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Neutron Activation Analysis of Rare Earth Elements in a Jurassic Limestone from Central Portugal and its Terra Rossa Derivates*

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The behaviour of rare earth elements (REE) during weathering of rocks, transport and deposition processes has been the object of several works [1, 2]. On the other hand, the REE pattern has been particularly useful in marine geochemistry studies, especially as far as the Ce anomaly is concerned [1, 3].

In this paper, some considerations are made about the behaviour of eight REE, namely La, Ce, Nd, Sm, Eu, Tb, Yb and Lu, during the chemical weathering of a Jurassic (Dogger) limestone. The REE contents in this limestone, as well as in its terra rossa derivates, were determined by instrumental neutron activation analysis (INAA). The terra rossa was divided into nine sieved fractions of different grain size in order to study how the REE are distributed in the separated sorts. These results are compared with the corresponding mineralogical compositions determined by X-ray diffraction (XRD).

Some considerations about the oxidation conditions of the bottom seawater of Dogger times, based on the observed Ce anomaly, are also made.

Experimental

The samples were collected near Arrifana (centre of Portugal); the terra rossa inside a cave and the limestone at its entrance. Whole rock samples were crushed using an agate mortar. The grains of the terra rossa were sorted into different grades, namely >1 mm, 500 μm–1 mm, 250–500 μm, 125–250 μm, 75–125 μm, 45–75 μm, 38–45 μm and <38 μm, by sieving in the presence of deionized water. The clay-sized (<2 μm) fraction was obtained by successive centrifuging and gravity settling.

The REE concentrations were determined by INAA according to the method developed at our laboratory [4, 5]. Six U.S. Geological Survey reference rocks, namely BCR-1, GSP-1, AGV-1, G-2, PCC-1 and DTS-1, were used as standards. Irradiations were made in the core grid of the RPI reactor (Sacavém) at a neutron flux of 1.6×10^{11} n cm^{-2} s^{-1} for 70 h (14 h periods on 5 successive days). A γ-ray spectrometer consisting of a 54 cm^3 Ge(Li) coaxial detector, or of a low energy photon detector (LEPD), connected through an 'Ortec' 472 amplifier to a 16K channel pulse-height analyser (Canberra S-80) was used.

Semi-quantitative mineralogical analyses were made by XRD. For analysing the clay-sized fraction, a sample of oriented aggregates was prepared.

Results and Discussion

The REE contents of the limestone, the terra rossa and its different fractions are given in Tables I and II, together with the values of total REE concentrations (taking into account only the elements determined) and the concentration ratios La/Lu, Eu/Sm and Ce_o/Ce_t (defined as the ratio of observed Ce abundance to that which would fall on the La–Nd join in the Masuda–Coryell plot). The mineralogical compositions of the terra rossa and the separated fractions are presented in Table III. Figures 1 and 2 show the chondrite-normalized [6] REE patterns of the limestone, the terra rossa and its fractions, respectively.

As seen in Table I and Fig. 1, the limestone and the terra rossa have quite different absolute REE contents ([REE] = 9 ppm for the limestone and 352 ppm for the terra rossa). The limestone presents a higher Ce anomaly than the terra rossa, but the Eu anomaly appears to be similar in both cases. Besides,

TABLE I. REE Contents in the Limestone and Terra Rossa

	Limestone (ppm)	Terra rossa (ppm)
La	3.86	91.0
Ce	1.7	135
Nd	2.2	96.2
Sm	0.57	18
Eu	0.106	3.2
Tb	0.090	1.9
Yb	0.25	5.40
Lu	0.04	0.78
Total REE	8.82	351.5
La/Lu	96.5	116.7
Eu/Sm	0.186	0.178
Ce_o/Ce_t	0.241	0.668

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TABLE II. REE Contents (ppm) in the Fractions Separated from the Terra Rossa

