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Oxygen isotope compositions and magmatic epidote from two contrasting metaluminous granitoids, NE Brazil

Abstract Oxygen isotope compositions of mineral separates were determined from two metaluminous granitoids (Emas and São Rafael plutons) from northeastern Brazil. The I-type Emas pluton has high $\delta^{18}O$ (WR) values (11.5–11.8‰), whereas the São Rafael pluton has low $\delta^{18}O$ (WR) values (7.5–8.1‰), but Sr and Nd are characteristics of S-type granitoids. Measured mineral–mineral fractionations suggest continuous sub-solidus inter-mineral isotope exchange among all minerals except zircon. There is a large and consistent quartz–epidote fractionation that gives apparent temperatures that are much lower than anticipated closure temperatures for epidote. Oxygen isotope fractionation between natural zircon and magmatic epidote is opposite to that predicted from theoretical determinations, as $\delta^{18}O$ (epidote) $< \delta^{18}O$ (zircon). An empirical calibration based on these results would suggests a closure T for oxygen in epidote of ~500 °C and Δ(qtz–epi) ~5.19 at 500 °C.

Introduction

Interest in magmatic epidote in granitic rocks has arisen in the last two decades since the experiments by Naney (1983) showed that the crystallization of epidote in magmas of granodiorite composition occurs at 6–8 kbar

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pressure. Zen and Hammarstrom (1984) emphasized the petrologic importance of magmatic epidote, and described textural criteria to identify magmatic epidote. Since then, many occurrences of magmatic epidote in granitoid rocks have been cited (e.g., Saavedra et al. 1987; Vyhnal et al. 1991; Farrow and Barr 1992; Schmidt and Thompson 1996; Sial et al. 1999). Most magmatic epidote crystallizes at near-solidus temperatures (e.g., Zen and Hammarstrom 1984; Schmidt and Thompson 1996; Sial et al. 1999), but Dawes and Evans (1991) reported early-crystallized epidote.

Few experiments have been run to establish the magmatic conditions for the crystallization of epidote. Naney (1983) demonstrated that epidote can be stable above the solidus in granites and granodiorites. Schmidt and Thompson (1996) showed that the minimum crystallization pressure of magmatic epidote depends on f_{O2}: when f_{O2} is high, near the magnetite–hematite buffer, the stability of epidote is expanded down to 3 kbar. Experiments on epidote dissolution kinetics (Brandon et al. 1996) indicate that epidote dissolution in granitic magmas is relatively fast. The presence of magmatic epidote in calc-alkalic granitoids implies rapid upward transport of magma or crystallization at high pressure. This would explain why plutons of similar chemical composition, which crystallized at similar pressure, may or may not bear magmatic epidote. Knowing the epidote dissolution rate and estimating the initial size of partially corroded epidote grains, the minimum speed of upward magma migration can be estimated (e.g., Sial et al. 1999). Epidote in slowly rising magmas, as in diapiric emplacement, is resorbed before the final crystallization. Fast migrating rapidly cooled magmas (diking) can preserve epidote grains before their complete resorption. Thus, magmatic epidote can be used as a time–pressure indicator in monitoring ascent rates of magmas.

The diffusion rates of oxygen under hydrothermal conditions indicate that zircon and titanite have slow diffusion rates (Watson and Chernick 1997; Peck et al. 2003), and among common minerals in a granitic rock,

such as hornblende, quartz, biotite, and feldspar, zircon and titanite are the first two minerals to close to oxygen diffusion during cooling. Data from natural titanite and zircon confirms that these are refractory phases to oxygen isotope exchange. Zircon has been shown to retain the magmatic oxygen isotope ratios in spite of events of metamorphism, magmatic contamination, and hydrothermal alteration (e.g., Valley et al. 1994; King et al. 1997; Monani and Valley 2001; Peck et al. 2003; see Valley 2003).

Theoretical calculations suggest that epidote is also a refractory phase to diffusive exchange of oxygen after crystallization (Fortier and Giletti 1989; Zheng and Fu 1998). However, few oxygen isotope data are available for natural igneous and metamorphic epidote. Experimental data are limited to the fractionation of zoisite and water (Matthews et al. 1983). Quartz–epidote and quartz–zoisite oxygen isotope fractionations calculated on the basis of the modified increment method are provided by Zheng (1993), and Matthews (1994) reports a coefficient for quartz–epidote that takes into account the pistacite content of epidote.

Keane and Morrison (1997) reported analyses on four textural varieties of epidote from the Mount Lowe quartz monzonite, California, in an attempt to discriminate between magmatic and subsolidus growth. Their work shows that both euhedral and anhedral epidote can have magmatic $\delta^{18}O$ values, and thus textural criteria alone are equivocal for distinguishing igneous vs. subsolidus epidote. Values of $\delta^{18}O$ for epidote and coexisting quartz, plagioclase, and biotite of rhyolites, rhyodacites, and tonalites are provided by Morrison et al. (1999). They found that oxygen isotope fractionations between quartz and magmatic epidote are quite different for the volcanic and plutonic rocks, and concluded that these differences reflect a combination of distinct crystallization temperatures and cooling rates, and variable post-crystallization diffusion.

In this paper, we report and discuss oxygen isotope compositions and fractionations of coexisting magmatic epidote, zircon, titanite, and quartz, from two compositionally contrasting granitoids crystallized at different pressures (Emas and São Rafael plutons) in the Borborema province, northeastern Brazil. We investigate magmatic and post-magmatic isotopic exchange of zircon, titanite, and quartz, besides epidote. Knowledge of exchange kinetics permits estimation of magmatic $\delta^{18}O$, which is important for determining the source of high and normal $\delta^{18}O$ I-type granitoids.

General geology

The major structural framework of the Borborema province, northeastern Brazil (Fig. 1), was attained during the Neoproterozoic through the reworking and amalgamation of several tectonostratigraphic terranes and major crustal blocks, previously deformed

during Meso and Paleoproterozoic orogenic cycles (Santos 1995). A large volume of diverse granitic magmatism in this province records the tectono-thermal evolution of the two major orogenic cycles in the region: Cariris Velhos (1.1–0.95 Ga) and Brasiliano (0.73–0.52 Ga). Undeformed Brasiliano-age granitoids are by far the most voluminous in the region, and among them six major petrological/geochemical types are recognized (Ferreira et al. 1998). Magmatic epidote is recorded in calc-alkalic, high-K calc-alkalic, shoshonitic, and trondhjemitic granitoids, which are intrusive into five different tectonostratigraphic terranes of this province.

Epidote-bearing calc-alkalic granitoids intruded low-grade metaturbidites in the Cachoeirinha-Salgueiro terrane, and they are regionally known as "Conceição-type granitoids" (Sial 1990), whereas high-K calc-alkalic granitoids intruded into gneisses and migmatites in the Seridó terrane, as well as other terranes (e.g., Alto Pajeu terrane). The Seridó and Cachoeirinha-Salgueiro terranes are adjacent NE–SW elongate belts separated by the E–W-trending Patos shear zone (Fig. 1).

