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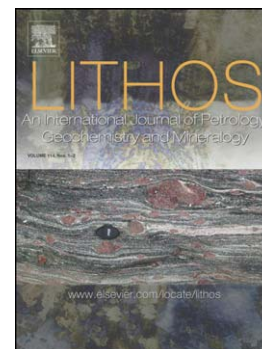
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**Insights into the Late-stage Differentiation Processes of the Catalão I Carbonatite
Complex in Brazil: New Sr-Nd and C-O Isotopic Data in Minerals from Niobium Ores**

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ABSTRACT

The Late Cretaceous Catalão I carbonatite complex consists of ultramafic silicate rocks, phosphorites, nelsonites and carbonatites. The latest stages of the evolution of the complex are characterized by several nelsonite (magnetite-apatite rock) and carbonatite dykes, plugs and veins crosscutting earlier alkaline rocks. The interaction between the latter and late-stage carbonatites and/or carbo-hydrothermal fluids, converted the original dunites and bebedourites to metasomatic phlogopitites. Late-stage nelsonites (N1), pseudonelsonites (N2) and various types of dolomite carbonatites (DC) including norsethite-, magnesite- and/or monazite-bearing varieties show significant whole-rock Nd and Sr isotopic variations. To elucidate whether magmatic or metasomatic processes, or both, were responsible for these isotope variations we characterized the Nd and Sr isotopic compositions of major mineral phases (i.e. apatite, dolomite, norsethite, pyrochlore and tetraferriphlogopite) in these late-stage rocks. Mineral isotope data recorded the same differences observed between N1 and N2 whole-rocks with N2 minerals showing more enriched isotopic signatures than minerals from N1. Sr isotopic disequilibrium among minerals from N2 pseudonelsonites and spatially related dolomite carbonatite pockets implies formation from batches of carbonate melts with distinct isotopic compositions. A detailed investigation of Nd and Sr isotopes from whole-rocks and minerals suggests that the most evolved rocks of the Catalão I complex probably derive from two different evolution paths. We propose that an earlier magmatic trend (path A) could be explained by several batches of immiscible and/or residual melts derived from carbonated-silicate parental magma (e.g. phlogopite picrite) contaminated with continental crust to a variable extent, in an AFCLI-like process. A second trend (path B) comprises highly variable $^{143}\text{Nd}/^{144}\text{Nd}$ at nearly constant $^{87}\text{Sr}/^{86}\text{Sr}$ coupled with high $\delta^{18}\text{O}$ in carbonates. This

is interpreted here as the result of the interaction of previously-formed dolomite carbonatites with carbo-hydrothermal fluids.

Keywords: Radiogenic isotopes; Carbonatite; Nelsonite; AFCLI; Subsolidus interactions.

1. Introduction

The isotopic compositions of carbonatites have established important constraints on the petrogenetic processes involved in the origin and evolution of alkaline-carbonatite complexes worldwide (e.g. Andersen, 1987; Bell, 1998; Ray, 2009; Simonetti and Bell, 1994). Radiogenic, stable and noble gas isotopic data show that: (a) carbonatites originate directly from the mantle or from mantle-derived magmas; (b) parts of subcontinental mantle may remain virtually undisturbed over billions of years (~ 3.0 Ga) and; (c) most worldwide carbonatites younger than 200 Ma have isotope signatures that can be explained in terms of mixtures of HIMU, EM-I and FOZO mantle components (Bell and Simonetti *et al.*, 2010 and references therein).

Recent works have reported radiogenic isotope studies in minerals from carbonatites and associated alkaline rocks providing new insights into the complicated histories for some alkaline-carbonatite complexes (e.g. Bell, 2001; Bizzarro *et al.*, 2003; Chen and Simonetti, 2015; Dunworth and Bell 2001; Tichomirowa *et al.*, 2006; Wu *et al.*, 2011; 2013; Ye *et al.*, 2013; Zaitsev and Bell, 1995). Open-system behaviour involving interaction between melts or fluids derived from mantle and/or crust levels, isotopically heterogeneous mantle sources, magma recharge, and crustal assimilation have been proposed to explain the major isotopic ratio variations. Therefore, mineral isotopic compositions may offer valuable information to clarify the evolution of some carbonatite complexes, particularly where isotope disequilibria have already been detected in whole-rock analyses.

Significant Nd and Sr isotopic variations have been reported in the niobium ores from the Catalão I complex (Cordeiro *et al.*, 2010; 2011b). Late-stage magmatic and/or metasomatic processes could explain such isotope signatures, but a detailed mineral isotope investigation may provide further insights into the mechanisms associated with these

variations. Hence, in this study, the Sr and Nd isotopic composition of several individual mineral phases separated from the samples described in Cordeiro *et al.* (2010, 2011b) are characterized in order to verify for isotopic equilibrium, provide additional stable (C, O) isotope data, and propose new constraints on the final stages of evolution of Catalão I complex.

2. Geological Setting

Catalão I is one of the northernmost alkaline-carbonatite complexes of the Late Cretaceous Alto Paranaíba Igneous Province (APIP). The APIP comprises ultrapotassic dykes, pipes, plugs and diatremes of kamafugitic, kimberlitic and rare lamproitic compositions along with extensive kamafugitic lava flows and pyroclastic deposits, and large carbonatite-bearing intrusions (Araújo *et al.*, 2001; Gibson *et al.*, 1995; Gomes and Comin-Chiaramonti, 2005). The carbonatites of the province belong to the rare carbonatite-kamafugite association (Brod *et al.*, 2000). The alkaline magmas were emplaced into the Neoproterozoic metasedimentary rocks of the Brasília Belt, between the SW border of the São Francisco Craton and the NE margin of the Phanerozoic Paraná Basin (inset Fig. 1). Such magmatism is attributed to the impact of the Trindade mantle plume beneath the previously metasomatized subcontinental lithospheric mantle in this region (Araújo *et al.*, 2001; Gibson *et al.*, 1995; 1997; Sgarbi *et al.*, 2004; Thompson *et al.*, 1998). However, some authors have argued against the plume hypothesis and claimed that APIP magmatism could be explained by long-lived deep mantle thermal anomalies (e.g. Riccomini *et al.*, 2005), or due to elevated homologous temperature (Guarino *et al.*, 2013).

The Catalão I carbonatite complex, located ca. 20 km northeast of the city of Catalão in central Brazil (18°08'S; 47°48'W), comprises a ~30 km² roughly circular, dome-shaped

multi-stage intrusion (Fig. 1) emplaced in quartzites and schists of the Araxá Group (Carvalho, 1974; Cordeiro *et al.*, 2010; Danni *et al.*, 1991). A ring of fenitized, weather-resistant country rocks favoured the development of an inward drainage pattern that preserves thick soil covers (> 150 m) over fresh rocks of the complex. This thick weathering profile hosts important supergene and residual deposits of phosphate, niobium, titanium, barium, rare earth elements and vermiculite (Carvalho and Bressan, 1997; Cordeiro *et al.*, 2011a; Danni *et al.*, 1991; Gierth and Baecker, 1986; Hirano *et al.*, 1990; Ribeiro, 2008).

The main rock types recognised in drill-core samples of Catalão I are dunites and bebedourites, both extensively transformed into metasomatic phlogopitites, together with phoscorites and several later-stage dykes, plugs and veins of nelsonites and carbonatites (Araújo, 1996; Carvalho, 1974; Danni *et al.*, 1991; Ribeiro, 2008). The metasomatic phlogopitites have been attributed to an intense auto-metasomatism due to interaction of early alkaline ultramafic rocks with fluids released by late-stage carbonatite intrusions (Araújo, 1996; Gaspar and Araújo, 1998). The later nelsonites and carbonatites are mineralized in Nb and REEs, and appear to be unaffected by the extensive phlogopitization that affected the early ultramafic and phoscoritic rocks of the complex (Cordeiro *et al.*, 2010; Ribeiro *et al.*, 2014).