	A >1000 μm 7.71 wt.%	B 500–1000 μm 4.99 wt.%	C 250-500 μm 6.28 wt.%	D 125–250 μm 5.51 wt.%	E 75–125 μm 3.32 wt.%	F 45–75 μm 3.41 wt.%	G 38–45 μm 1.14 wt.%	H <38 μm 67.3 wt.%	$\phi < 2$ μm
La	28.4	36.7	35.3	40.3	47.1	50.7	44.6	112	108
Ce	14.7	15.7	16.9	26.3	42.0	59.7	57.2	180	219
Nd	27.0	40.7	39.7	46.7	52.9	53.1	42.8	109	84.0
Sm	5.6	8.7	8.7	10	12	12	9.5	22	16
Eu	1.2	2.0	2.0	2.3	2.5	2.4	1.8	4.4	3.5
Tb	0.66	1.1	1.1	1.4	1.4	1.6	1.3	2.6	2.1
Yb	1.43	2.81	2.76	3.17	3.65	4.90	3.89	7.59	5.80
Lu	0.20	0.41	0.42	0.54	0.56	0.68	0.55	1.1	0.95
Total REE	79.2	108.1	106.9	130.7	162.1	185.1	161.6	438.7	439.4
La/Lu	142	89.5	84.0	74.6	84.1	63.4	81.1	101.8	113.7
Eu/Sm	0.214	0.230	0.230	0.230	0.208	0.200	0.189	0.200	0.219
Ce_o/Ce_t	0.260	0.214	0.240	0.330	0.446	0.662	0.788	0.744	0

TABLE III. Minerals Present in the Terra Rossa and Separated Fractions

	Terra Rossa	Fractions								
		A	B	C	D	E	F	G	H	$\phi < 2$ μm
Quartz	XX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	X	
Calcite	XX	XXX	XXX	XX	XX	X	XX	XX	X	
Feldspar K	X						XX	XX		
Plagioclase						X	XXX	XX	X	
Kaolinite	X								X	XXX
Illite										X
Chlorite										X
Goethite										X

A = >1 mm; B = 500 μm–1 mm; C = 250–500 μm; D = 125–250 μm; E = 75–125 μm; F = 45–75 μm; G = 38–45 μm; H = <38 μm.

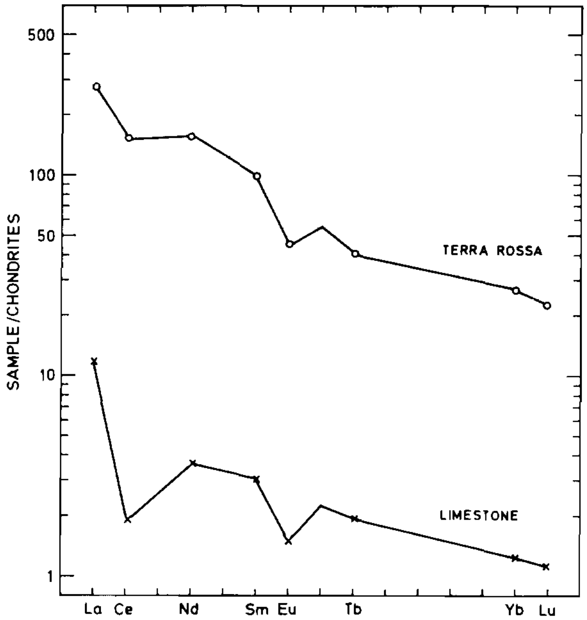

Fig. 1. REE contents of the limestone and the terra rossa relative to chondrites.

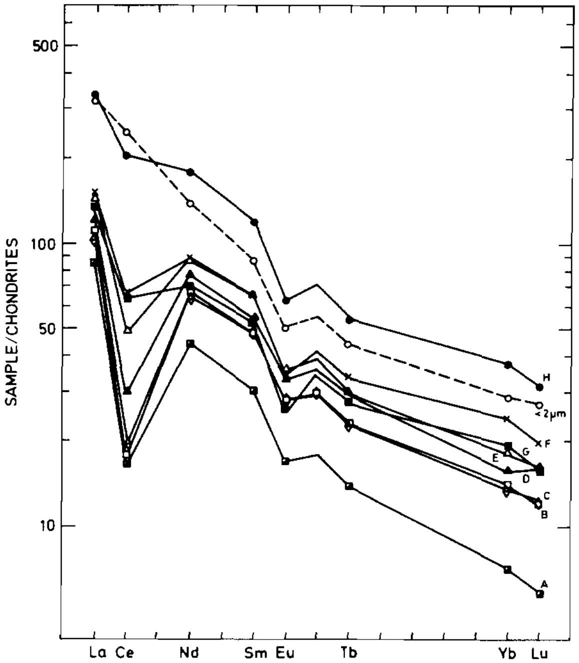

Fig. 2. REE patterns: A = >1 mm; B = 500 μm–1 mm; C = 250–500 μm; D = 125–250 μm; E = 75–125 μm; F = 45–75 μm; G = 38–45 μm; H = <38 μm; and <2 μm.

the light REE (LREE), especially Ce and Nd, are more enriched in the terra rossa relative to the heavier REE (HREE).

As shown in Table II and Fig. 2, the REE abundance in the terra rossa increases as the particle size decreases. On the contrary, the Ce anomaly decreases so that it becomes absent in the clay-sized fraction. The Eu anomaly seems not to vary significantly with grain size.

