

Understanding the Mechanisms of Rare Earth Element (REE) Enrichment in the Organic and Inorganic Phases of the Middle Devonian Sequence of the Appalachian Basin

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Abstract

While the mechanism of REE (lanthanides + Sc + Y) enrichment in the silicate, carbonate, and phosphate phases that comprise the bulk of shales is generally well-understood, the degree to which the REE are incorporated into organic matter is less certain. Despite a recent increase in studies on this topic, the relative fractionation of light, middle, and heavy REE (LREE, MREE, and HREE) into organic matter requires more documentation. The current study uses high-quality elemental (ICP-OES/MS), mineralogical (XRD), and TOC (Leco) data from 15 core and cuttings samples from the Middle Devonian sequence of the Appalachian basin to inventory REE and infer mineralogical and organic-matter affinities. Inferences made from bulk-rock data are checked against the results of a sequential leaching procedure. A range of fine-grained lithologies is represented by the sampled sequence. The lower part generally consists of higher-carbonate (11% - 56%), organic-rich rocks, while the upper part comprises clay-rich (48% - 61%) rocks, with lower TOC and little to no carbonate. When normalized to Post-Archean Average Australian Shale (PAAS), REE patterns of bulk-rock analyses show slight to moderate MREE enrichments, and slight to pronounced HREE enrichments for the entire section. This contrasts with the relatively flat PAAS-normalized REE patterns typically displayed by most organic-lean shales. Sc and the light REE show an overall poor correlation with TOC but a good correlation with siliciclastic indicators (e.g., TiO₂, Al₂O₃, K₂O, Zr). These relationships weaken in the MREE and ultimately reverse for the HREE and Y, which are generally well-correlated with TOC and poorly correlated with refractory elements. Phosphates (mainly apatite) can be a significant reservoir of REE (particularly MREE), but no apatite was detected by XRD. The leachates from the organic matter fraction account for 0.44 - 5.26% of the bulk-rock REE. This is generally less than the percent of REE recovered in the carbonate, oxy-hydroxide, and sulfide leachates. However, the organic leachate REE patterns also suggest the traditional reagents used in this study have not fully extracted all REE and are more effective in extracting LREE than HREE. Y and Tb in particular, could not be effectively extracted from organic matter, suggesting these HREE are more strongly complexed than other REE. While detailed petrological data for organic-rich shales are still underrepresented in the literature, this study supports the recognition that organic-rich shales may show “disturbed” REE patterns, with HREE enrichments relative to those seen in the “normal” REE patterns of organic-lean shales. Also, the data cannot completely rule out that some LREE may have been mobilized and depleted in the studied interval. The exact geochemical mechanisms behind the observed enrichments and fractionations, particularly the timing of REE redistribution during diagenesis, require further investigation.