Ultrapotassic, olivine- and CO₂-rich phlogopite picrites (Gibson *et al.*, 1995) occur mainly as dykes geographically associated with the alkaline-carbonatite complexes of the province and represent their most primitive magmas (Brod *et al.*, 2000; 2013). Phlogopite picrites are extremely silica-undersaturated (SiO₂ < 33.4 wt.%) rocks characterized by high CO₂ (up to 21.9 wt.%), MgO (up to 21 wt.%), Cr (up to 1000 ppm) and Ni (up to 900 ppm). They are chemically similar to the APIP kamafugites (Brod *et al.*, 2000, 2013), although potassic feldspathoids and melilite have not yet been recognized. Phlogopite picrite dykes may crosscut all other rock types of the Catalão I complex (Ribeiro *et al.*, 2005a).

Cordeiro *et al.* (2010; 2011b) detailed the petrography and mineral chemistry of phoscorites, nelsonites and dolomite carbonatites formed during mid to late-stage evolution of the complex, and associated with the phosphate and niobium ores from Catalão I. These authors define four units: (a) Earlier P1 phoscorites consisting of coarse- to medium-grained rocks composed essentially of olivine, apatite, phlogopite and magnetite. (b) Late-stage P2 apatite-rich nelsonites and (c) P3 magnetite-rich nelsonites; both composed of apatite, carbonates, magnetite, tetraferriphlogopite and pyrochlore, the latter mineral varying from accessory to up to 50% vol. in very enriched specimens. The main difference between P2 and P3 nelsonite types is the amount of apatite, magnetite and carbonates, the latter reaching up to 20% vol. in P2 and up to 40% vol. in P3. Following the suggestion of Palmieri (2011), P2 and P3 were renamed respectively as N1 and N2. (d) Dolomite carbonatite (DC) pockets coeval with N1 and N2, ranging in size from centimetre to meter, and often comprise an inner zone composed of dolomite, norsethite, and rare barite, surrounded by an outer zone of radial prismatic apatite and elongated crystals of ilmenite, magnetite, pyrochlore and tetraferriphlogopite, similar to a comb-layering texture (Cordeiro *et al.*, 2010).

Field observations at the Boa Vista Niobium Mine, in the nearby Catalão II complex (Palmieri, 2011), show that the DC pockets within N1 and N2 nelsonites have distinct origins. DC pockets in N1 (Fig. 2a) have diffuse outlines, grade to interstitial carbonate and probably represent immiscible carbonate liquids segregated from the host nelsonite. On the other hand, DC pockets in N2 seem to be related with the percolation of carbonatitic magma through fractures (Fig. 2b) leading to progressive incrustation of the walls with different inward-growing mineral phases (e.g., apatite, Fe-Ti oxides, pyrochlore) until the passage becomes finally blocked with carbonate crystals, forming pockets. In this scenario, carbonates and other solidified phases within these pockets would represent the composition of the last carbonatite magma to pass through that conduit. It is important to stress that this indicates that

N2, although mineralogically similar to nelsonites, are actually produced as wall cumulates from carbonatite, instead of *bona fide* phoscoritic magmas. Palmieri (2011) argues that these N2 nelsonitic cumulates should be named pseudonelsonites to reflect their genesis from a carbonate instead of a phosphate-oxide magma.

3. Sample descriptions

A brief petrographic description of the four studied niobium ore samples is presented below. These were carefully selected in order to avoid any noticeable alteration. One is an apatite-rich nelsonite (N1, sample NRD339B) consisting of fine- to medium-grained apatite, magnetite, and tetraferriphlogopite, with minor amounts of scattered yellowish-brown pyrochlore and rare clear carbonate crystals. The other three samples (NRD149; NRD170; NRD339B) characterize the association between N2 pseudonelsonites and dolomite carbonatites. The samples are composed of 30-40% of carbonates, essentially concentrated in pockets surrounded by rims of cumulate, fine- to coarse-grained apatite, Fe-Ti oxides, tetraferriphlogopite and pyrochlore. Rare barite crystals may occur within the DC pockets (e.g. sample NRD170). Detailed mineral descriptions and modal compositions are given in Supplementary Material.

4. Analytical procedures

Stable C-O isotope measurements were carried out using a Gas Bench II System connected to a Delta V Advantage gas-source mass spectrometer after the reaction of carbonate samples with 99% H_3PO_4 at 72°C. The results are expressed as $\delta^{13}\text{C}_{\text{V-PDB}}$ and $\delta^{18}\text{O}_{\text{V-SMOW}}$ relatively to reference V-PDB and V-SMOW standards and are complementary to

those data reported by Cordeiro *et al.* (2011b). Analytical uncertainties expressed as absolute deviation of repeated analyses of international standards (e.g. NBS-19) are $\pm 0.05\%$ and $\pm 0.10\%$ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively.

Nd and Sr isotopic ratios were determined for two whole-rock samples, in order to complement the whole-rock dataset of Cordeiro *et al.* (2010; 2011b), and in individual mineral separates comprising apatite, barite, dolomite, magnetite, norsethite, pyrochlore and tetraferriphlogopite from nelsonite, pseudonelsonites and DC pockets. To obtain the mineral separates, the rock samples were processed by electrodynamic disaggregation using a SELFRAG[®] Lab S2.0 High Voltage Pulse Power Fragmentation at voltages of 100-140 kV. After disaggregation, all samples were dried and screened in sieves matching the crystal size observed in thin section, to facilitate hand-picking. The minerals of interest were then separated using a Frantz[®] magnetic separator and careful hand-picking under a binocular microscope to ensure high purity (~99%) for each mineral concentrate. Unfortunately, magnetite and pyrochlore separates could not achieve such level of purity due to their close association. Given the extremely low concentrations of Rb, Sr, Sm and Nd in magnetite, significant impact is not expected on the isotopic signature of pyrochlore. However, the opposite assumption is not valid, and results obtained from magnetite separates may reflect the isotope composition of pyrochlore. Thus, magnetite isotopic data reported should be considered as representative of the associated pyrochlore.

Next, leaching procedures as outlined in Wittig *et al.* (2009) were applied to our mineral separates. All minerals except apatite were washed with ultra-pure Milli-Q[®] water at room temperature (16-18 °C) in an ultrasonic bath for 30 minutes (step 1). After removing this water, minerals were repeatedly rinsed with Milli-Q[®] water before a second wash under the same conditions (step 2). At this stage, carbonates were dried out since they readily dissolve in inorganic acids. Barite, pyrochlore and tetraferriphlogopite were leached with 2.5

N HCl for 30 minutes at 80-100 °C (step 3). Magnetite concentrates were leached as in step 3 and one more time with 6 N HCl for 30 minutes at 80-100 °C (step 4). Between the leaching steps 2, 3, and 4 the minerals were exhaustively rinsed with Milli-Q[®] water prior to drying out. Apatite was leached following the procedure developed by Oliveira (2015), which uses dilute acetic acid (0.5 N) at 80-100 °C. All procedures described above were conducted in class 10,000 cleanrooms.

Aliquots of 5 to 10 mg of apatite and pyrochlore, and ~100 mg of the other minerals, were spiked with a mixed ¹⁴⁹Sm-¹⁵⁰Nd tracer before digestion. Barite, magnetite, pyrochlore, tetraferriphlogopite and whole-rock samples (~100 mg of sample powder) were dissolved in a mixture of HF-HNO₃ in Parr Teflon[®] bombs according to the method of Gioia and Pimentel (2000). For the barite sample, the digestion procedure was repeated because of the very low solubility of this mineral, adding only HNO₃ in the second run, as recommended by Puchelt and Setiobudi (1989). Apatite and carbonate samples were digested with 2 ml of HCl 6 N (carbonates) and 2 ml of concentrated HNO₃ (apatite) in Savillex[®] vials placed on a hot plate for 1 day at 80-100 °C. Once the mineral separates were completely dissolved, two-step ion exchange chromatography was carried out in order to separate Sm and Nd fractions from the matrix, following the method developed by Gioia and Pimentel (2000). An aliquot of 0.5 ml of each sample solution was loaded on quartz glass columns packed with DOWEX[®] AG-50W-X8 cation exchange resin (100-200 mesh) to extract the REE. Sm and Nd fractions were collected via Eichrom[®] LN-Spec 100-150 µm resin in Teflon[®] columns. Another aliquot of 0.5 ml of the solutions was directly loaded onto Teflon[®] columns containing approximately 83 mg of Eichrom[®] Sr-Spec resin (50-100 µm) to separate the Sr fraction from the matrix.