These observations suggest that the REE tend to remain in the residual material instead of being dissolved out by groundwater, and possibly also that the higher REE abundances in the terra rossa may essentially be a reflection of the REE patterns in the groundwater. The REE removed from other regions may be transported in solution by groundwater and redeposited in the weathering minerals of the limestone, possibly in response to an increase in pH. In fact, if one assumes that the REE pattern of river water [7] is indicative of the distribution of these elements in groundwater, a great similarity is observed between REE distributions in the terra rossa and in groundwater (Fig. 3), except as far as the Ce anomaly is concerned. However, this anomaly might have been inherited from the limestone. Moreover, it should be noted that the most abundant mineral in the clay-sized fraction of the terra rossa is kaolinite, which could account for the higher REE contents in this fraction [8], and that the clay-sized fraction does not show any Ce anomaly. It seems, therefore, that the high REE contents observed in the terra rossa may be principally due to the deposition of REE from groundwater in the kaolinite. The fact that the heavy REE are preferentially transported in solution relative to the lighter REE may be explained by the increase in the stability of carbonate and perhaps organic complexes of the REE from La to Lu, as has already been suggested by other researchers [1].

It is well known that the REE pattern in carbonates is an important redox indicator of bottom seawater. If seawater is in an oxidizing condition, it will be depleted in Ce, and so will be the carbonate. If seawater is in a reducing condition, all Ce will be in the III oxidation state and no Ce anomaly will be found in the carbonate. Thus, the strong Ce anomaly seen in the limestone (Fig. 1) suggests that the bottom seawater of the area during Dogger times was in an

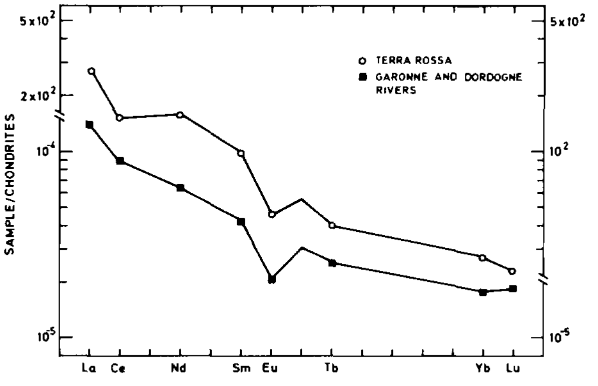

Fig. 3. REE abundances in the terra rossa and in water (soluble contents) of the Garonne and Dordogne rivers (0.1 °/oo salinity) relative to chondrites.

oxidizing condition. The same strong anomaly is observed in the flint concretions that mainly constitute the coarser fractions of the terra rossa (Fig. 2). Shimizu and Masuda [9] have shown that deep-sea cherts have negative Ce anomalies, but that cherts formed in extensive shelves have not, suggesting that Ce is depleted in the water of the open ocean but not in waters of shallow seas. Our results suggest, therefore, that in Dogger times an open ocean with oxidizing conditions in the bottom seawater existed over the area.

References

1 S. E. Humphris, in P. Henderson (ed.), 'Rare Earth Element Geochemistry', Developments in Geochemistry, Vol. 2, Elsevier, Amsterdam, 1984, p. 317.

2 A. J. Fleet, in P. Henderson (ed.), 'Rare Earth Element Geochemistry', Developments in Geochemistry, Vol. 2, Elsevier, Amsterdam, 1984, p. 343.

3 H. Elderfield and M. J. Greaves, *Nature (London)*, *296*, 214 (1982).

4 J. M. P. Cabral, M. A. Gouveia and M. I. Prudêncio, *Bol. Lab. Min. Geol. Faculd. Ciên.*, *16*, 205 (1979).

5 M. I. Prudêncio, M. A. Gouveia and J. M. P. Cabral, *Geostand. Newsl.*, *10*, 29 (1986).

6 M. A. Haskin, L. A. Haskin, F. A. Frey and T. R. Wildeman, in L. H. Ahrens (ed.), 'Origin of the Distribution of the Elements', Pergamon, Oxford, 1968, p. 889.

7 J. M. Martin, O. Høgdahl and J. C. Philppot, *J. Geophys. Res.*, *81*, 3119 (1976).

8 M. I. Prudêncio and J. M. P. Cabral, *Int. Conf. on Methods and Application of Radioanalytical Chemistry*, Kona, Hawaii, U.S.A., April 5–10, 1987.

9 H. Shimizu and A. Masuda, *Nature (London)*, *266*, 346 (1977).