

Geochemical Characteristics of REE+Y in Middle-Upper Jurassic Phosphate Nodules From the Silesian-Cracow Homocline (Southern Poland)

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This study combines multiple data to constrain the origin and environmental controls on REE+Y uptake into Middle-Upper Jurassic phosphate nodules from southern Poland. The nodules were sampled from the Upper Bajocian-Bathonian (B-B) ore-bearing clays and Callovian-Middle Oxfordian (C-O) marly-limestone. Ammonite assemblages allow dating of the nodule-bearing horizons. The B-B clays are marked by nodules confined to zones of siderite concretions. In contrast, in the C-O strata, nodules are found in condensed marly beds associated with marine transgression.

Petrographic observations, combined with XRD and SEM analyses, indicate that the nodules are mainly composed of a carbonate-rich variety of fluorapatite (francolite), replacing bioclasts and the matrix. They contain silica, clay minerals, and sulphides. ICP-ES/MS analyses of nodules exhibit elevated P_2O_5 levels, ranging from 20 to 25 wt.%. A enrichment in REE+Y relative to the host sediments is observed, averaging 2740 ppm for the B-B nodules and 1420 ppm for the C-O nodules. In both cases, Y, La, Ce, and Nd dominate the REE+Y budget. The Ca-phosphate/Ca-carbonate ratio is higher in B-B nodules, reflecting more intense phosphatization. PASS-normalized patterns show middle REE+Y enrichments and negative Ce anomalies, which are pronounced in the B-B samples, along with positive Y anomalies. The normalized La/Sm to La/Yb ratios point to the REE+Y uptake from marine-derived pore waters under variable rate of diagenetic substitution and adsorption processes. A lack of Eu anomalies argues against a substantial hydrothermal contribution.

The spatial and stratigraphic variability in REE+Y concentrations in the nodules reflects variations in sedimentation rate and in the intensity of early diagenetic incorporation of these elements. Nodule formation was closely associated with microbial degradation of organic matter, pH fluctuations, and shifts between oxic and suboxic conditions at the sediment-water interface. Such environmental conditions contributed to the enrichment of REE+Y, suggesting the potential economic significance of these nodules.