Sedimentary-volcanic sequences in the Cachoeirinha-Salgueiro terrane record the opening of a rift in the Mesoproterozoic (1.1–1.15 Ga), subduction and magmatic arc development (1.03–0.98 Ga), and its closure, constituting the Cariris Velho orogeny (de Brito Neves et al. 1995). The basal, rift-stage sedimentary sequence (pelites, graywackes) was deposited in a shallow-water marine environment, and is characterized by bimodal volcanism, and low- to intermediate-grade metamorphism. This unit overlies a sequence of low-grade metapelites, banded iron formation, and basaltic-andesitic metavolcanic rocks. Lower continental platform unit (metaturbidites), and a deep-marine water unit (metarhythmites) overly these sequences, with a final deposition at around 0.95 Ma, during the collisional stage (Campos Neto et al. 1994).

The Seridó terrane is a collisional and transpressive belt inprinted over reworked Archean and Paleoproterozoic terranes (Santos et al. 2001). Accretion of juvenile crust around 3.2 and 2.0 Ga characterizes this terrane, which includes a platformal-like Jucurutu–Equador supracrustal sequence, probably of Neoproterozoic age, and a turbiditic-filled Neoproterozoic Seridó sequence. The Cachoeirinha-Salgueiro and Seridó terranes were reworked during the Brasiliano orogeny, during which a large volume of granitic magmatism took place.

In this study, one representative epidote-bearing granitic pluton from the Seridó terrane (São Rafael pluton) and one from the Cachoeirinha-Salgueiro terrane (Emas pluton) are examined in detail for oxygen isotope ratio. These plutons were chosen because they are known to be contrasting in terms of heavy radiogenic isotope signatures, even though both carry magmatic epidote, and have similar geochemical (major elements) compositions.

Fig. 1 Geological map of the Neoproterozoic Borborema province, northeastern Brazil, emphasizing the Brasiliano-age granitoids and syenites, the Emas and São Rafael plutons. *1* Phanerozoic undeformed sedimentary cover; *2* major shear zones and terrane boundaries; *3* magmatic epidote-bearing granitoids; *4* other granitoids and syenitoids; *5* São Francisco craton. *SD* Seridó terrane; *CS* Cachoeirinha-Salgueiro terrane; *AP* Alto Pajeú terrane and the Emas and São Rafael plutons (from Ferreira et al. 1998)
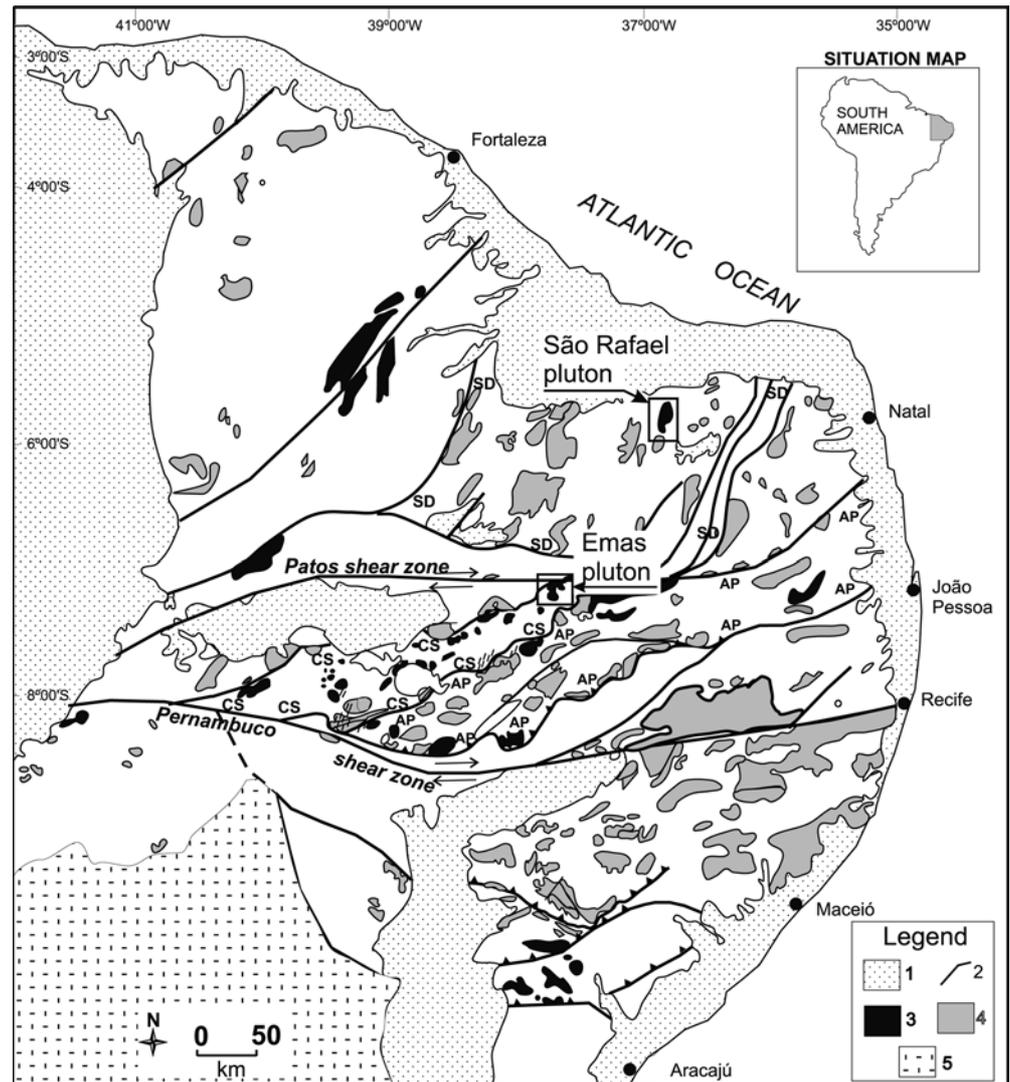
Petrology and geochemistry

Emas pluton

The elongate Emas pluton (Fig. 2) consists of unfoliated, medium-grained equigranular tonalites to granodiorites that intruded low-grade metapelites of the Cachoeirinha-Salgueiro terrane. The tonalites-granodiorites are composed of zoned plagioclase, quartz, calcic amphibole, biotite, microcline, epidote, sphene, zircon, and apatite. Iron oxides are rare to absent. Angular, fine-grained, up to 15 cm long amphibole-rich clots and microgranular mafic inclusions are common in this pluton, and are observed either within quartz diorite enclaves or in the host granodiorite, many times fringed by biotite or amphibole. Sial et al. (1998), on the basis of textural relationships and mineral chemistry, proposed that these clots are fragments derived from the source rock (metabasalts). This conclusion and the mineral assemblage for the Emas granitoid indicate an I-type granite, according to the Chappell and White (1974)

classification. Low magnetic susceptibility ($0.15–0.40 \times 10^{-3}$ SI) is a characteristic of all plutons of this type thus far studied in the Cachoeirinha-Salgueiro terrane (Sial et al. 1999), which is compatible with low modal contents of magnetite.

