APIP magma types are also postulated by Carlson *et al.* (1996) and Araújo *et al.* (2001), comparing the Re-depletion ages of the kimberlites with Nd-depleted mantle model ages of all their analyzed rock-types. The Os isotope data for the APIP rock-types are indicative of lithospheric mantle sources for the kimberlites (^{187}Os/^{188}Os ratios 0.11 to 0.13) that were variously Re depleted, probably at Neoarchean to Mesoproterozoic times. These lithospheric sources 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. Kamafugites have radiogenic ^{187}Os/^{188}Os ratios (up to 0.15) suggestive of source veins that appear to have been stabilized in the lithospheric mantle in the Meso- to Neoproterozoic.

Finally, it should be stressed that Carlson *et al.* (1996) proposed that the Os isotope compositions, coupled with Sr-Nd-Pb isotope systematics, most likely represent the influence of delaminated Brazilian lithospheric mantle mixed into mantle circulation beneath the South Atlantic and are not related to the plume(s) activity commonly associated with the APIP magmatism (cf. Gibson *et al.*, 1995a).

CONCLUDING REMARKS

The alkaline-carbonatitic magmatism from the PAN is distributed along tectonic lineaments in both American and African continents. The intruded crystalline basement is generally observable. 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. Liquid immiscibility processes played an important role in the genesis of the PAN carbonatites.

The large variations of incompatible elements and REE appear to be in many cases mainly related to hydrothermal processes (up to low thermality). This evidence is also supported by the O-C isotope systematics and by the calcite-dolomite isotopic equilibrium temperatures indicating complex trends from magmatic to hydrothermal environments at variable CO_2/H_2O ratios. On the other hand, many O-C isotopic ratios data, falling into the primary carbonatite box and strictly linked to orthomagmatic phases, are believed to represent primary isotopic signature of the mantle, as suggested also by the isotopic systematics regarding the noble gases.

On the whole, the geochemical data show that the genesis of the PAN magmatism requires heterogeneous mantle sources, also in terms of radiogenic isotopes. Such heterogeneity is probably related to metasomatic l.s. processes which would have occurred between Neoarchean and Neoproterozoic times, as also confirmed by Re-Os systematics on mafic-ultramafic rock-types associated with the alkaline-carbonatitic complexes.

The areal distribution of the magmatism seems indicate that the time-integrated isotopic enrichment of the carbonatites and associated alkaline rocks decreases from West (Eastern Paraguay) to East (Angola and Namibia), concomitantly with the decreasing age of the magmatism (Early to Late Cretaceous). This supports the view that the PAN alkaline-carbonatitic magmatism originated from large- to small-scale heterogeneous subcontinental mantle. Sr-Nd-Pb-Os isotope data yield clear evidences that HIMU and EMI mantle components were important in the genesis of the PAN magmatism.

All the results are indicate that the contribution of asthenospheric components derived from mantle plumes (i.e. Tristan da Cunha and Trindade hot spots; cf. Stefanick and Jurdy, 1984) to the genesis of the PAN alkaline-carbonatitic magmatism was not significant. This is also consistent with the conclusions reached by Piccirillo and Melfi (1988), Comin-Chiaramonti *et al.* (1997a), Marques *et al.* (1999a) and Ernesto *et al.* (2002) for the petrogenesis of the Paraná flood tholeiites.

Regional thermal anomalies in the deep mantle, mapped by geoid and seismical tomography, are supporting a non-plume-related heat source for the PAN magmatism according to Ernesto *et al.* (2002) and Comin-Chiaramonti *et al.* (2004). The hotspot tracks of Walvis Ridge and Rio Grande Rise, as well as the Victória-Trindade chain, might reflect the accomodation of stresses in the lithosphere during rifting rather than continuous magmatic activity induced by mantle plumes beneath the moving lithospheric plates.

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