Nd isotope measurements were performed using a Thermo Scientific TRITON[™] Plus Thermal Ionization Mass Spectrometer (TIMS) operating in the static multi-collector mode whereas Sr isotopic compositions were determined with the same equipment in the multi-

dynamic mode. The average $^{143}\text{Nd}/^{144}\text{Nd}$ obtained for the USGS BHVO-1 standard was 0.512996 ± 0.000006 (2SD; $n = 7$) and the average $^{87}\text{Sr}/^{86}\text{Sr}$ obtained for the NBS-987 standard was 0.710257 ± 0.000007 (2SD; $n = 9$) during the course of this study. The BHVO-1 result is in excellent agreement with the most recently published values (e.g. 0.512986 ± 0.000009 ; Weis *et al.*, 2005). The value obtained for standard NBS-987 also agrees with the recommended $^{87}\text{Sr}/^{86}\text{Sr} = 0.71025$ (Thirlwall, 1991). The analytical precision of $\pm 0.1\%$ is estimated for Sm and Nd concentrations determined by isotope dilution. Sm and Nd blanks were less than 40 pg and 250 pg, respectively. Although the Rb and Sr contents of mineral separates could not be determined in this work, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of minerals with extremely low Rb/Sr (in our study, apatite, carbonates and pyrochlore) can be considered initial ratios (Zaitsev and Bell, 1995). For details regarding mass fractionation corrections, see the footnotes of Table 1. All sample preparation procedures and isotope determinations were carried out at the Laboratory of Geodynamics, Geochronology and Environmental Studies of the Institute of Geosciences, University of Brasília.

5. Results

Sm-Nd and Sr isotopic data for mineral separates and whole-rock samples are given in Table 1. All initial Sr and Nd ratios were back-corrected to 85 Ma. Unfortunately, there is no high-resolution geochronology of Catalão I. However, several authors have consistently reported K-Ar (Gibson *et al.*, 1995; Sonoki and Garda, 1988), Rb-Sr (Machado Junior, 1991) and U-Pb perovskite ages (Sgarbi *et al.*, 2004, Guarino *et al.*, 2013) within a range of 80-90 Ma for all rocks of the Alto Paranaíba Igneous Province, including carbonatite complexes elsewhere in the province (e.g. Catalão II, Salitre, Serra Negra, and Tapira). Such a narrow range is unlikely to produce significant variation in the calculated initial Sr and Nd isotope

ratios. We therefore assumed a whole-rock K-Ar age of 85.0 ± 6.9 Ma, reported by Sonoki and Garda (1988) as the age of Catalão I. This is also consistent with the assumption of Gibson *et al.* (1995) for the whole of the APIP.

In general, Sr isotopic compositions show a remarkable variation within minerals taken from the different samples. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for all mineral separates range from 0.705284 to 0.705404. N1 apatite has the least radiogenic $^{87}\text{Sr}/^{86}\text{Sr}_i$ (0.705284) among all analysed minerals and, albeit the only mineral phase analysed from N1 nelsonite, its isotopic composition is consistent with whole-rock data (Fig. 3a). Minerals from N2/DC pseudonelsonites display more enriched $^{87}\text{Sr}/^{86}\text{Sr}_i$, varying from 0.705353 to 0.705404, when compared with N1 apatite and whole-rock values. It is clear that Sr isotopic disequilibrium occurs between the late-crystallizing carbonates and the earlier formed pyrochlore in all samples (Fig. 3b). Interestingly, pyrochlore exhibits $^{87}\text{Sr}/^{86}\text{Sr}_i$ that are systematically higher than those of the corresponding latest-crystallizing carbonate in each sample, by a factor of ~ 0.000030 . Considering our Sr mineral isotopic data in-run precisions (Table 1), such differences are particularly significant. If there is within-grain isotopic disequilibrium in pyrochlore, some of the carbonate melts involved in the generation of N2/DC rocks could be even more enriched in radiogenic ^{87}Sr than the average values obtained here. For a discussion on within-grain isotopic disequilibrium see Davidson *et al.* (2007).

The range of $^{143}\text{Nd}/^{144}\text{Nd}_i$ in our mineral separates is 0.512138 to 0.512216. If only individual minerals from each rock type are considered, N1 concentrates exhibit a much narrower range of $^{143}\text{Nd}/^{144}\text{Nd}_i$ than N2/DC minerals (Table 1). Furthermore, there is a large difference between the Nd isotopic compositions of N1 and N2 minerals, similar to the behaviour observed in the Sr isotope data. This probably reflects the highly variable Nd results noted by Cordeiro *et al.* (2010, 2011b) between whole-rock samples.

Apatite and tetra-ferriphlogopite from N1 nelsonite have the highest $^{143}\text{Nd}/^{144}\text{Nd}_i$ among our samples (0.512216 and 0.512211, respectively). These minerals are in equilibrium with the N1 whole-rock range (Fig. 4a). Apatite contains very high concentrations of Sm and Nd, in comparison with tetra-ferriphlogopite, but both minerals show similar Sm/Nd in N1 samples (Table 1). Minerals from N2 pseudonelsonites and associated DC pockets have more enriched Nd isotopic compositions, ranging from 0.512138 to 0.512182. Initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of mineral separates are slightly higher than their corresponding DC pockets, although some overlap exists (Fig. 4b, c, d). Despite minor variations between mineral and whole-rock data, no clear distinction can be made between N2 and DC Nd isotopic compositions. Except for barite in sample NRD170, which has a slightly higher $^{143}\text{Nd}/^{144}\text{Nd}_i$ than that of other coexisting mineral phases, as a general rule all minerals from a particular sample are in isotopic equilibrium, considering the analytical uncertainties. It should be noted that bulk analyses of the DC pockets (Cordeiro *et al.*, 2011b) show lower Sm/Nd ratios than the carbonate phases separated from them, indicating that bulk samples are more enriched in LREE than single dolomite/norsethite crystals. This may be due to unidentified phases crystallized during post-magmatic processes that did not affect the main minerals.

6. Discussion

6.1. Source of the Catalão I magmas

On a Sr-Nd initial isotope ratios plot (Fig. 5), all our analysed minerals fall in the lower-right quadrant, within the field of APIP carbonatites (inset Fig. 5), consistent with derivation from an enriched mantle source (e.g. Carlson *et al.*, 2007; Gibson *et al.*, 1995; Gomes & Comin-Chiaramonti, 2005; Guarino *et al.*, 2013). The isotopic compositions of both

whole-rocks and minerals from the most evolved stages of the Catalão I complex (i.e. N1, N2, and associated late-stage carbonatites) seem to split between two different trends (Fig. 6): path A may be considered a continuation of the trend of primitive phlogopite picrite dykes (see Figs. 5 and 6), whereas path B comprises a set of samples plotting in the direction of enriched Nd compositions at nearly constant Sr ratios.

Heterogeneous mantle sources have been systematically invoked to explain many of radiogenic isotope variations of alkaline-carbonatite complexes (e.g. Chen and Simonetti, 2015; Dunworth and Bell, 2001; Morikiyo *et al.*, 2000; Zaitsev and Bell, 1995). Although the Catalão I data indicate a mixture of at least three isotopic components, these are difficult to reconcile with distinct mantle compositions for the following reasons: (1) the Nd isotope compositions for Catalão I spans a narrow range when compared with the province as a whole (inset Fig. 5), and the Sr isotope range is even narrower; (2) evidence was presented earlier (Brod *et al.*, 1999) to show that parental magma such as phlogopite picrite can be readily contaminated with crust due to their expected high temperature and low viscosity, which could explain path A (Fig. 6); (3) an end-member mantle component with extremely enriched Nd isotope signature, such as suggested by path B (Fig. 6) is very uncommon. Mantle source regions containing an old, recycled crustal component, similar to those interpreted for some Russian (Aldan Shield, Davies *et al.*, 2006) and North American lamproites (Leucite Hills and Smoky Butte, Mitchel and Bergman, 1991) would have a suitable unradiogenic signature to explain path B. However, if such a mantle source was involved in the origin of the APIP carbonatite complexes, then primitive phlogopite picrites would plot along the same trend, which is clearly not the case.