São Rafael pluton

The São Rafael batholith (Fig. 3) is a N–S elongated pluton that has intruded biotite schists of the Seridó Formation along its eastern margin, and gneisses of the Jucurutu Formation along the northern and western contacts. It is a composite batholith containing two major intrusions: one, the Serra pluton, is medium-grained equigranular two-mica granite forming the southern part of the batholith. The northern portion is porphyritic quartz monzonite to granite (Sial 1990). The porphyritic pluton is characterized by microcline megacrysts up to 4 cm long that often exhibit inclusions of biotite in rows parallel to the feldspar faces, and that are randomly oriented in a coarse-grained

Fig. 2 Simplified geological map of the Emas pluton, Cachoeirinha-Salgueiro terrane, Borborema province, northeastern Brazil (modified from da Silva Filho 1985), showing the location of the studied samples
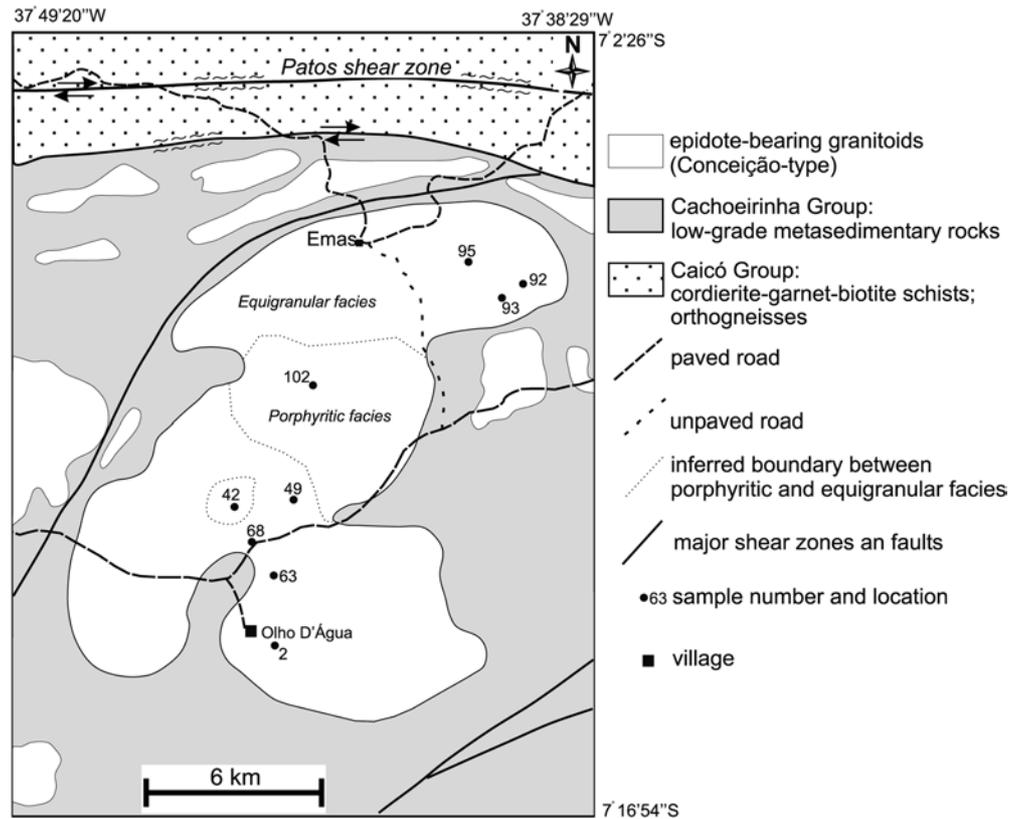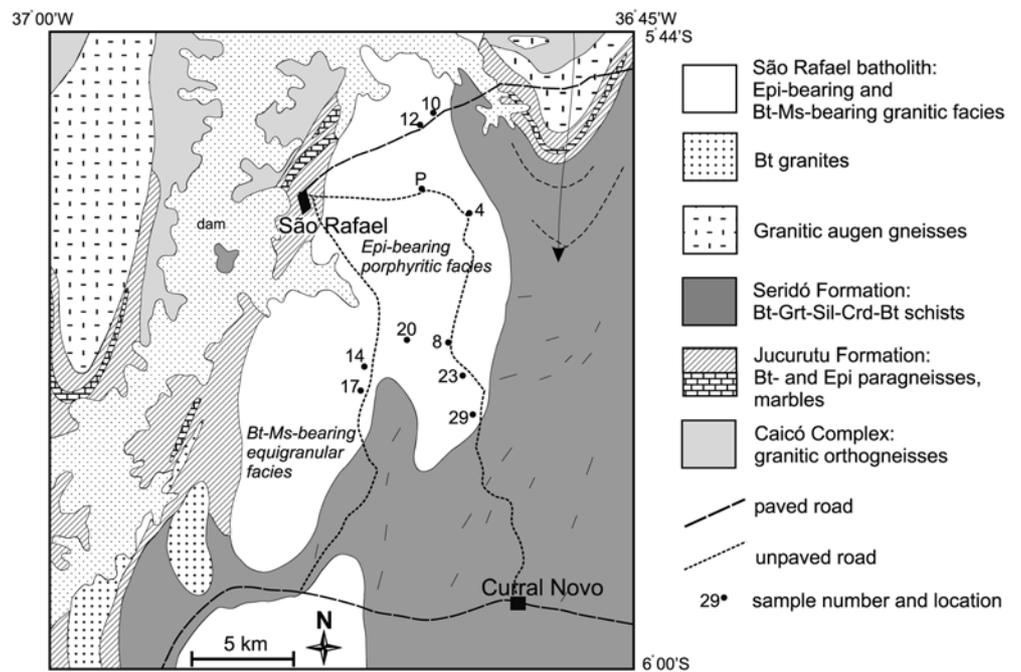

Fig. 3 Simplified geological map of the São Rafael pluton (modified from Jardim de Sá 1994), Seridó terrane, Borborema province, northeastern Brazil, showing the location of the studied samples. *Epi* Epidote; *Bt* biotite; *Ms* muscovite; *Grt* garnet; *Sil* sillimanite; *Crd* cordierite

equigranular groundmass. The groundmass is composed of zoned microcline and plagioclase, quartz, biotite, hornblende, epidote, titanite, apatite, allanite within epidote and as isolated crystals, zircon, and magnetite. Locally, this epidote-bearing porphyritic granitoid contains quartz diorite enclaves that show pillow-like or stromatic structures. High magnetic susceptibility for this pluton (1.0–4.0×10^{-3} SI; Sial et al. 1999) is compatible with higher modal magnetite than in the Emas pluton.

