

Enhancing extraction of rare earth elements from West Virginia bituminous coal

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Abstract

Rare earth elements (REE) are essential for manufacturing technologies vital to economic and national security. As the demand for REE increases and conventional ores are depleted, attention has turned to coal as a promising unconventional resource for these elements. As the nation's second-largest coal producer, West Virginia (WV) can transition into the production of these critical elements. But it is imperative to understand REE modes of occurrence in these coals in order to identify promising coal seams and design efficient extraction techniques. To this end, four WV bituminous coal samples were subjected to a standard sequential leaching process to quantify REE concentrations and identify their modes of occurrence. The leaching procedure targeted individual coal fractions including ion-exchange sites; carbonates, oxides, and monosulfides; pyrite; and organic matter. More than 50% of the extracted REE in each sample were leached from the HCl-soluble carbonate, oxide, and monosulfide fraction. However, overall extraction efficiency was low (< 17%), indicating that the majority of REE are associated with or shielded by aluminosilicate minerals or are present in other resistant phases. Additional experiments will be conducted to identify more efficient extraction techniques for WV coals, using a combination of roasting additives and acid leaching.

Materials & Methods

- Four bituminous coal samples provided by the West Virginia Geological and Economic Survey
- Samples ground to < 149 μm
- Rare earth elements in individual coal fractions targeted by sequential extraction method based on Tessier et al. (1979) and Riley et al. (2012)
- Samples washed with D.I. water between steps
- Filtrate collected after each step, acidified, and analyzed by ICP-MS
- Whole coal REE analysis performed by the Energy Institute Analytical Lab at West Virginia University