Extensive sampling and description of fresh rock samples from mining pits and drill-cores of all APIP carbonatite complexes, conducted by the authors over the last two decades, showed that phlogopite picrite dykes are abundant, both within and in the immediate vicinity

of the complexes. Furthermore, and perhaps more importantly, these rocks are remarkably similar in chemistry, mineralogy and textures from one complex to another, have chemically and mineralogically primitive compositions, and typically contain immiscible carbonate globules that indicate a strong link between them and the associated carbonatites (e.g. Brod *et al.*, 2000; 2013). So far, no other fine-grained, carbonated-silicate ultramafic rocks that could represent alternative primitive magmas were identified in such complexes, leading us to interpret phlogopite picrite as the parental magma from which Catalão I and other APIP carbonatite complexes evolved.

Nevertheless, the current knowledge of the petrogenesis of the APIP alkaline-carbonatite complexes indicates that they are multi-stage intrusions with a very complex differentiation history (see below). Although there is no direct evidence for different parental magmas, it is conceivable that a contribution of different mantle sources could, potentially, be masked or overprinted by several other processes. In this sense, a robust isotopic investigation of the postulated parental magma (i.e. phlogopite picrite) is still required to definitely rule out the participation of varied mantle sources in their origin.

6.2. Differentiation of the Catalão I carbonatite complex

According to Ribeiro *et al.* (2014) a multi-stage magmatic system with successive and recurrent crystal fractionation and liquid immiscibility is required to explain the petrogenetic evolution of the Catalão I complex. Similar concepts were also applied to other APIP complexes (e.g. Barbosa *et al.*, 2012; Brod *et al.*, 2013). Figure 7 illustrates an evolution scheme for Catalão I, which is discussed below.

The starting point is a parental alkaline carbonated-silicate magma such as phlogopite picrite. Fractional crystallization of olivine, chromite, perovskite, and minor

clinopyroxene/phlogopite produced ultramafic cumulates such as the perovskite dunites and perovskite bebedourites occurring in Catalão I (Ribeiro, 2008; Ribeiro *et al.*, 2014). The fractionation of this assemblage of CO₂-free minerals from an already CO₂-rich magma leads to increase in the amount of dissolved CO₂ and, eventually, to the onset of carbonate-silicate liquid immiscibility. Nucleation of immiscible carbonate globules taken place and later coalescence gives rise to small veins, and then, to pockets and dykes of carbonate melt (Ribeiro *et al.*, 2005a). The occurrence of liquid immiscibility in phlogopite picrites from Catalão I and other APIP complexes is demonstrated by field (Ribeiro *et al.* 2005a), mineral chemistry (Brod *et al.*, 2001), and whole-rock geochemistry (Brod *et al.*, 2013) evidences.

After the initial separation of an immiscible carbonate melt, the CO₂-depleted silicate conjugate liquid continues to evolve through fractional crystallization of clinopyroxene, apatite and phlogopite, generating evolved bebedourites. Further residual carbonatites could be produced at the end of silicate magma evolution (Ribeiro *et al.*, 2014). The carbonate conjugate melt, in turn, evolves through fractionation of high-temperature minerals, giving rise to olivine- and apatite-rich cumulates (e.g. Brod, 1999; Ribeiro, 2008). Estimates from sulphur isotope fractionation in early-stage carbonatites from Catalão I indicate a temperature of ca. 750°C for these liquids (Gomide *et al.*, 2013), in good agreement with temperatures expected for Catalão I carbonatite magmas based on oxygen isotopes (e.g. Cordeiro *et al.*, 2011b).

The presence of phoscorite and nelsonite dykes with magmatic textures requires a second liquid immiscibility event in order to produce a phosphate-oxide melt. This crystallizes initially as phoscorite, and then evolves toward nelsonites (N1) by olivine removal. After crystallization of N1 nelsonites, a residual carbonate melt percolates fractures that are progressively infilled by cumulates of apatite, Fe-Ti oxides, tetra-ferriphlogopite and

pyrochlore that constitute the N2 pseudonelsonites. This carbonate melt eventually crystallizes in residual voids within the N2 cumulates as dolomite carbonatite (DC) pockets.

All perovskite-rich dunites and bebedourites are extensively transformed in metasomatic phlogopites by interaction with carbonatite-derived fluids (Araújo, 1996; Brod *et al.*, 2001; Ribeiro, 2008), indicating volatile loss from evolved carbonatites into the previously formed alkaline rocks. Phoscorites are also affected by this process, which results in the conversion of the original olivine to phlogopite. The presence of primitive phlogopite picrite dykes, with or without immiscible globules that crosscut all other (petrologically more evolved) rocks as well as breccias containing fragments of almost all rock types from Catalão I in a phlogopite picrite matrix (Ribeiro *et al.*, 2005a), provide strong evidence for the recurrence of all the petrogenetic processes described above.

6.3. Isotope signatures of the late-stage rocks of Catalão I

Cordeiro *et al.* (2010; 2011b) recognized important variations in $^{87}\text{Sr}/^{86}\text{Sr}_i$ and, particularly, in $^{143}\text{Nd}/^{144}\text{Nd}_i$ ratios of the late-stage rocks from Catalão I. Our mineral and additional whole-rock isotopic data support their previous results (Fig. 2, 3 and 5), and rule out a simple liquid line of descent between N1 and N2/DC. Furthermore, there is systematic Sr isotopic disequilibrium among minerals from pseudonelsonites (N2) and those of spatially related dolomite carbonatite (DC) pockets (Fig. 3b), indicating that these rocks were formed from multiple batches of isotopically distinct carbonate melts.

A detailed examination of the initial Nd and Sr isotope ratios of the late-stage rocks from Catalão I suggests two possible arrays (Fig. 6), indicating the mixing of at least three distinct isotopic components (inset Fig. 6).

Path A comprises N1 nelsonites, N2 pseudonelsonites and some DC pockets in a continuous array, extending from the APIP phlogopite picrites trend toward more enriched compositions, consistent with crustal contamination. However, the feasibility of direct contamination of such late-stage magmas, particularly the carbonatites is small because of their low liquidus temperatures. Also, these magmas have very high contents of both Sr and Nd (i.e. 100's to 1000's of ppm; Bell and Simonetti, 2010), such that the required amount of crustal contamination would be unrealistically high, and extensively alter the predominant composition of the magma.

On the other hand, if contamination occurred at the early evolution stages, such constraints would not apply. Wall-rock assimilation is favoured at the early stages of the magmatic evolution of an ultramafic carbonated-silicate parental magma (phlogopite picrite) due to the high temperature and low viscosity of these magmas, resulting in a turbulent flow and high wall-rock/magma ratios. Radiogenic isotope evidence for crustal assimilation in phlogopite picrites have been reported by Brod *et al.* (1999) for the Tapira complex and by Oliveira (2015) for the Salitre complex, both in the APIP. A contaminated isotopic signature acquired by the parental magma would persist through differentiation. Therefore, if variable degrees of assimilation occurred, this should be reflected in the whole differentiation sequence.

In alkaline-carbonatite complexes, further complexity is added by the possibility of liquid immiscibility. Ray (1998, 2009) demonstrated that assimilation taking place simultaneously with fractional crystallization of a parental carbonated-silicate magma, followed by liquid immiscibility can reproduce the isotopic variations observed at several alkaline-carbonatite complexes worldwide. Recurrent liquid immiscibility events throughout the evolution of a silicate conjugated-pair that have been continuously contaminated may generate isotopic contrasts between the immiscible carbonate melts produced at various

stages. Multiple batches of variously contaminated carbonated-silicate parental magma, undergoing liquid immiscibility, could produce the range of Nd and Sr isotope ratios observed in the late-stage rocks from the Catalão I complex along path A (Fig. 6). This interpretation is consistent with the postulated petrogenetic model of the Catalão I complex (see Fig. 7) and with the Assimilation - Fractional Crystallization - Liquid Immiscibility (AFCLI) concept devised by Ray (1998, 2009). However, we do not attempt to mathematically model this process for Catalão I in this work, because our samples are restricted to the final stages of the complex evolution.

