

REE distribution as an indicator of the origin of carbonates and silicates in basaltic rocks

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Introduction

The rare earth elements (REE) distribution in minerals and hydrothermal fluids has been used for a better understanding of the behaviour of these elements during interactions of hydrothermal solutions with hot rocks (Alderton *et al.*, 1980; Michard & Albarede, 1986). Eu, in particular, has been used for temperature determination. Eu³⁺ dominates at low temperatures, decreases with increasing temperature, and around 250°C Eu²⁺ should predominate (Sverjensky, 1984).

In this work, REE patterns were used as a contribution for the meteoric or hydrothermal origin of carbonates (calcite) and silicates (palygorskite and smectites) occurring filling

fissures and vacuoles in basaltic rocks at central (Lisbon) and southern Portugal (Budens, Algarve). Calcite from a caliche profile in Alentejo was also analysed to be used as a low temperature carbonate term.

The REE data were obtained by using the instrumental neutron activation analysis method. The mineralogical analyses were made by X-ray diffraction.

Results and discussion

The REE data obtained are given in Table 1. The concentrations were normalized relative to the chondrite (Haskin *et al.*, 1971) and to the respective adjacent basaltic rocks (Fig. 1).

TABLE 1. REE contents (ppm) in minerals samples from Restelo (Lisbon), Budens (Algarve) and Beringel (Alentejo). Cal = calcite; Pal = palygorskite; Sm = smectites.

Profile	Restelo (Lisbon)				Fissure Palygorskite 100% RF2	Budens (Algarve)			Beringel, (Alentejo) Caliche Calcite 100% CA
	Vacuoles Calcite 100% RVC	Calcite 100% RF1.1	80% Cal + 20% Sm RF1.2	50% Cal + 40% pal + 10% Sm RF1.3		Fissure Calcite 100% BFC	Accumulation Calcite 100% BBC1	Calcite 100% BBC2	
La	5.4	15	8.7	3.8	7.2	1.6	5.8	4.7	0.62
Ce	8.5	23	13	5.0	12.0	3.0	8.1	6.7	1.07
Nd	4.1	11	7.6	4.5	5.8	1.9	5.0	4.9	n.d.
Sm	0.80	1.99	1.45	0.82	1.20	0.46	0.92	0.92	0.123
Eu	0.33	0.71	0.51	0.28	0.37	0.16	0.35	0.37	0.05
Tb	0.12	0.26	0.20	0.11	0.17	0.06	0.12	0.10	0.02
Yb	0.38	0.42	0.39	0.30	0.38	0.12	0.24	0.20	0.09
Lu	0.06	0.06	0.07	0.05	0.06	0.02	0.04	0.03	0.015
ΣTR	19.7	52.4	31.9	14.9	27.2	7.3	20.6	17.9	> 1.99
(La/Yb) _{ch}	8.6	21.6	13.5	7.7	11.5	8.1	14.6	14.2	4.2
Ce/Ce*	0.73	0.72	0.68	7.7	0.77	0.79	0.63	0.62	
Eu/Eu*	1.26	1.87	1.09	1.07	0.95	1.09	1.20	1.31	1.21

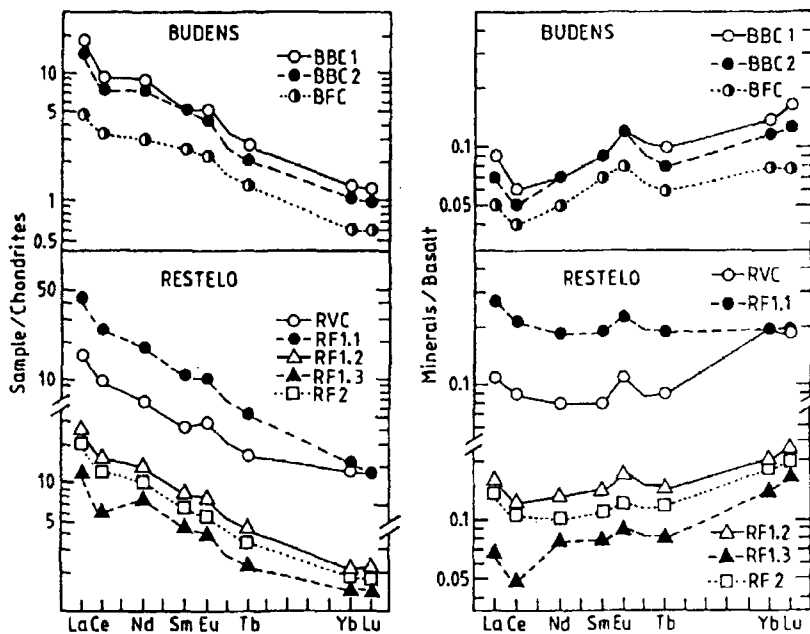


Fig. 1. REE distributions relative to chondrites and to the respective adjacent basaltic rocks.

The REE patterns of calcites from Restelo and Budens are similar, with negative Ce anomalies and positive Eu anomalies. The presence of positive Eu anomalies could justify an hydrothermal origin for these minerals (Sverjensky, 1984; Prudêncio *et al.*, 1992). However, this anomaly was also found in the calcite ($\text{Eu}/\text{Eu}^* = 1.21$), which together with the existence of negative Ce anomalies (due to meteoric processes, Prudêncio, 1993) indicate a low-temperature origin for those calcites. A positive Eu anomaly in meteoric calcites may be explained as follows: (1) an important amount of Eu is present in feldspars as Eu^{2+} ; (2) Eu^{2+} maintains in solution, possibly as stable carbonate complexes with Eu^{2+} (carbonate complexes predominate at near-neutral to basic pH, Wood, 1990) until the precipitation of calcite; and (3) Eu^{2+} is taken up by calcite (in substitution of Ca^{2+}) in a greater proportion than the other trivalent REE. Palygorskite and calcite-palygorskite-smectite assemblages REE patterns have positive Eu anomalies due to the calcite presence and negative Ce anomalies. RF2 sample (palygorskite) has no Eu anomaly. The heavy REE are enriched in the carbonates and silicates analysed relative to the respective adjacent basaltic rocks, which may be explained by the fact of these REE form more stable soluble complexes than the light REE. The results obtained suggest a supergenic origin for

these minerals, in agreement with previous isotopic data (Gauthier-Lafaye *et al.*, 1993).

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