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Early-diagenesis carbonation of biogenic apatite: the pathway for the past-seawater REE conservative uptake.

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Phosphorite are primarily composed of nanocrystalline biogenic apatite ($Ca_5(PO_4\text{-}CO_3)_3F$) which hosts rare earth elements (abbreviated REE, including lanthanides and Yttrium) which are extensively used in marine geochemistry as a proxy to investigate paleo-marine conditions [1]. Although it is conceded that biogenic apatite preserves an unaltered pas-seawater record, the REE enrichment mechanism is still open to debate [2]. Therefore, elucidate the crystal chemistry of REEs in biogenic apatite is necessary to fathom their conservative uptake. To clarify this issue, we conducted a mineralogical study on a Moroccan phosphorite sample using a combination of SEM images, SXRF elemental mappings, and in-situ micro-XAS measurements on both La*LIII*-edge and Y *K*-edge.

We found that REEs are heterogeneously distributed into fluorapatite grains with enrichments located in micro/nanoporous carbonated-fluorapatite regions. Regardless of their distribution, XAS analysis reveals that the REEs are uniformly substituted for the Ca2 fluorapatite site with a concomitant CO_3^{2-}-PO_4^{3-}substitution and a calcium vacancy, suggesting the (3Ca, REE, □) ($2PO_4$, CO_3)F charge compensated equation. Such results suggest that the porosity and the nanocrystalinity promote the congruent migration of both $CO_3^{2-}$and REE ions; initially adsorbed onto the hydrated layer; to the apatite lattice during crystal growth and/or during dissolution-recrystallisation processes. This idea is consistent with the observed X-Y axis elongated plate-like crystals and the seawater/porewater REEs speciation predominantly represented by REE carbonates complexes. Thus, we propose that the uptake of non-fractionating and relatively preserved past-seawater REEs composition in marine biogenic apatite is an outcome of: I) their subsequent elemental accommodation abilities, II) their peculiar nanocrystals morphologies and hydrated layers presence; III) the REE affinity with carbonate in marine systems.

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