

Rare earth elements abundance in Tunisian phosphorites

Ounis Anouar^{1,3}, Kocsis Laszlo², Pfeifer Hans-Rudolf³ and Chaabani Fredj¹

¹ Laboratory of the Mineral Resources and Environment, Faculty of Sciences of Tunis, University of Tunis El Manar.

² Institute of Mineralogy and Geochemistry, Faculty of Geosciences and Environment, University of Lausanne.

³ Center of Mineral Analysis, Faculty of Geosciences and Environment, University of Lausanne.

The purpose of this study is to advance our understanding of how the redox condition and the depositional environment changed during the formation of the diverse phosphatic layers of the Late Cretaceous and Early Eocene phosphorites in the Gafsa-Metlaoui basin, south western Tunisia. To constrain this former environment Rare earth elements (REE) composition were analyzed mainly from phosphatic coprolites. The samples were collected from different phosphatic layers, from Late Cretaceous locality (K) and two Early Eocene sections (CAC and ZT).

The coprolites have sub-rounded, rounded or cylindrical shape and their diameters changed from 0.05 to a few mm. They appear to be internally structureless but their colour is changing. Mineralogical data was determined by DRX and the grains show only carbonate fluorapatite mineral. Chemical analyses of phosphatic coprolites were determined by XRF, contained CaO an average of 41.5 wt% for the Cretaceous and 49.5 wt% for the Eocene samples.

The REE concentrations were determined by LA-ICP-MS at the Institute of Mineralogy and Geochemistry of University of Lausanne, Switzerland. To guarantee the quality of the data NIST 612 reference standard were analyzed parallel and the data were evaluated by LAMTRACE program using the wt% of CaO values as internal standard.

The Post Archean Australian Shale (PAAS) - normalized (McLennan, 1989) REE patterns of Early Eocene coprolites are significantly different from Late Cretaceous coprolites with having negative Cerium anomalies and less total REE concentration (Σ REE). The patterns of older samples show middle REE (MREE) enrichment while the Eocene samples have flat or slightly heavy REE (HREE) enrichment. The variation in the total REE concentration for the Early Eocene coprolites is between 26.86 and 187.80 ppm with average of 88.87 ppm, the cerium anomaly (Ceanom) is quantified by $\log(\text{Ce}/\text{Ce}^*)$ where the ratio $\text{Ce}/\text{Ce}^* = 3\text{CeN}/(2\text{LaN} + \text{NdN})$, the Eu/Eu^* denotes $\text{EuN}/(\text{SmN} + \text{GdN})^{0.5}$ where N refers to normalization of concentrations against the standard PAAS (Chen et al., 2003). The Ceanom are significant with value varying between -0.08 and -0.20. The average of total concentration of REE in Late Cretaceous coprolites is 209 ppm and no Ceanom was recorded in this sample. Slightly HREE enrichment for the Eocene samples indicate the weathering depositional environment (McArthur and Walsh, 1984)

The cross-section study of a coprolite (CAC5) show that the borders have higher REE concentration than the inner part this could be due to the direct contact with the seawater with additionally adsorption process. The REE patterns inner and outside however are very the same showing similar condition during its re-crystallization. The REE characteristics suggested that the Early Eocene coprolites recorded a depositional condition that very similar to modern oxic seawater pattern (e.g Elderfield and Pagett, 1986), showing these phosphatic remains has up-taken the

REEs at the sediment surface and/or the well oxygenated upper part of the sediment. On the other hand, the enrichment in the MREEs of Late Cretaceous coprolites might have resulted from late diagenetical alteration and/or indicating anoxic bottom/pore water, where the MREE might derive from FeO source (Haley et al., 2004).

The two studied Eocene sections were localised according to an east-western line which occupied the center of the Gafsa-Metlaoui basin and distant of some ten kilometres. The comparison of the distribution of the REE into the two Eocene sections showed the presence of cerium anomaly and has the same patterns in all samples. This confirms the presence of same redox condition in the entire basin but the degree of this oxidation and the abundance of REE between the phosphatic layers and the sections was not the same.

REE data for the Tunisian phosphorites in west Gafsa-Metlaoui Basin document a variable paleoenvironmental conditions during the Late Cretaceous and Early Eocene. To better understanding characterization, other trace elements and stable isotope approaches have been used for further study.

REFERENCES

- Ilyin, A.V., 1998: Rare-earth geochemistry of 'old' phosphorites and probability of syngenetic precipitation and accumulation of phosphate. *Chem. Geol.* 144, 243–256.
- Chen D. F., Dong W. Q., Qi L., Chen G. Q., Chen X. P., 2003: Possible REE constraints on the depositional and diagenetic environment of Doushantuo Formation phosphorites containing the earliest metazoan fauna. *Chem. Geol.* 201, 103-118.
- McArthur, J.M., Walsh, J.N., 1984: Rare-earth geochemistry of phosphorites. *Chem. Geol.* 47, 191– 220.
- McLennan, S.M., 1989: Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. In: Lipin, B.R., McKay, G.A. (Eds), *Geochemistry and Mineralogy of Rare Earth Elements*. *Min. Soc. Am. Rev. Mineral.* 21, 169–200.
- Haley, A. B., Klinkhammer, P. G., and McManus, J., 2004, Rare earth elements in pore waters of marine sediments: *Geochimica et Cosmochimica Acta*, v. 68, p. 1265–1279.
- Elderfield, H., and Pagett, R., 1986, Rare Earth Elements in ichthyoliths: Variations with redox conditions and depositional environment: *The Science of the Total Environment*, v. 49, p. 175–197.