Rare earth elements distribution of Tertiary phosphorites in Tunisia

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Abstract. REE concentrations and distribution have been established for the Upper Palaeocene-Lower Eocene sedimentary phosphorites, southern Tunisia. REE contents of phosphatic beds vary according to the paleogeographic environments, granulometry and grain types. Shale normalized REE patterns are characterized by a slight depletion in HREE and a negative Ce anomaly. The Ce/Ce* and La/Yb indexes indicate Ce deficit and the LREE-HREE fractionation, range from 0.35 to 0.86 and from 11.7 to 17.1, respectively. These ratios are variable and reflect important variations from basin to basin. The high REE contents correlate with the high bulk porosity and the specific surface of cryptocrystalline apatite The REE content, the enrichment and depletion in HREE and the Ce-anomaly may reflect diverse environmental conditions of each basin.

Keywords. REE, Tunisia, phosphorites, fluorapatite, fractionation, Ce-anomaly

1 Introduction

Results related to the presence of Rare Earth Elements (REE) in phosphocalcic apatite were first described by Altshuler (1967) and Baturin et al. (1972), Numerous works established the affinity of REE for this mineral, which they tend to replace calcium (Fleet and Pan 1997).

In this study the authors attempt to gain a better understanding of REE distribution in phosphorites, and use these elements as tracing tools to establish genetic relationships to environment, the source and the mechanism of their incorporation in apatite.

We are presenting the REE contents and distribution in Paleogene phosphatic samples from Tunisia, with the attempt to gain a better understanding of the genesis of these phosphorites and their paleoenvironment.

2 Geological setting, lithostratigraphy and analytical techniques

Figure 1 shows the position of the Tunisian phosphate basins that are located around the Kasserine Island which has been an emerged area since the Upper Cretaceous (Sassi 1980 Beji Sassi 1999; Zaier 1999). The main lithologic profiles of the phosphatized series around the Kasserine Island are shown in Figure 2.

In this study our sampling targeted all the phosphate types based on their size and nature.

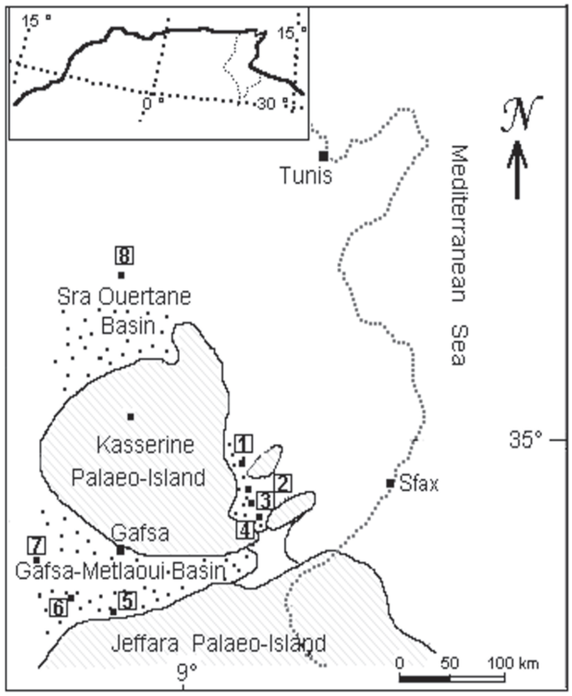

Figure 1: Paleogeographic map of the Tunisian phosphate basins during the Paleogene. [1- Ahzem . 2 Jebs-Abdallah; 3- Oued Abiod; 4- Kef Nsour-Rouijel; 5 – Atra; 6 – Selja; 7 – M'Rata; 8 – Sra Ouertane]

Hence, the coprolites, pellets, bony fragments, bioclasts, etc, were analyzed separately. We also analyzed the REE in grains of various sizes (800µm, 315µm, 80µm, 40µm).

A hundred samples were analyzed for REE in this study. Some samples were analyzed by neutron activation in the Centre of Nuclear Studies in Saclay (France) (Tlig and al. 1987). Other samples were analysed by ICP-MS in the CRPG of Nancy (France) and at the BRGM in Orleans (France).