Epidote and Al-in-hornblende barometry

In these two plutons, epidote occurs in four different textural relationships (Fig. 4): (1) euhedral to subhedral, enclosed or partially enclosed by biotite, up to 2 mm long, is the most common type; (2) euhedral to subhedral, with euhedral allanite core, totally rimmed by biotite; (3) euhedral to subhedral, sometimes elongate
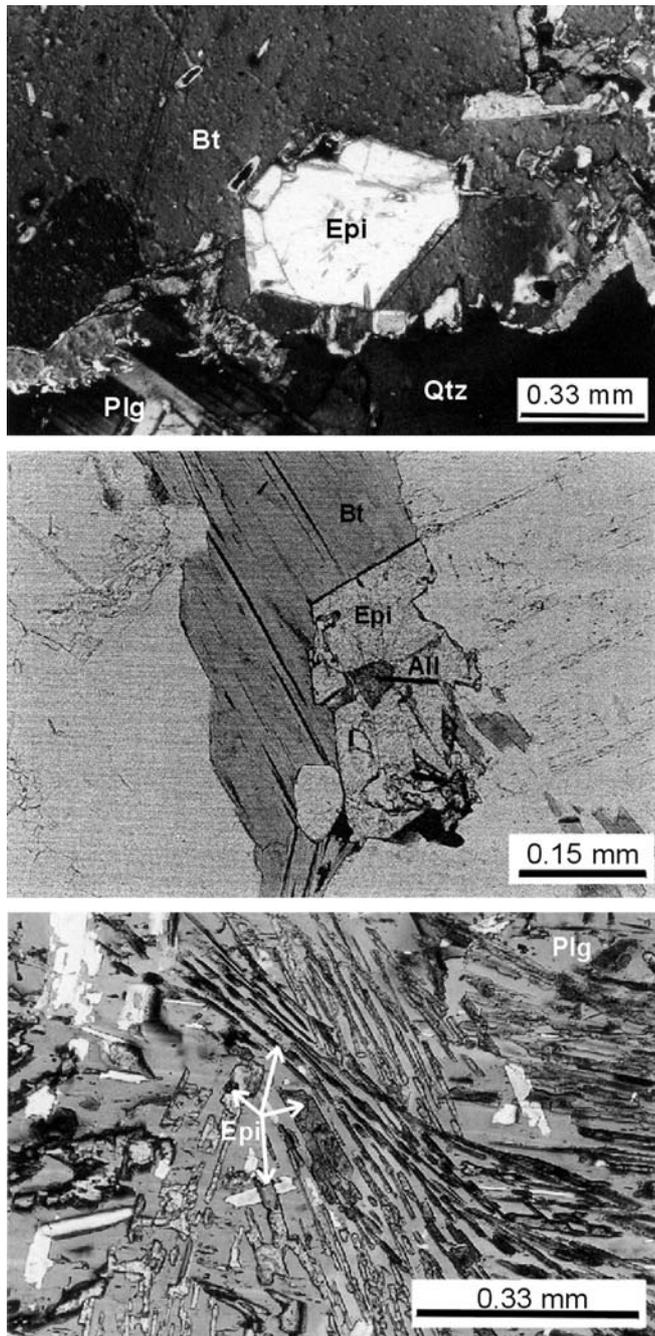

Fig. 4a–c Textural relationships of magmatic epidote from the Emas and São Rafael granitoids. **a** euhedral epidote enclosed by biotite (Emas pluton); **b** epidote with allanite core enclosed by biotite (São Rafael pluton); **c** elongate and needle-like epidote included in plagioclase crystal (Emas pluton)

crystals, with length/width of 3/1 to 10/1, included in the core of plagioclase phenocrysts; and (4) granular, along the boundary of amphibole in contact with plagioclase (Sial 1990). The first two types are believed to be magmatic in origin, on the basis of textural relationships and mineral chemistry (Sial 1993; Sial et al. 1999). The last two are found in the Emas pluton only, and the last one is thought to be of subsolidus growth.

Al-in-hornblende pressure estimates (Schmidt 1992), indicate that the Emas pluton solidified between 6 and 9 kbar, and the São Rafael pluton between 3 and 5 kbar (Sial 1993). Kyanite-bearing thermal aureoles were developed around two granitoids similar to the Emas pluton in the Cachoeirinha-Salgueiro terrane. Metamorphic equilibria constrains T $\sim$670 °C and P = 7.5 ± 0.5 kbar (Caby and Sial 1997; Sial et al. 1999), compatible with the pressure estimate for the Emas granitoid. The calculated pressure for the São Rafael pluton is in agreement with pressure estimates for the nearby metapelites of the Seridó Group (3–4 kbar, de Lima 1987).

Magmatic epidote in the Emas granitoid displays a composition of Ps_{20-24}, and in the São Rafael pluton Ps_{27-29}, suggesting the latter crystallized under higher f_{O2} conditions (Sial et al. 1999). This is in agreement with a higher abundance of magnetite in the São Rafael granitoid and is consistent with its lower pressure, in accord to the experiments by Schmidt and Thompson (1996) that show that epidote can be stable at lower pressures in high f_{O2} conditions.

Geochemistry

Major and minor element chemistry (Sial 1990) indicates that the Emas granodiorite is metaluminous to slightly peraluminous, has $Na_2O < K_2O$, is Ba enriched (650–1,500 ppm), and has moderate Sr (500–1,250 ppm) and Zr (180 ppm) contents, and low Nb (< 20 ppm). A whole rock Rb–Sr isochron for the Conceição granodiorite, the representative pluton of this type in the Cachoeirinha-Salgueiro terrane, indicates an age of 633 ± 0.9 Ma and an initial $^{87}Sr/^{86}Sr$ of 0.70598 ± 0.00001 (Sial 1993). Hornblende and biotite have internally discordant $^{40}Ar/^{39}Ar$ age spectra, suggesting that initial post-magmatic cooling occurred between 625 (hornblende) and 604 Ma (biotite; Dallmeyer et al. 1987). This is compatible with high pressure crystallization, and indicates a cooling rate of ca. 15 °C/million years. Slightly negative ϵNd values (–1 to –2; Sial et al. 1999) suggest an I-type source for these granodiorites.

The porphyritic monzonitic pluton of the São Rafael batholith is metaluminous, and has higher Sr (600–1,000 ppm) and Zr (250 ppm) contents than the Emas pluton (Sial 1990). The Serra pluton of the São Rafael batholith has a Rb–Sr age of 0.6 Ga (Ketcham et al. 1995). The porphyritic epidote-bearing granitoid; however, has inhomogeneous initial Sr ratios, anomalous whole rock Sm–Nd data (that provide age of 1.1 Ga, inconsistent with field evidence for Neoproterozoic

emplacement of the pluton), and a discordant U–Pb zircon data consistent with presence of inherited component with 2.0 Ga minimum age, all indicating an inhomogeneous source. Strongly negative ϵNd (0.6 Ga) values (–18 to –21), Sm–Nd model age of 2.7 ± 0.3 Ga, and high initial $^{87}Sr/^{86}Sr$ (0.713 ± 0.001; projected back to 0.6 Ga), all suggest that the source rock was ancient radiogenic crust (Ketcham et al. 1995).

Only samples from the porphyritic epidote-bearing granitoid of the São Rafael batholith, hereafter called São Rafael batholith, were analyzed in this work.

Oxygen Isotopes

Analytical techniques

Zircon, titanite, epidote, and quartz separates were obtained from several kilograms of sample using standard procedures including initial crushing, gold panning, sieving (300 μm mesh), and heavy liquid and Frantz magnetic separations. Final hand picking under a binocular microscope ensured purity of mineral separates. Epidote grains with visible allanite cores as well as titanite with opaque mineral inclusions, were excluded. Zircon samples were cleaned in cold hydrofluoric acid, followed by cold sulfuric acid, and hot nitric acid when sulfides were present. Only the least magnetic fraction of zircon was analyzed. This procedure has been shown to remove mineral impurities and radiation damaged zircons without altering $\delta^{18}O$ of residual zircon (Valley et al. 1994; King et al. 1998).