Interestingly, $\delta^{18}\text{O}$ values reported for samples belonging to path A do not show a positive correlation with more enriched Nd and Sr isotope compositions (Fig. 6), contrarily to what would be expected in AFC-like processes. We interpret this lack of correlation as a result of superimposed post-magmatic hydrothermal alteration given that such samples show nearly constant mantle-derived $\delta^{13}\text{C}$ compositions (i.e. $\delta^{13}\text{C} = -5.66$ to -6.31 ‰; see Table 2 and Cordeiro *et al.*, 2011b).

Path B comprises some DC pockets and monazite-bearing carbonatites plotting toward much more enriched Nd isotope compositions at a nearly constant $^{87}\text{Sr}/^{86}\text{Sr}_i$ (Fig. 6). A similar “vertical array” is noted by Ye *et al.* (2013) in apatites from the Qieganbulake carbonatite complex (NW China). Those authors suggest that such isotope signatures could be explained by either crustal contamination or magma mixing of multiple mantle sources. The latter explanation is unlikely in the case of late-stage Catalão I carbonatite samples plotted along path B, as discussed in section 6.1. Moreover, contrasting behaviour between paths A and B (Fig. 6) argues against a simple AFCLI model for path B.

Stable C-O isotope data given in Table 2, as well as previous data from Cordeiro *et al.* (2011b) reveal that many of the samples in path B are strongly enriched in $\delta^{18}\text{O}$, and although $\delta^{13}\text{C}$ remains mostly within the compositional range of mantle carbon (Deines, 1989) it still

shows significant variation ($\delta^{13}\text{C} = -3.55$ to -7.01 ‰; Cordeiro *et al.*, 2011b). We interpret the most unradiogenic Nd signatures of these samples as a result of subsolidus interaction of the late-stage magmatic carbonatites with isotopically enriched carbo-hydrothermal fluids. These CO_2 - H_2O -rich fluids may have mixed with an old continental crust component, acquired an extremely enriched Nd isotope composition, and then affected previously-formed dolomite carbonatites from the Catalão I complex.

Other authors argue in favour of a widespread interaction of Catalão I rocks with crustal materials and/or low-temperature fluids (Morikiyo *et al.*, 1990; Santos and Clayton, 1995; Toyoda *et al.*, 1994). Gomide *et al.* (2013) estimate that late-stage carbonatites of the Catalão I complex were formed around 550°C , near to the limit between magmatic and carbo-hydrothermal systems. Evidence from sulphur stable isotopes (Gomide *et al.*, 2013) also points out to recurrent degassing events at the final stages of the Catalão I evolution, suggesting a major role of carbonatite-derived fluids in the formation of late-stage rocks. These are in agreement with the interpretation by Ribeiro *et al.* (2014) that REE-rich carbonatites of the Catalão I complex are products of the interaction of previously formed carbonatites with carbo-hydrothermal fluids.

7. Conclusions

Our study is the first to report Nd and Sr isotope ratios in minerals, some of them very uncommon (i.e. norsethite and pyrochlore), separated from a carbonatite complex of the Alto Paranaíba Igneous Province. The new mineral isotopic data exhibit variations comparable to those previously observed between N1 and N2 late-stage rocks of the Catalão I complex (Cordeiro *et al.*, 2010; 2011b). Besides, the isotope results reported here reveal significant Sr isotope disequilibrium among minerals from pseudonelsonites (N2) and spatially related

dolomite carbonatite (DC), indicating the occurrence of various batches of carbonate melts with distinct isotopic compositions in Catalão I.

Detailed $^{143}\text{Nd}/^{144}\text{Nd}_i$ and $^{87}\text{Sr}/^{86}\text{Sr}_i$ investigation shows that the final stages of the evolution of the Catalão I carbonatite complex were marked by significant isotope variations that can be attributed to two different trends (Fig. 6). Similar isotopic evidence in alkaline-carbonatite complexes worldwide has often been interpreted as indicative of an isotopically heterogeneous mantle source (e.g. Chen and Simonetti, 2015; Mitchell *et al.*, 1994; Morikiyo *et al.*, 2000; Zaitsev and Bell, 1995; Wu *et al.*, 2011). However, we propose that the varied isotope signatures of Catalão I late-stage rocks could be explained by: (1) several batches of immiscible and/or residual melts derived from carbonated-silicate parental magma (phlogopite picrite) contaminated to a variable extent with continental crust, in an AFCLI-like process (Path A); or (2) as a result of the interaction of previously-formed magmatic carbonatites with late-stage or post-magmatic carbo-hydrothermal fluids that have a very enriched Nd isotope composition (Path B). Stable isotopes (C-O and S) indicate that the formation of trend B it is most certainly related to a final event in the whole evolution of the Catalão I carbonatite complex, although the origin of the extremely enriched Nd isotope signatures is unclear. Moreover, the distinct trends (A and B) coincide with the shift from a Nb-rich to a REE- and Ba-rich mineralization environment (e.g. Ribeiro, 2008; Ribeiro *et al.*, 2014) and may constitute a metallogenic, as well as a petrogenetic indicator.

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Figure Captions

Fig.1. Geological sketch from the Catalão I carbonatite complex (after Cordeiro *et al.*, 2010; Ribeiro *et al.*, 2014). (1) Early alkaline ultramafic rocks; (2) Phoscorites and early-stage carbonatites with minor alkaline ultramafic rocks; (3) Late-stage nelsonites and dolomite carbonatites; (4) Late-stage REE-rich and monazite-bearing carbonatites; (5) Fenitized quartzites; (6) Area without outcrops or drill-core information. Approximate sample locations are marked by dashed lines in the centre of the complex. Faults and fractures are shown by straight black lines. Inset shows the location of APIP (square) between the NE margin of the Phanerozoic Paraná Basin (PB - light grey) and the SW border of the São Francisco Craton (SFC - dark grey). Blank areas between cratons and basins are Neoproterozoic mobile belts.

Fig.2. Drill-core samples from the Catalão I complex. (a) Apatite-rich N1 nelsonite with diffuse DC pockets texture (white parts). (b) Magnetite-rich N2 pseudonelsonite dyke and

associated DC pockets crosscutting earlier metasomatized rocks. Note that DC pockets are constrained by the dyke walls.

Fig.3. Variation of $^{87}\text{Sr}/^{86}\text{Sr}_i$ for Catalão I mineral separates from N1 (red diamond) and N2 (purple diamonds) nelsonites. Open symbols are carbonates from the DC pockets associated with each nelsonite. All symbols are larger than their associated analytical errors ($\pm 2\text{SE}$). Grey field in (a) mark the variation for whole-rock (Data from Cordeiro *et al.*, 2011b). Tie lines in (b) join the minerals from the same sample. Note that N2 minerals are systematically more enriched than N1 signatures. In the sample NRD339B (N2/DC), norsethite is the latest carbonate phase to crystallize. Ap, apatite; Dol, dolomite; Nor, norsethite; Pcl, pyrochlore.

Fig.4. Variation of $^{143}\text{Nd}/^{144}\text{Nd}_i$ for Catalão I mineral separates from N1 (red diamonds) and N2 (purple diamonds) nelsonites. Open symbols are the DC pockets associated with each nelsonite. The error bars represents $\pm 2\text{SE}$ and are plotted only when they are larger than the symbol size. Grey field in each chart mark the variation for whole-rock (N1) and DC pockets (N2) compositions; Data from Cordeiro *et al.* (2011b) and this study. All charts are to the same vertical scale. Ap, apatite; Brt, barite; Dol, dolomite; Mag, magnetite; Nor, norsethite; Pcl, pyrochlore; TfPhl, tetra-ferriphlogopite.