3 Results

The mineral apatite, the main constituent of phosphorites, is a carbonate sulphate fluorapatite with a parameter a ranging approximately between 9.32-9.33 Å (Beji

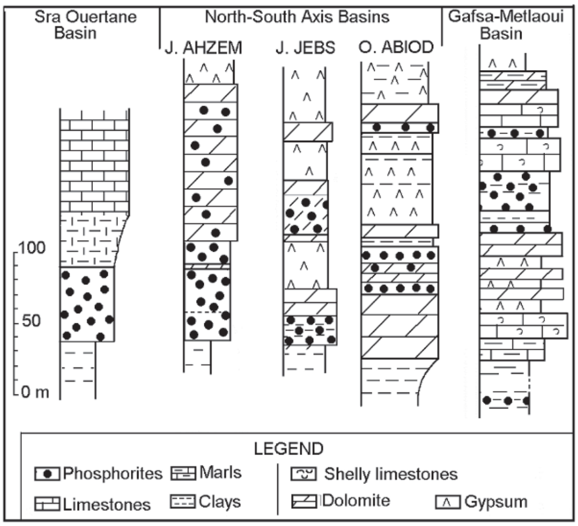

Figure 2: Lithological profiles of the main phosphatic basins

Sassi 1999).The REE contents vary between 420 and 1700 ppm (Table 1). To the north and the east of the Kasserine Island, the REE contents show a considerable increase with values ranging between 800 and 1700 ppm. On the other hand, in the Gafsa-Métlaoui Basin, the averages are only comprised between 400 and 950 ppm.

Generally and independently of nature, origin and size, the sum of the light REE contents (LREE) is far higher than heavy HREE (Fig. 3). The first three REE elements constitute up to 80% of the total. On the other hand, the sum of all the REE shows a good correlation with La ($R^2 = 0.97$).

In addition, the variation of this element concentration reflects that of the lanthanids group and represents the abundance of the REE in the analyzed grains. The concentrations of REE are variable in different types of grains.

The average content is around 700 ppm in phosphatic pellets whereas the irregular grains, coarser than the pellets, contain approximately 600 ppm, bioclasts contain up to 500 ppm and coprolites contain 400 ppm only. The highest REE concentrations characterize the fine fractions, especially pelletoïds which are less than 100 µm in size whereas the coarser grains are less enriched in REE.

The comparison of the REE contents of the different grain size classes shows the existence of a clear cut between the bigger grains (>315µm) and the small ones (40-100µm). It is noticed that the highest REE contents characterize the finer fractions (870 ppm) whereas the coarser grains are less enriched with 513 ppm.

4 REE fractionation and distribution patterns

In this study, the La/Yb ratio was used as a fractionation index. It was compared with the result of average shales (11.6) proposed by Piper (1974). The means of La/Yb ratios from our sectors are: Sra Ouertane: 13.6 – Ahzem: 13.5 - Jebs: 16.2 – Abdallah: 15.1– Abiod: 17.1 – Kef Nsour: 16.4 – Rouijel: 15.6 – Atra: 15.3 – Selja: 12.8 – M'Rata: 11.7 . The fractionation is variable. Although little accentuated, it characterizes the whole samples. Several patterns show an impoverishment in heavy REE with an average of the La/Yb ratio higher than the shales average. Averages of REE contents are higher in the North-South Axis phosphorites than in those of the others basins. Th values for J Ahzem are similar to those found in Sra Ouertane.

Table 1: Mean REE content of the phosphorites (I.K.: Kasserine Island)

	Localities	10 elements	14 elements
North I.K.	Sra Ouertane (AT1)	1560	
	j. Ahzem)	1300	
	j. Jebs	1100	1200
East I.K.	j. Abdallah	1000	
	O. Abiod	1500	
	j. Rouijel	1700	
	Atra		950
South I.K.	Selja		497
	M'rata	420	
	Phosphate marchand		460

The distribution patterns of REE normalized to shale values are shown in Figure 3. The high content of REE in phosphorites is shown by the values of the Y-axis which approach 10, in comparison to the shales values. The general shape is a concave-down type. Concavity is generally moderate. The shape of the curves is rarely flat and the fractionation is rarely in favour of the HREE. The main distribution of the REE patterns is characterized by a variable negative cerium anomaly exhibited by a large number of samples (Fig. 3). The cerium deficit is described by the distribution patterns of its peak shape and its intensity. It is also expressed by the relation Ce/Ce *, with Ce * = 2/3La Sh + 1/3Nd Sh (Ce Sh and Nd Sh are the values of these two elements normalized to the shales).

It is worthwhile to mention that when Ce/Ce * value approaches 1, the negative cerium anomaly, observed with the distribution patterns, is more attenuated. For each basin we obtained the following average values: Sra Ouertane: 0.64 - Ahzem: 0.35 – Jebs: 0.74 – Abdallah: 0.81– Abiod: 0.71– Kef Nsour: 0.73– Rouijel: 0.78- Atra: 0.86– Selja: 0.77– M'Rata: 0.73. These variations are similar to those occurring usually. When the environment evolves to a more reducing pole, we observe a decreasing of the Ce-negative anomaly as it was mentioned by Watkins et al. (1995).