

Rare Earth Element Biogeochemistry in the mid-2020s: Living with Anomalies

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The fundamental reason why geochemists fell in love with rare earth elements (REE) long before politicians, investors and the media did, is that the REE's relative behavior is predictable. Their ionic radii decrease with increasing atomic number and because of their electron configuration most of them are exclusively trivalent, as had already been recognized by V.M. Goldschmidt, the godfather of geochemistry. Hence, REE concentrations produce smooth patterns without any anomalies when normalized against a reference system. Until the end of the 20th century, only two exceptions were known: In oxic low-temperature systems, Ce³⁺ may be oxidized and subsequently be decoupled from the other, still trivalent REE, and in reducing systems at temperatures exceeding ca 200°C, Eu³⁺ is reduced and may be decoupled. The results are Ce anomalies (e.g., in seawater and zircons) and Eu anomalies (e.g., in black smoker fluids and post-Archean shales).

Inclusion of Y in the discussion (i.e. moving from REE to REY) in the mid-1990s revealed Y anomalies and hence fundamental differences between trace element behavior in igneous vs aqueous systems and confirmed the lanthanide tetrad effect in natural materials.

By the mid 2020s, the picture has changed again. Biological La anomalies are related to methanotrophy, while anthropogenic La anomalies resulting from catalyst production have been found in atmospheric dust, river water and mussels. Cerium anomalies are no longer exclusively considered redox-proxies, but may be produced by biogenic siderophores or even be of purely biological origin such as in marine mussel shells. Micropollution produced Sm anomalies for several years in river water and in the shells of related mussels. Anthropogenic Gd anomalies resulting from Gd use in MRI contrast agents, are ubiquitous in rivers, lakes, shallow aquifers and many coastal waters worldwide and are present in tapwater and beverages. Anomalies of Yb have been observed in river sediments in the vicinity of steelworks, and most recently, Lu anomalies were found in the Isère River in southern France.

Today, anomalies in REE patterns of samples from the Critical Zone have become the new normal and unlocked the door to numerous new ways of making use of REE biogeochemistry.