

Distribution and Speciation of Rare Earth Elements in Clay Deposits via Synchrotron μ XRF and μ XANES

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Underclay, the layer of stratum beneath a coal bed, are being explored as a potential mining source of rare earth elements (REE). This study utilized micro-X-Ray fluorescence (μ XRF) and micro X-Ray near edge structure (μ XANES) to characterize the Ce speciation and REE distribution from four underclay samples (total REE content: 250-450 ppm) from clay deposits associated with Central Appalachian coal seams. The following REE binding environments have been identified in our study: (1) micro-scale trace minerals (10-40 μ m) with various co-localization pattern with Ca, P, and Al; (2) large-scale light REE (e.g., Ce, La, Sm, and Nd) zones (>200 μ m) colocalizing with Sr and Ba, whose Ce μ XANES displayed a Ce(III) species distinctively different (with shorter post-edge oscillation) from micro-scale Ce hotspots and previously collected Ce(III) references for fly ash study [1], and (3) The heavy REEs (e.g, Gd, Yb) often co-localize with Fe and sometimes with S, P and Y, indicating presence of xenotime or REE-bearing pyrite. Our results indicate the REE mineralization may occur in the presence of Ba, Sr and LREE-rich hydrothermal fluids, highly charged with volatile constituents (e.g., carbon dioxide, fluorine, and phosphorus). The characterization of REE-bearing phases in underclay deposits provides key mineralogical data to develop targeted and more efficient methods for the recovery of REE from domestic geological deposits.

[1] Stuckman et al. (2018) *International Journal of Coal Geology*, Special Issue of "Critical Elements in Coal and Coal Ash and their Recovery", submitted.