Oxygen isotope ratios of 1–2 mg mineral separates (2–3 mg for zircon) were analyzed at the University of Wisconsin by laser fluorination. Oxygen was liberated by reaction with BrF_5, reacted with hot graphite, and converted into CO_2, following the procedures described by Valley et al. (1995). Values of $\delta^{18}O$ were determined in a Finnigan MAT 251 mass-spectrometer. On each analysis day, four to six aliquots of UWG-2 garnet standard were analyzed, and daily precision averaged $0.06 \pm 0.03\%_0$. Daily averages of UWG-2 differed by 0.02–$0.28\%_0$ from the accepted value of $5.80\%_0$ VSMOW, and mineral analyses of samples have been corrected, as described in Valley et al. (1995). Quartz was analyzed using the rapid heating and defocused laser beam technique as described by Spicuzza et al. (1998). Zircon grains were crushed in a boron carbide mortar and pestle before loading. Two zircon samples from the Emas plutons (E-49, E-92) and four from the São Rafael pluton (DSR-4, DSR-14, DSR-23, DSR-29) were analyzed in duplicate, yielding an average reproducibility of $\pm 0.04\%_0$. All results are reported in the standard notation, in permil relative to Vienna standard mean ocean water (VSMOW). Measured oxygen isotope compositions of zircon, titanite, epidote, and quartz, and calculated apparent temperatures for the different mineral-pair fractionations, are listed in Table 1. Sample locations are shown in Figs. 2 and 3.

Oxygen isotope ratios

Values of $\delta^{18}O$ of the different minerals are homogeneous within each pluton, but quite different between the plutons. Values for all minerals are higher in the Emas pluton than in the São Rafael batholith. Values of $\delta^{18}O$ (zircon) in the São Rafael pluton are very homogeneous (average $\delta^{18}O = 5.98 \pm 0.16\%_0$, for nine rocks collected as much as 12 km apart), in spite of the presence of inherited cores as suggested by U–Pb zircon data obtained by Ketcham et al. (1995). These $\delta^{18}O$ values are much lower that the average value in the Emas pluton [$\delta^{18}O$ (zircon) $= 10.04 \pm 0.21\%_0$; $n = 8$ rocks collected over 15 km apart].

The average oxygen isotope ratios for other minerals in the Emas pluton are $14.32 \pm 0.42\%_0$ (quartz), $9.17 \pm 0.51\%_0$ (epidote), and $8.79 \pm 0.13\%_0$ (titanite). These values are more variable than those for zircon, but are similar to the preliminary analyses reported by Sial (1990), who found average $\delta^{18}O$ (quartz) $= 14.30\%_0$ and $\delta^{18}O$ (epidote) $= 9.55\%_0$. The average $\delta^{18}O$ values in the São Rafael batholith are $9.81 \pm 0.41\%_0$ (quartz), $5.15 \pm 0.25\%_0$ (epidote), and $4.83 \pm 0.19\%_0$ (titanite).
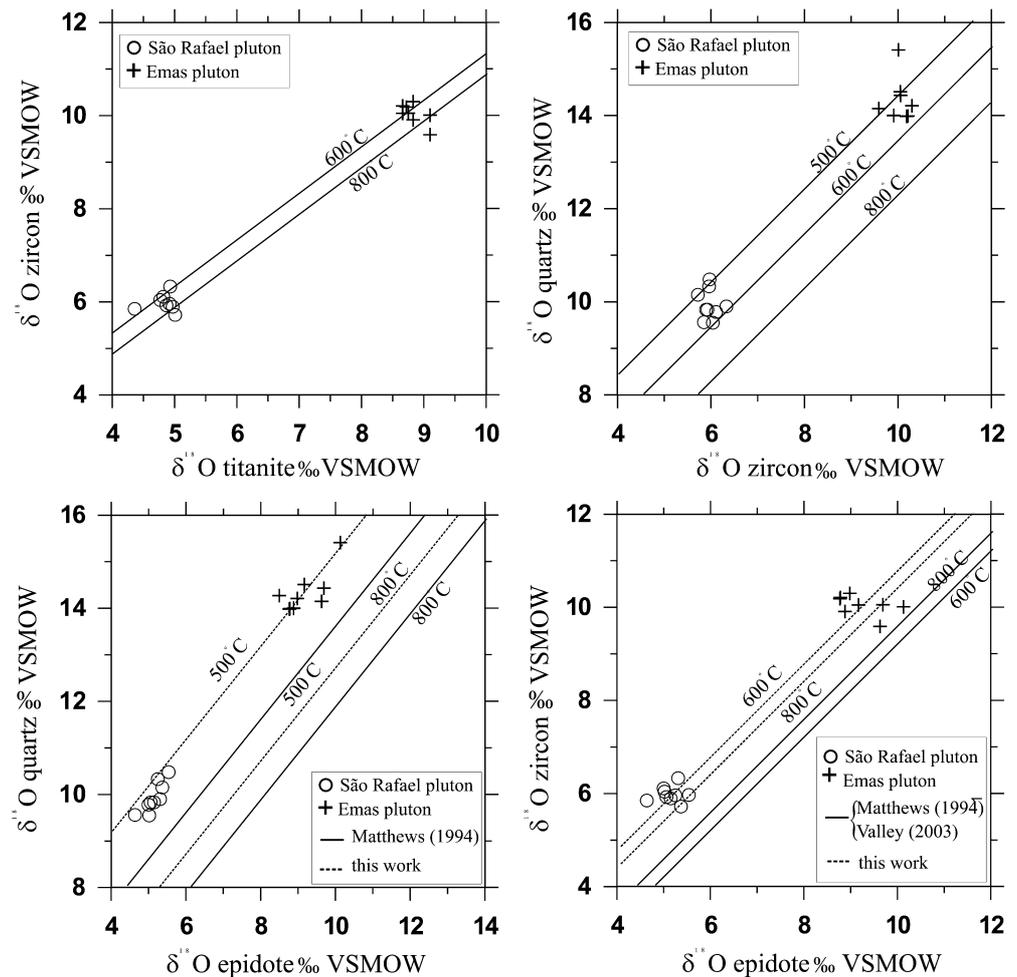
Oxygen isotope fractionation among minerals

Measured oxygen isotope fractionation of coexisting zircon and titanite (Fig. 5A) is highly consistent in the two plutons [Δ(zircon–titanite) $= 1.15 \pm 0.25\%_0$ (1SD) and $1.21 \pm 0.34\%_0$ (1SD) for the São Rafael and Emas plutons, respectively], in spite of a $4\%_0$ difference in absolute $\delta^{18}O$. These fractionations are larger than the expected values for Δ(zircon–titanite) in equilibrium, estimated to be $0.88\%_0$ at 800 °C (King et al. 2001). Average calculated apparent temperatures are 618 ± 85 °C for the Emas pluton and 690 ± 117 °C for the São Rafael granitoid. These lower than expected temperatures may be due to different closure temperatures for oxygen isotope exchange, which for zircon can be as high as liquidus temperatures (see cooling history discussion later in this paper).

