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Rare earth geochemistry and phosphogenesis in the Miocene of Patagonia, Argentina

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Abstract

The abundance and distribution patterns of rare earth elements (REEs) in phosphorites reflect the source and the mechanism of their incorporation. providing an interesting tool to understand the depositional environment. Pore waters can also acquire characteristic REE patterns in different early-diagenetic environments. Phosphatic concretions originated in the Early Miocene, shallow-water marine, clastic beds of the Gaiman Formation, present a characteristic REE pattern and an unusual association with fallout tuffs. The concretions show typical major element ratios, REE patterns and total REE contents. These characteristics are common to different stratigraphic levels and geographic locations of the unit in central-north Patagonia, Argentina and suggest a common process for the origin of the concretions. Major elements in concretions are grouped into an aluminosilicate-clastic group (Si, Al, Ti, K and Fe), which correspond to the clastic fraction, and a chemical-authigenic group (P, Ca and total REEs), which corresponds to francolite, a rare-earth oxihydroxide and calcite. Mn is the only element which has a separate behaviour, most likely because of its high mobility in seawater. Major element ratios in host shales are similar to those of the clastic fraction within the concretions and coquinas. Concretions are slightly depleted in LREEs and slightly enriched in HREEs in comparison to shales and display a weak negative Ce anomaly. Their La/Yb and La/Sm ratios point to REEs incorporation preserving the pore seawater or pore water ratios without strong postdepositional recrystallization or strong adsorption. Y anomaly and La/Nd ratio in concretions are equivalent to seawater or slightly lower, pointing out that Gaiman concretions did not

undergo intense diagenesis, but they were probably formed from phosphatic solutions impoverished in Y and La as a result of REEs release to solution from organic complexes in the early diagenesis. Flat, linear REE pattern in the concretions of Gaiman Fm. suggest quantitative precipitation from early diagenetic pore waters, reproducing the flat pattern of oxic-suboxic recent pore waters, which results from remineralization of organic coatings rich in LREEs and Ce. Water circulation through burrows at the Miocene seawater-sediment interface improved ion diffusion and pore water renewal in the sediments, allowing the development of a widened early diagenetic oxic-suboxic zone.