Fig.5. $^{143}\text{Nd}/^{144}\text{Nd}_i$ vs $^{87}\text{Sr}/^{86}\text{Sr}_i$ comparing the isotopic compositions of Catalão I whole-rocks and minerals with APIP phlogopite picrites. Whole-rock symbols as in Fig. 4. Minerals are green triangles. Phlogopite Picrites are grey circles. Data source: Catalão I whole-rocks and minerals – Cordeiro *et al.* (2010; 2011b) and this study; APIP phlogopite picrites – Brod (1999), Gibson *et al.* (1995), Gomes and Comin-Chiaramonti, 2005, Guarino *et al.* (2013). All isotope data were recalculated at 85 Ma using decay constants $\lambda_{87}\text{Rb}$ and $\lambda_{147}\text{Sm}$ of 1.393×10^{-11}

$^{11} \text{ a}^{-1}$ (Nebel *et al.*, 2011) and $6.54 \times 10^{-12} \text{ a}^{-1}$ (Lugmair and Marti, 1978), respectively. Inset shows the APIP carbonatite field (Oliveira, 2015) with the Catalão I mineral isotope data plotted for comparison (black crosses). Arrow indicate the average composition of the continental crust ($^{87}\text{Sr}/^{86}\text{Sr} = 0.720$; $^{143}\text{Nd}/^{144}\text{Nd} = 0.5118$; Hofmann, 1997). Dashed lines show the model values of BSE (Bulk Silicate Earth) and CHUR (Chondritic Uniform Reservoir) calculated at 85 Ma. DMM, HIMU, EM-I e EM-II are mantle end-member components from Hart *et al.* (1992).

Fig.6. $^{143}\text{Nd}/^{144}\text{Nd}_i$ vs $^{87}\text{Sr}/^{86}\text{Sr}_i$ showing in detail the Catalão I isotopic data (Symbols as in Fig. 5). The APIP phlogopite picrites compositional trend (Fig. 5) is extended by the grading grey field. Label numbers close to whole-rock symbols are the respective $\delta^{18}\text{O}_{\text{V-SMOW}}$ values. Oxygen isotope data are from Table 2 (bold numbers) and from Cordeiro *et al.* (2011b). Nd and Sr isotope data sources are the same of Fig. 5. All radiogenic isotope data were recalculated at 85 Ma as in Fig. 5. Inset shows an illustration of the two possible arrays (paths A and B) and their postulated relationship with three distinct isotopic components (see text for details).

Fig.7. Schematic evolution of the Catalão I complex (see text for details). Grey boxes represent the studied late-stage rocks. FC, fractional crystallization; LI, liquid immiscibility.