The average quartz–mineral fractionation is higher in both plutons than predicted for equilibrium at magmatic temperatures of 800 °C. Samples from the Emas pluton have an average Δ(quartz–zircon) of $4.30 \pm 0.50\%_0$, and from the São Rafael pluton the average is $3.96 \pm 0.36\%_0$. Values of $\delta^{18}O$ for coexisting quartz–zircon (Fig. 5B) define a trend almost parallel, but at lower temperature than the isopleth for equilibrium fractionation at 800 °C [Δ(quartz–zircon) $= 2.29\%_0$; calculated after Valley et al. (2003)], suggesting elevation of the $\delta^{18}O$ quartz values relative to those for zircon by post-magmatic exchange of quartz, feldspar, and mica. The measured quartz–zircon fractionations yield average apparent temperatures of 514 °C for the Emas granitoid and of 546 °C for the São Rafael pluton, compatible with oxygen isotope closure temperature of quartz [461 °C, calculating using experimental data for oxygen diffusion in quartz at $P_{(H2O)} = 1$ kbar, the Dodson (1973) closure temperature

Table 1 Oxygen isotope ratios (‰ VSMOW) of mineral separates from the São Rafael and Emas plutons of the Borborema province, northeastern Brazil. Apparent temperatures calculated according to: King et al. (2001) *1* zircon–titanite; Valley et al. (2003) *2* quartz–titanite; *3* quartz–zircon; this work *4* quartz–epidote; (see text for discussion); Watson (1987) *5* zircon saturation. δ18O (WR) values calculated after Valley et al. (1994) with a correction for the composition of garnet (Kohn and Valley 1998). SiO$_2$ and Zr values marked with * are from Goist (1989); all others are from this work. *SR* and *DSR* São Rafael pluton samples; *E* Emas pluton samples

	$\delta^{18}O$ zir	$\delta^{18}O$ ttn	$\delta^{18}O$ qtz	$\delta^{18}O$ epi	Δ(zir-ttn)	Zir-ttn (1) (°C)	Δ(qtz-ttn)	Qtz-ttn (2) (°C)	Δ(qtz-zir)	Qtz-zir (3) (°C)	Δ(qtz-epi)	Qtz-epi (4) (°C)	SiO$_2$ (wt%)	Zr (ppm)	Zir. sat. (5) (°C)	Calculated $\delta^{18}O$ (WR)
SR-P	6.04	4.77	9.55	5.02	1.33	603	4.78	602	3.51	594	4.72	537	-	-	-	-
DSR-4	5.85	4.36	9.56	4.64	1.49	554	5.20	566	3.71	570	4.92	521	68.47	202	814	7.6
DSR-8	5.97	-	10.48	5.54	-	-	-	-	4.51	491	5.00	514	65.21	154	789	7.5
DSR-10	6.11	4.82	9.78	5.00	1.29	616	4.96	586	3.67	575	4.78	532	69.45	151	788	8.0
DSR-12	5.96	4.92	10.33	5.25	1.04	717	5.41	549	4.37	504	5.08	508	71.95	146	785	8.0
DSR-14	5.72	5.01	10.15	5.37	0.71	926	5.14	571	4.43	499	4.78	532	72.83	182	804	7.8
DSR-17	6.33	4.93	9.90	5.31	1.40	581	4.97	585	3.57	587	4.59	549	70.63	180	803	8.2
DSR-23	5.90	4.97	9.83	5.15	0.93	774	4.86	595	3.94	545	4.68	541	71.17	161	793	7.9
DSR-29	5.93	4.87	9.83	5.06	0.99	742	4.96	586	3.91	549	4.77	541	-	-	-	-
Average	5.98 ± 0.16	4.83 ± 0.19	9.81 ± 0.41	5.15 ± 0.25	1.15 ± 0.25	689 ± 117	5.04 ± 0.19	580 ± 17	3.96 ± 0.36	546 ± 39	4.81 ± 0.15	531 ± 13	69.96 ± 2.4	168 ± 20	797 ± 10	7.9 ± 0.2
E-02	9.59	-	14.15	9.63	-	-	-	-	4.56	488	4.52	555	64.52*	210*	817	11.2
E-42	10.01	9.10	15.41	10.13	0.91	786	6.31	488	5.40	426	5.28	493	-	-	-	-
E-49	10.06	8.75	14.43	9.69	1.31	609	5.68	530	4.38	503	4.74	536	62.04	217	820	11.5
E-63	10.30	8.83	14.21	8.98	1.47	560	5.38	552	3.91	549	5.23	497	-	-	-	-
E-68	9.91	8.83	14.00	8.88	1.08	699	5.17	568	4.09	530	5.12	507	63.85	217	820	11.4
E-92	10.19	8.72	13.98	8.77	1.47	560	5.26	561	3.80	560	5.21	498	67.18*	189*	808	11.9
E-93	-	8.78	14.27	8.50	-	-	5.49	543	-	-	5.77	460	65.11	197	811	-
E-95	10.21	8.66	13.99	8.78	1.55	530	5.33	556	3.78	563	5.21	498	66.45	170	798	11.9
E-102	10.05	8.66	14.51	9.17	1.39	584	5.85	518	4.46	496	5.34	489	-	-	-	-
Average	10.04 ± 0.21	8.79 ± 0.13	14.32 ± 0.42	9.17 ± 0.51	1.21 ± 0.34	618 ± 85	5.56 ± 0.35	540 ± 26	4.30 ± 0.50	514 ± 46	5.16 ± 0.34	504 ± 26	64.86 ± 1.69	200 ± 18	812 ± 8	11.6 ± 0.3

Fig. 5a–d Plot of coexisting minerals for magmatic epidote-bearing granites from the Borborema province, NE Brazil: **a** $\delta^{18}O$(zircon) vs. $\delta^{18}O$(titanite). Isotherms for equilibrium fractionation are after King et al. (2001); **b** $\delta^{18}O$(zircon) vs. $\delta^{18}O$(quartz). Isotherms for equilibrium fractionation are calculated after Matthews (1994), Valley et al. (2003); **c** $\delta^{18}O$(quartz) vs. $\delta^{18}O$(epidote). Isotherms for equilibrium fractionation are calculated after Matthews (1994) and this study; **d** $\delta^{18}O$(epidote) vs. $\delta^{18}O$(zircon). Isotherms for equilibrium fractionation are calculated after Matthews (1994), Valley et 3al. (2003), and this study

for quartz at 2 mm diameter, and 15 °C/my cooling rate].

Oxygen isotope fractionation between quartz and titanite is large in both plutons [Δ(quartz–titanite) is 5.56 ± 0.35 and $5.04 \pm 0.19\permil$ for the Emas and São Rafael plutons, respectively], resulting in low average apparent temperatures of 540 and 580 °C (equation of Valley et al. 2003), again, probably because of post-magmatic exchange of quartz.

The average Δ(quartz–epidote) is also high ($5.16 \pm 0.34\permil$ for the Emas pluton and $4.81 \pm 0.15\permil$ for the São Rafael pluton), above the equilibrium fractionation at magmatic temperatures [Matthews 1994, at 800 °C Δ(qtz–epi) = 1.88 for Ps_{22}, and 1.92 for Ps_{28}]. This is illustrated in Fig. 5C that shows the fractionation equilibration curve for Ps_{22}. The application of the correction factor for different epidote pistacite contents makes no significant difference in the results. The measured average fractionations result in apparent temperatures below 400 °C for both plutons and this implies that $\delta^{18}O$ (epidote) values have suffered post-magmatic exchange.

