

## REE geochemistry and tetrad effects in F-rich magmatic-hydrothermal systems with Sn-Nb-cryolite deposits

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The tetrad or double-double effect is caused by subtle variations of the 4f-orbital configuration of some particular REE –Nd, Gd, Ho-Er, Lu - which produce typical complementary chondrite-normalised patterns named W- and M-type. Tetrad effect is observed particularly where REE complexes are formed, as for instance, in highly evolved F-rich granitic magmas, such as those that generated the Sn-Nb-cryolite ore bearing Madeira Granite in the Brazilian Amazonia. Nd, Gd, Ho-Er, and Lu form less stable complexes than their neighbors REE, therefore, they are relatively more compatible during granitic melt crystallization and that causes the development of M-type patterns in the highly evolved melts as well as in zircons and cryolite (Na<sub>3</sub>AlF<sub>6</sub>) crystallized from them. W-type complementary patterns are generally not formed because the more compatible REE are distributed among the earlier crystallized magmatic phases. M-type patterns are, therefore, typical of highly differentiated magmatic rocks and minerals, when complexes were abundant in the melts. Melts and their crystallized products that, were leached by fluids capable of complexing REE, would be expected to show W-type patterns. The metal partitioning between fluid and melts in hydrothermal-granitic systems is however, too low to yield significant W-type patterns. In the hydrothermal phases, however, as in cryolite from Madeira Granite, the W-type patterns are frequent and well developed. The identification of tetrad effect in rocks and minerals can be a powerful tool for metallogenetic, provenance and exploration studies.

## C and O-isotope stratigraphy of carbonates at the K-T boundary of the Paraíba Basin, NE Brazil

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### Introduction

The Paraíba coastal basin, northeastern Brazil, contains a complete carbonate sequence that records the K-T boundary.

C and O isotopes and major, minor and trace elements have been analyzed in carbonate samples from drill holes from three localities (Poty quarry, Olinda and Itamaracá island). C, O, Mg/Ca, Si, Al, Mn/Sr, Rb and Sr stratigraphic profiles have been compared with similar stratigraphic profiles from elsewhere in the pertaining literature.

### Results and Discussions

Deposition of carbonates under consideration was initiated in a period of marine transgression in the Early Maastrichtian, under increasing temperature and bioproductivity, according to isotopic signals ( $\delta^{18}\text{O}$  values vary from -3 to -5‰<sub>PDB</sub>; and  $\delta^{13}\text{C}$ , from -1.2 to 0.1‰) reaching their maximum in the Late Maastrichtian, with values of  $\delta^{13}\text{C}$  around +2‰. The early Danian, has recorded a small positive C-isotope excursion with values around +2‰, falling to values of +1‰, right after the Maastrichtian-Danian transition. After this transition, an increase of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> is recorded that was associated to the contribution of terrigenous material. Upsection, carbonates recorded a period of marine regression and bioproductivity fall as recorded in the  $\delta^{13}\text{C}$  curve (+1‰) and carbonate sediments with higher Mg/Ca ratios (dolomitic limestones) possibly deposited in shallow-marine environment. Mn/Sr ratios are all <2 and guarantee that C isotopic signals are near primary near.

C and O isotope pathways in carbonates of the Paraíba coastal Basin as registered in the Poty quarry, Olinda and Itamaracá island localities, are similar to each other and to those observed worldwide.