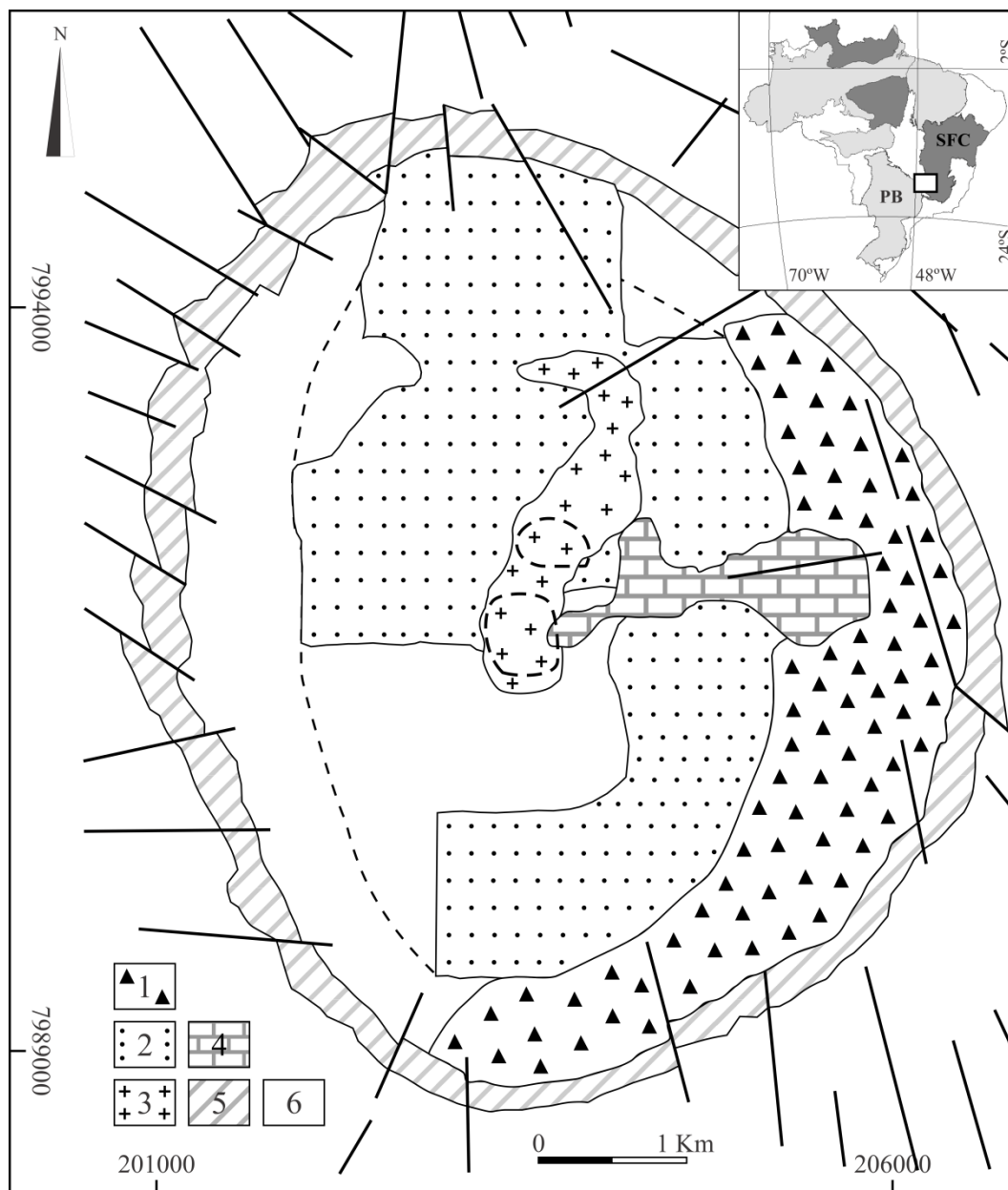


Figure 1

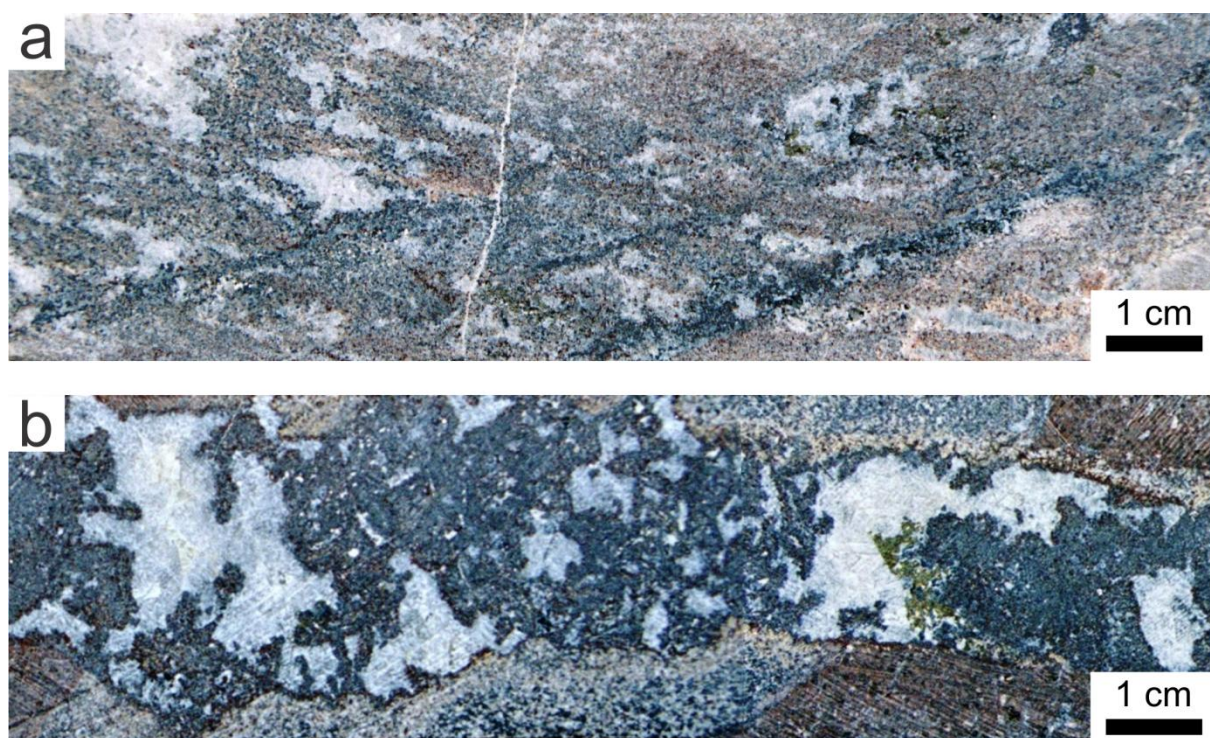


Figure 2

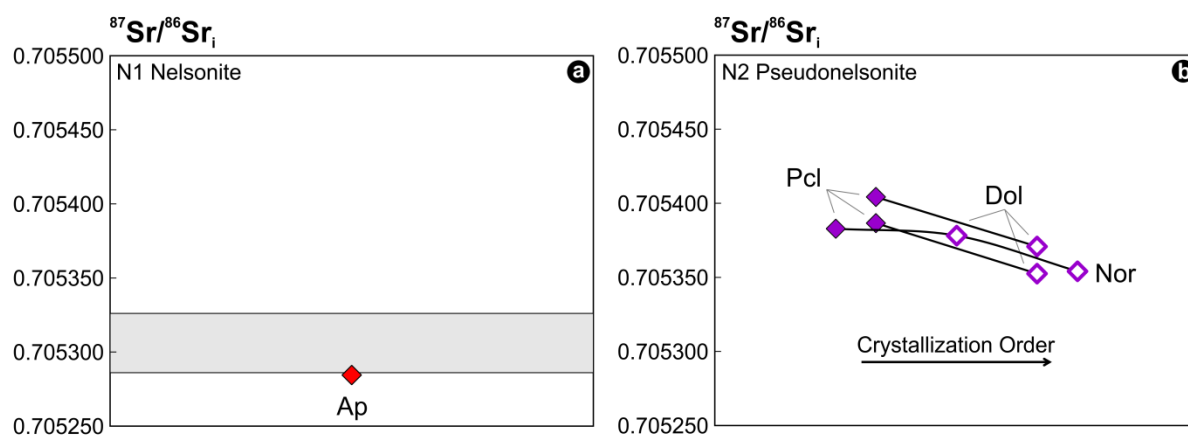


Figure 3

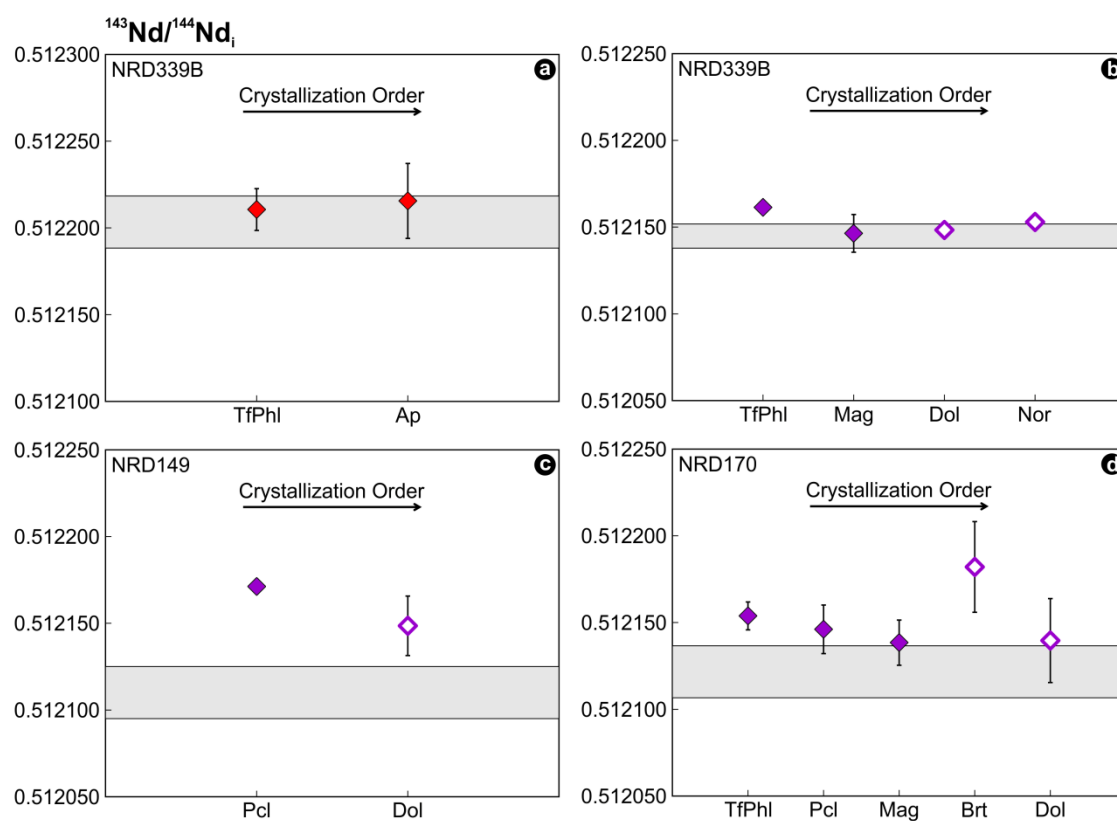


Figure 4

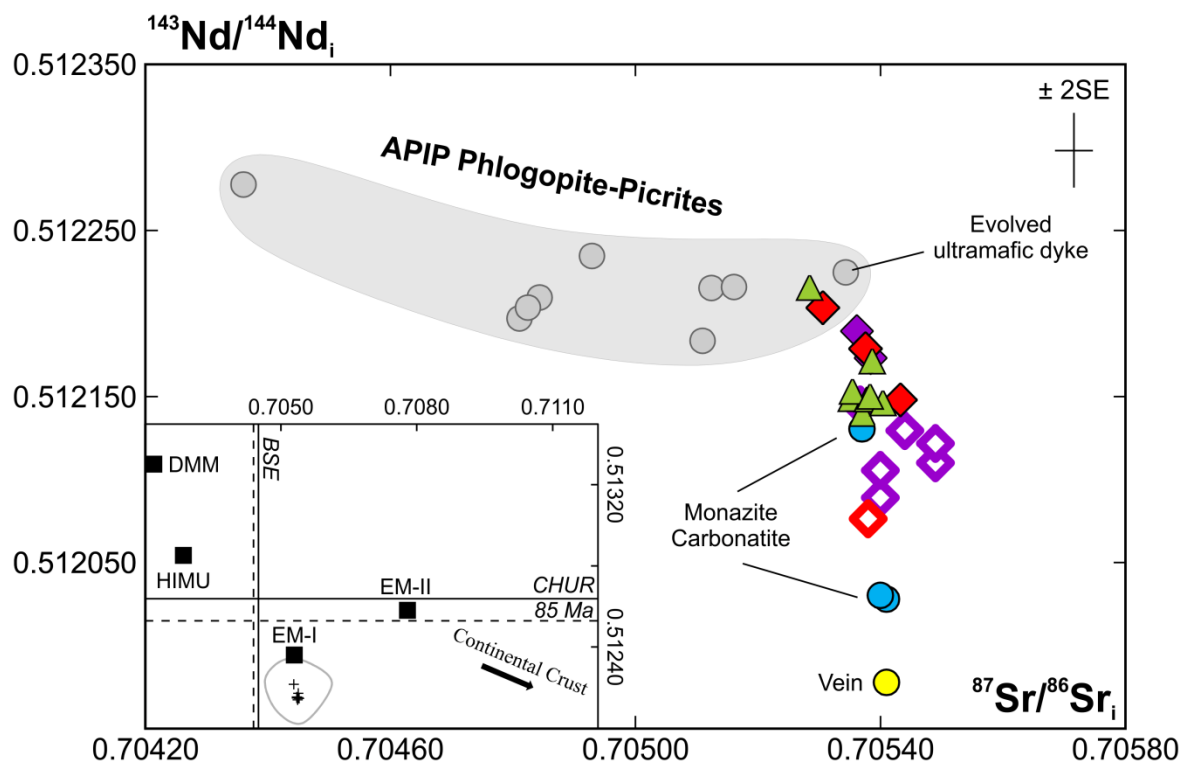


Figure 5

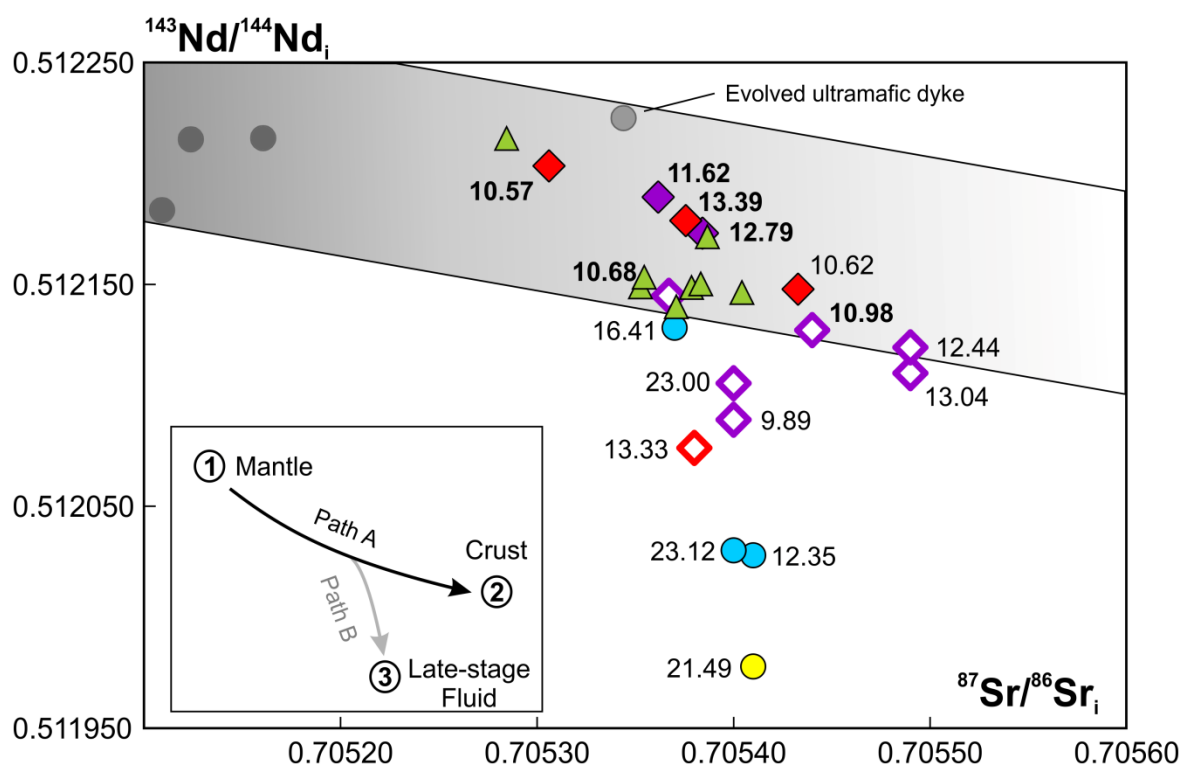


Figure 6



Figure 7

Table 1: Sr and Nd isotopic data of the Catalão I samples.

Sample	Mineral	Unit	Sm ^a	Nd ^a	¹⁴⁷ Sm/ ¹⁴⁴ Nd ^b	¹⁴³ Nd/ ¹⁴⁴ Nd _m ^c	¹⁴³ Nd/ ¹⁴⁴ Nd _i ^d	⁸⁷ Sr/ ⁸⁶ Sr _m ^c	⁸⁷ Sr/ ⁸⁶ Sr _i ^d
NRD339B	Ap	N1	243.58	1940.57	0.0759	0.512258 ± 0.000022	0.512216	0.705284 ± 0.000003	0.705284
NRD339B	Tfphl	N1	11.43	86.63	0.0798	0.512255 ± 0.000012	0.512211	-	-
NRD149	WR	N2	93.7	817.8	0.0692	0.512212 ± 0.000023	0.512173	0.705420 ± 0.000010	0.705384
NRD149	Pcl	N2	386.31	4353.09	0.0536	0.512201 ± 0.000003	0.512171	0.705387 ± 0.000003	0.705387
NRD149	Dol	DC	8.88	81.63	0.0657	0.512185 ± 0.000017	0.512149	0.705353 ± 0.000003	0.705353
NRD170	Mag	N2	31.61	323.45	0.0591	0.512171 ± 0.000013	0.512138	-	-
NRD170	Pcl	N2	404.57	4983.03	0.0491	0.512173 ± 0.000014	0.512146	0.705404 ± 0.000003	0.705404
NRD170	Tfphl	N2	0.99	8.86	0.0676	0.512191 ± 0.000008	0.512154	-	-
NRD170	Dol	DC	13.00	105.84	0.0742	0.512181 ± 0.000024	0.512140	0.705371 ± 0.000002	0.705371
NRD170	Brt	DC	3.49	30.40	0.0694	0.512221 ± 0.000026	0.512182	-	-
NRD339B	Mag	N2	5.95	66.78	0.0538	0.512176 ± 0.000011	0.512146	-	-
NRD339B	Tfphl	N2	0.66	6.61	0.0600	0.512195 ± 0.000006	0.512161	-	-
NRD339B	Pcl	N2	-	-	-	-	-	0.705383 ± 0.000003	0.705383
NRD339B	WR	DC	11.2	123.8	0.0548	0.512175 ± 0.000007	0.512145	0.705367 ± 0.000006	0.705367