Oxygen isotope fractionations between coexisting zircon and epidote are illustrated in Fig. 5D. In both plutons, $\delta^{18}O$(epidote) is lower than $\delta^{18}O$(zircon), with average Δ(zircon–epidote) = $0.87 \pm 0.60\permil$ for the Emas

pluton, and $0.83 \pm 0.28\permil$ for the São Rafael batholith. This fractionation is reversed from that expected for equilibrium between zircon and epidote, as estimated by combining published fractionation factors for zircon–grossularite [$1,000\ln\alpha(zrn–grs) = 0.39 \times 10^6/T^2$; Valley et al. 2003], quartz–grossularite [$(1,000\ln\alpha(qtz–grs) = 3.03 \times 10^6/T^2$); Matthews 1994], and quartz–epidote [$(1,000\ln\alpha(qtz–epi) = (2 + 0.75X_{Ps}) \times 10^6/T^2$]; Matthews 1994]. This yields an A-factor in the equation $1,000\ln\alpha$ (zir–epi) = $A \times 10^6/T^2$ for the equilibrium zircon–epidote of $-(0.64–0.75X_{Ps})$, i.e., $\delta^{18}O$(epidote) is expected to be higher than $\delta^{18}O$(zircon). The range in the measured $\delta^{18}O$(epidote) is large compared with the measured range of $\delta^{18}O$(zircon), especially in the Emas pluton, where the $\delta^{18}O$(epidote) range is 1.37‰, almost twice as high as the range for $\delta^{18}O$(zircon; 0.71‰), indicating that epidote does not preserve magmatic oxygen isotope ratios. This reversal is expected due to late exchange of epidote with higher $\delta^{18}O$ minerals such as quartz and feldspar.

Epidote grain size

Epidote samples analyzed in this study were hand picked after sieving (300-μm sieve), i.e., they represent a mixture

of grains < 300 μm in size. Textural relationships indicate that magmatic epidote grains, which are more abundant (up to 6%) than secondary epidote ($<<1\%$), are larger (average 670 μm) than the subsolidus crystals (average 280 μm). Grain size dependence of δ^{18}O(epidote) was tested in one sample from each pluton. Aliquots of sieved epidote (149–300 and <105 μm) were analyzed. Differences in the δ^{18}O values are not significant as Δ(small–large) are 0.30 and 0.09‰, for the São Rafael and Emas plutons, respectively, and values of δ^{18}O of mixed grains are close to those of larger epidote [Δ(mixed–large grains) is 0.17 and 0.14‰ for the São Rafael and Emas pluton, respectively]. These small differences in the oxygen isotope compositions suggest that there is no substantial influence of epidote grain size on the determined magmatic oxygen isotope compositions of mixed epidote grains. In any case, even if none of these oxygen isotope compositions represent the actual compositions of the magmatic epidote, all values are clearly systematically lower than δ^{18}O values of all other minerals (zircon, titanite, and quartz) in the two plutons, as discussed in the previous sections.

Significance of the δ^{18}O (epidote)

Theoretical calculations of oxygen diffusion rates suggest that epidote is a refractory phase to diffusive exchange at lower temperatures after crystallization (Fortier and Giletti 1989; Zheng and Fu 1998). The systematic mineral fractionations observed in this study suggest that δ^{18}O(epidote) reflects subsolidus diffusive exchange at high temperature during slow cooling.

King and Valley (2001) found δ^{18}O(epidote) values lower than those for coexisting δ^{18}O (zircon) for the Atlanta lobe of the Idaho batholith, western USA, with Δ(zircon–epidote) ranging from 0.68 to 1.40 and Δ(quartz–epidote) varying from 4.35 to 4.49. The quartz–epidote fractionations yield subsolidus temperatures from 420–440 °C (Matthews 1994), assuming $Ps_{20–30}$. Apparent temperatures estimated using the equation of Zheng (1993) are still lower (370–380 °C).

Morrison et al. (1999) found Δ(quartz–epidote) of 3.1 ± 0.12 for rapidly cooled Sutter Butte rhyolites, 3.12 ± 0.06 for Boulder County rhyodacites, and 4.19 ± 0.17 for Ellicott City tonalites, USA. All epidote were interpreted as magmatic. Applying the equation of Matthews (1994), low temperatures would be estimated even for the quenched volcanic rocks (560–574 °C for $Ps_{20–30}$), which are thought to preserve the magmatic oxygen isotope composition. Using the equation of Zheng (1993), the apparent temperature for the volcanic rocks is 543 °C. This finding suggests that both Matthews (1994) and Zheng (1993) equations yield Δ(quartz–epidote) values that are too small.

In an attempt to better estimate the natural quartz–epidote fractionation, data reported by Morrison et al (1999) for volcanic rocks were used in this study to infer an A-factor for the equilibrium Δ(quartz–epidote) at magmatic temperatures. Assuming that quartz and epidote preserved their magmatic oxygen isotope compositions in the rapidly cooled volcanic samples and a $1/T^2$ dependence, the empirical A-factor is 3.1 for the quartz–epidote fractionation in the equation 1,000ln α(quartz–epidote) = $Ax10^6T^{-2}$. The resulting equation predicts larger fractionation between quartz and epidote than the A factors of 2.0 and 0.42 (B = 3.05; C = –1.77) reported by Matthews (1994) and Zheng (1993), respectively.

Applying A = 3.1 for Δ(quartz–epidote), the average apparent temperature is 504 °C for the Emas pluton and 531 °C for the São Rafael pluton. Although still lower than magmatic values, these apparent temperatures are compatible with the closure temperature of quartz (460 °C; Dodson 1973). Apparent temperatures calculated using this equation are also rather low for the tonalites studied by Morrison et al. (1999; around 522 °C), as well as for the Idaho batholith (571–558 °C), studied by King and Valley (2001).

A fractionation factor for zircon–epidote can also be obtained by combining the published experimental and empirical A-factors, but using the new empirical quartz–epidote A-factor (3.1) discussed here. The combination of these factors yields an A (zircon–epidote) of 0.46, in agreement with natural coexisting epidote and zircon found in this study. This fractionation factor results in average apparent temperatures of 490 °C for the Emas pluton and 480 °C for the São Rafael granitoid.

Cooling history

The cooling history for the two plutons is similar, although a slightly higher mineral apparent closure temperature is calculated for the São Rafael batholith. Under wet conditions, a 20-μm radius zircon closes to diffusion of oxygen (Dodson 1973; see Valley 2001) at 520 °C, a 100-μm radius zircon at 600 °C, and a 180-μm radius zircon at 640 °C in a pluton with a cooling rate of 10 °C/Ma if the hydrothermal diffusion data of Watson and Cherniak (1997) are used. Closure temperatures are around 40–60 °C higher at a faster (100 °C/Ma) cooling rate. However, the applicability of these data has been questioned and diffusion may have been significantly slower (Peck et al. 2003). A low cooling rate estimated for the Emas pluton (15 °C/Ma), together with the presence of hydrous minerals in the studied plutons indicating rather high f_{H2O} conditions, results in a calculated closure temperature between 700 and 600 °C for diffusion of oxygen in zircon.

Zircon saturation temperatures (Watson 1987) can be used to determine the temperature at which the magma began crystallizing zircon. Textural relationships in both Emas and São Rafael plutons indicate that zircon was one the first minerals to crystallize from magma, and so calculated zircon saturation temperatures should be close to the liquidus temperature, and possibly be higher than oxygen closure temperature for zircon. However, Peck et al. (2003) found that the inherited cores of some

detrital zircons from granulite-facies quartzites are up to 5.6‰ lower in $\delta^{18}O$ than apparently igneous overgrowths, showing that gradients of 5‰ per 50 μm can be preserved even at magmatic conditions. This finding implies that the closure temperature for oxygen diffusion of zircon might be as high as the liquidus temperature. The calculated zircon saturation temperatures for the Emas granitoids range from 798 to 820 °C (average 812 °C), and for the São Rafael granitoid, from 785 to 814 °C (average 797 °C; Table 1).

The oxygen isotope data for the analyzed minerals indicate that at high magmatic temperatures, zircon is closed to diffusion, and titanite, epidote, and quartz continued to exchange oxygen as the rock cooled, until titanite closed to oxygen diffusion, at around 690 °C in the São Rafael pluton, and 620 °C in the Emas pluton. As cooling continued, quartz and epidote were still open to oxygen isotope exchange. Closure temperature for quartz seems to be slightly higher than for epidote, as suggested by the different mineral–epidote and quartz–mineral fractionations (Table 1). Estimated closure temperature of epidote ranges from 500 to 490 °C in the Emas pluton and from 530 to 480 °C in the São Rafael pluton. For quartz, these temperatures are 540–500 °C (Emas pluton) and 580–530 °C (São Rafael pluton). Oxygen isotopic ratios of feldspar, an important mineral phase, have not been measured in this study, but it is predicted that feldspar exchanges with quartz and epidote, after titanite closure. Oxygen exchange with feldspar explains why $\delta^{18}O(quartz)$ and $\delta^{18}O(epidote)$ exchange to low subsolidus temperatures.

Magmatic oxygen isotope ratios

Zircon is a refractory phase to oxygen exchange and non-metamict, low magnetic, igneous zircons can preserve primary magmatic oxygen isotope ratios even after granulite-facies metamorphism (e.g., Valley et al. 1994; Peck et al. 2003), magmatic contamination, and hydrothermal alteration (e.g., King et al. 1997; King and Valley 2001; Monani and Valley 2001). Valley et al. (1994) showed that fractional crystallization in a closed system results in values of $\delta^{18}O$ (zircon) that show no variation with whole-rock SiO_2 contents, and there is a positive correlation between Δ(whole rock–zircon) vs. weight % SiO_2 in rocks crystallized in a closed system. Values of $\delta^{18}O(zircon)$ for both Emas and São Rafael plutons are also independent of corresponding SiO_2 contents, as expected in a closed system during fractional crystallization (Fig. 6). Whole-rock SiO_2 contents in the Emas pluton vary from 62.0 to 67.2 wt%. Applying the estimate of Valley et al. (1994), and a correction for the composition of garnet (Kohn and Valley 1998), whole-rock $\delta^{18}O$ values for these rocks range from 11.1 to 11.8‰. SiO_2 contents vary from 65.2 to 72.8 wt% in the São Rafael pluton, implying $\delta^{18}O$(whole rock) = 7.5 to 8.1‰. In both plutons the estimated

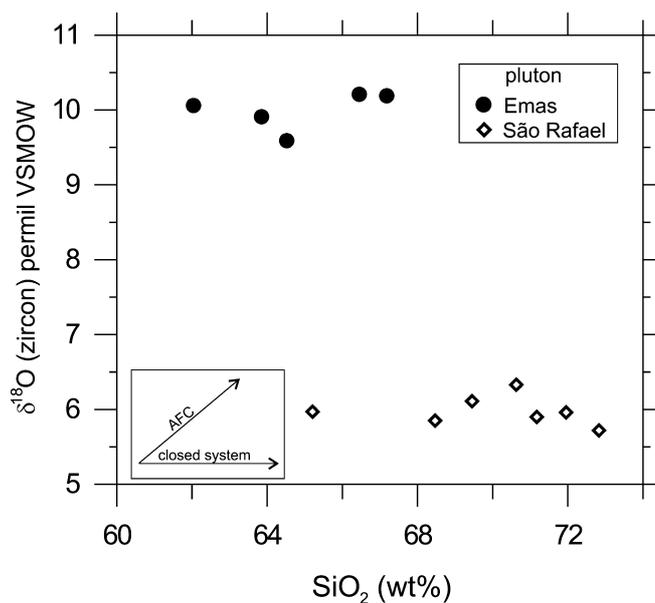**Fig. 6** Plot of $\delta^{18}O(zircon)$ versus SiO_2 contents of corresponding rocks for the Emas and São Rafael plutons, Borborema province, northeastern Brazil. Values of $\delta^{18}O(zircon)$ for both plutons are independent of SiO_2 contents, as expected in a closed system fractional crystallization (*horizontal line in the insert*) as opposed to assimilation and fractional crystallization (AFC) of high $\delta^{18}O$ rocks (AFC trend) that tends to increase the slope

$\delta^{18}O$(whole rock) should be close to the $\delta^{18}O$ of the original magmas, assuming a closed system.

Discussion and conclusion

The mineralogical characteristics, and the predominantly metaluminous nature of the Emas granitoid, together with low $^{87}Sr/^{86}Sr$ initial ratio (0.70598), and values of ϵNd close to 0 (–1 to –2) are all compatible with an igneous source in the lower crust. The high $\delta^{18}O$(whole rock) (11.5–11.8‰) on the other hand is consistent with the hypothesis that amphibole-rich clots, which have high $\delta^{18}O$(whole-rock) (9.9–11.5‰), found in the Emas pluton are source rock fragments, transported by the host granitic magma (Sial et al. 1998). The high $\delta^{18}O$(whole-rock) values for the amphibolite clots probably resulted from melting of seafloor basalt that exchanged with low-temperature water.

The $\delta^{18}O$ values of the São Rafael pluton (7.5–8.1‰) could be derived either from direct differentiation from unaltered basaltic or andesitic magmas, or by partial melting of deep-seated rocks of the lower crust. Sr (initial $^{87}Sr/^{86}Sr$ > 0.708, with variable $^{87}Sr/^{86}Sr$ ratios) and Nd (ϵNd below –9.8) isotopic characteristics, however, all suggest an ancient radiogenic crust as the source rock, and variable degrees of interaction of mantle- and crust-derived melts.

The measured mineral-mineral fractionations in the Emas and São Rafael plutons suggest continuous inter-mineral isotope exchange (exchange rates zircon

< titanite < quartz < epidote) through diffusive processes at high temperature. This is consistent with the slow cooling rate (15 °C/million years) estimated for the Emas pluton, and with field relationships that indicate high-pressure contact aureoles around two Conceição-type plutons in the Cachoeirinha-Salgueiro terrane.

The systematic mineral–epidote fractionations in the two studied plutons suggest that epidote cooled in a closed system, and is magmatic in origin. Oxygen diffusion is not as slow as theoretically predicted by ionic porosity models. Values of $\delta^{18}O$(quartz) and $\delta^{18}O$ (epidote) reflect continuous isotopic exchange through diffusive processes during slow cooling at high temperatures following solidification. Mineral–epidote and quartz–mineral fractionations suggest that the closure temperature of epidote is higher than that of quartz. Oxygen fractionation between natural zircon and epidote is opposite to that predicted from theoretical-empirical determinations due to subsolidus exchange, and $\delta^{18}O$ (epidote) is lower than $\delta^{18}O$ (zircon).

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