NRD339B	Dol	DC	6.14	44.95	0.0826	0.512194 ± 0.000009	0.512148	0.705379 ± 0.000006	0.705379
NRD339B	Nor	DC	75.18	556.63	0.0817	0.512198 ± 0.000008	0.512153	0.705355 ± 0.000004	0.705355

^a Sm and Nd concentrations (in ppm) determined by isotopic dilution.

^b Atomic ratios calculated from Sm and Nd concentrations according to Gioia and Pimentel (2000).

^c Measured ratios normalized to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 and ⁸⁸Sr/⁸⁶Sr = 8.375209 using an exponential law; errors are two standard errors (2SE) of the in-run means, at 95% confidence level (2σ).

^d Initial ratios calculated at 85 Ma using the ¹⁴⁷Sm decay constant of 6.54 × 10⁻¹² a⁻¹ (Lugmair and Marti, 1978) and the ⁸⁷Rb decay constant of 1.393 × 10⁻¹¹ a⁻¹ (Nebel *et al.*, 2011).

WR, whole-rock; Ap, apatite; Brt, barite; Dol, dolomite; Mag, magnetite; Nor, norsethite; Pcl, pyrochlore; Tfphl, tetraferriphlogopite.

- not determined.

Table 2: C and O isotopes of carbonates from Catalão I late-stage rocks.

Sample	Rock Type	$\delta^{13}\text{C}$ (V-PDB)	$\delta^{18}\text{O}$ (V-SMOW)
339	N1	-6.15	10.57
230A	N1	-5.86	13.39
149	N2	-6.26	12.79
304BR	N2	-6.16	11.62
304BG*	DC	-5.82	10.98
NRD339B	DC	-5.99	10.68

* Unpublished data from Cordeiro (2009).

HIGHLIGHTS

- Nd and Sr isotopic compositions in mineral separates of the late-stage rocks.
- Isotopic signatures become more enriched from early to later nelsonites.
- Evidence of several batches of carbonate melts with different $^{87}\text{Sr}/^{86}\text{Sr}_i$.
- Two distinct evolution paths for the most evolved rocks emerge from Nd-Sr isotopes.
- AFCLI model evolution and subsolidus interaction with carbo-hydrothermal fluids.