Sequential Extraction

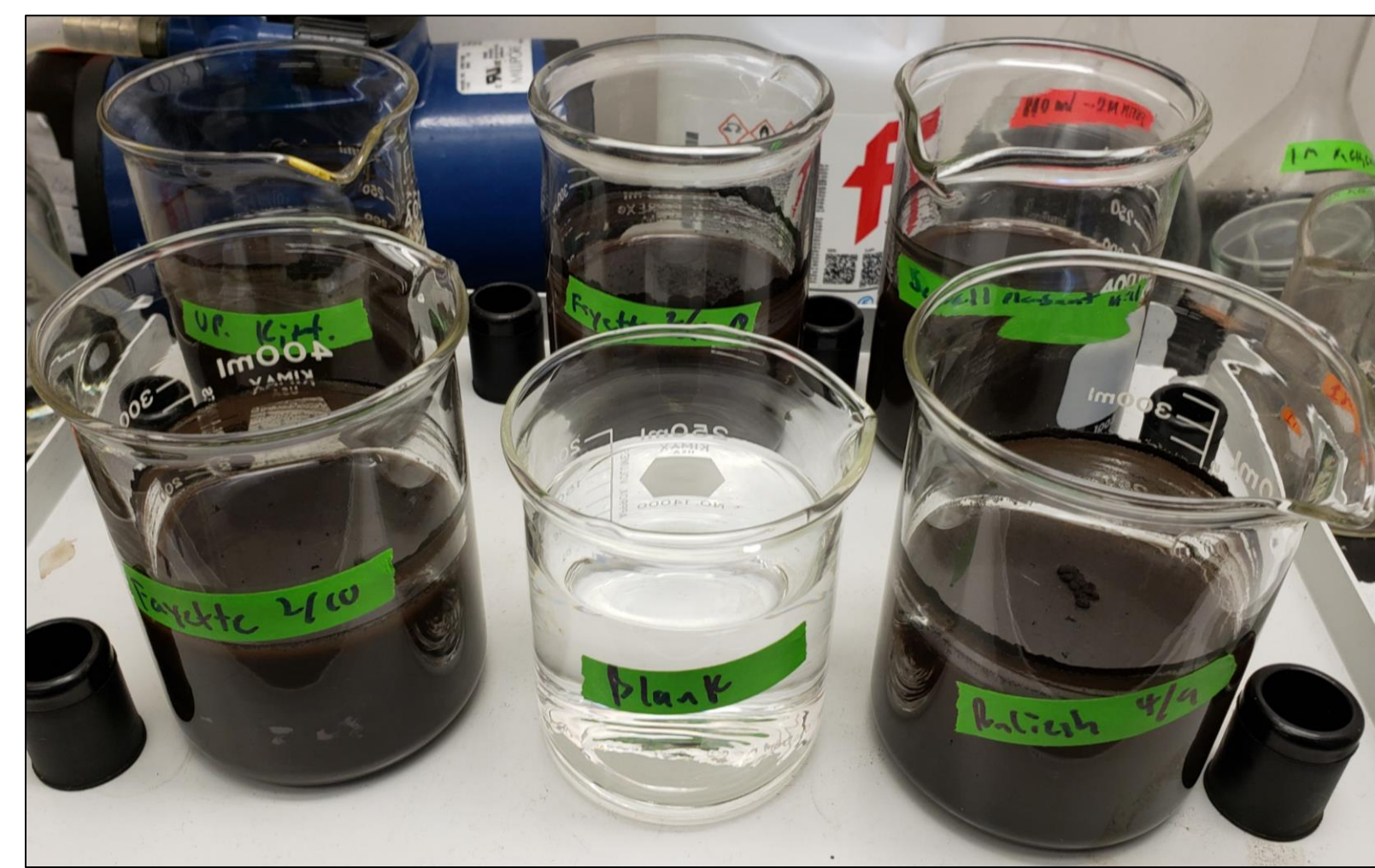
Ion Exchangeable
1M sodium acetate
1 hr

Carbonates, Oxides, Monosulfides
6M HCl
18 hr

Pyrite
2M HNO₃
18 hr

Organics
.02M HNO₃; 30% H₂O₂; 3.2M ammonium acetate
5.5 hr

Residue
Assumed to be silicates and other resistant mineral phases



Results & Discussion

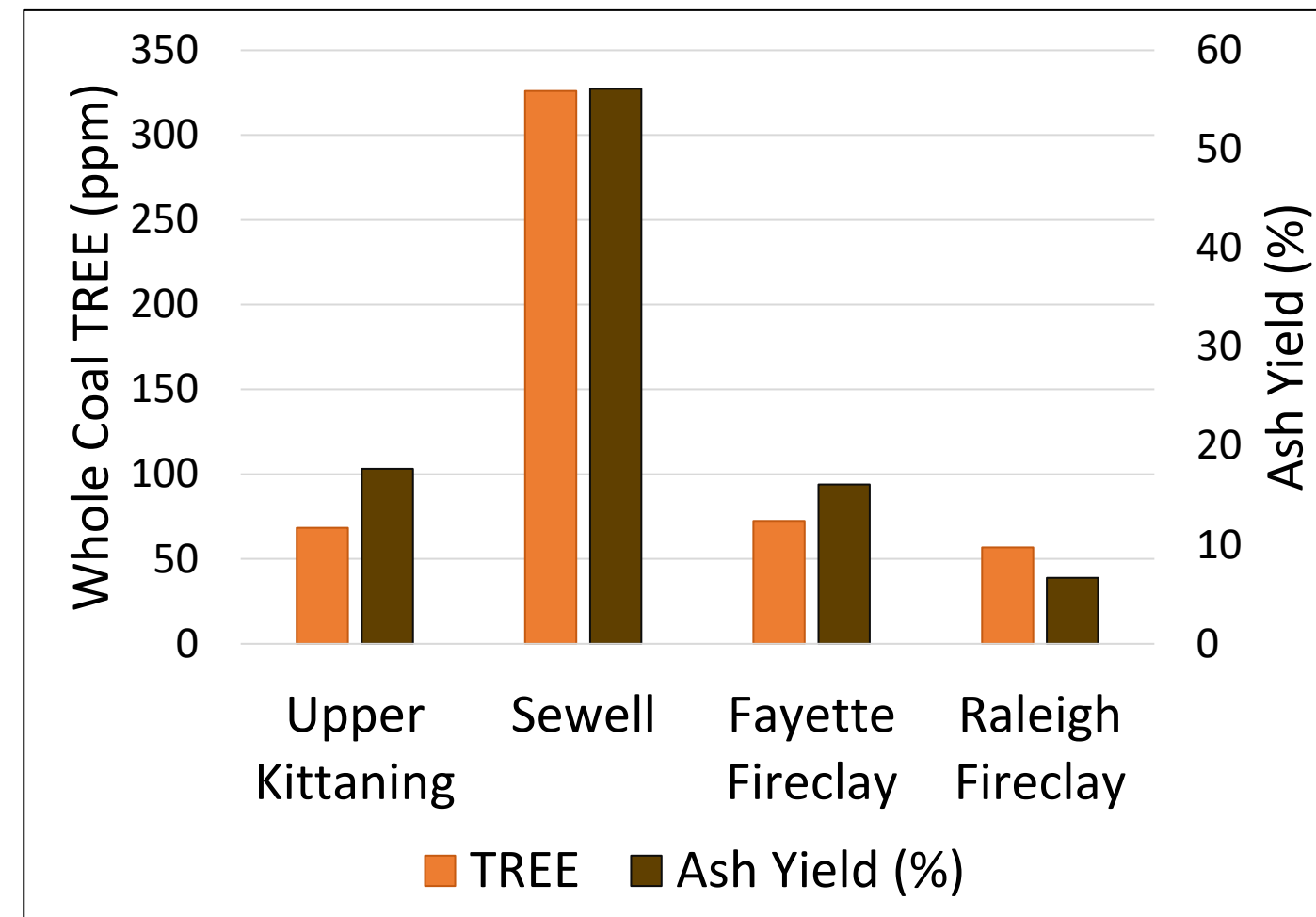


Fig. 1) Ash yield correlates well with total rare earth (TREE) concentration because mineral matter is generally the primary contributor of REE in coal. With the highest ash yield, Sewell has the highest TREE concentration. However, REE can also be introduced through secondary processes such as leaching or hydrothermal fluid flow. Secondary enrichment processes may have influenced the REE content of the Raleigh Fireclay sample.

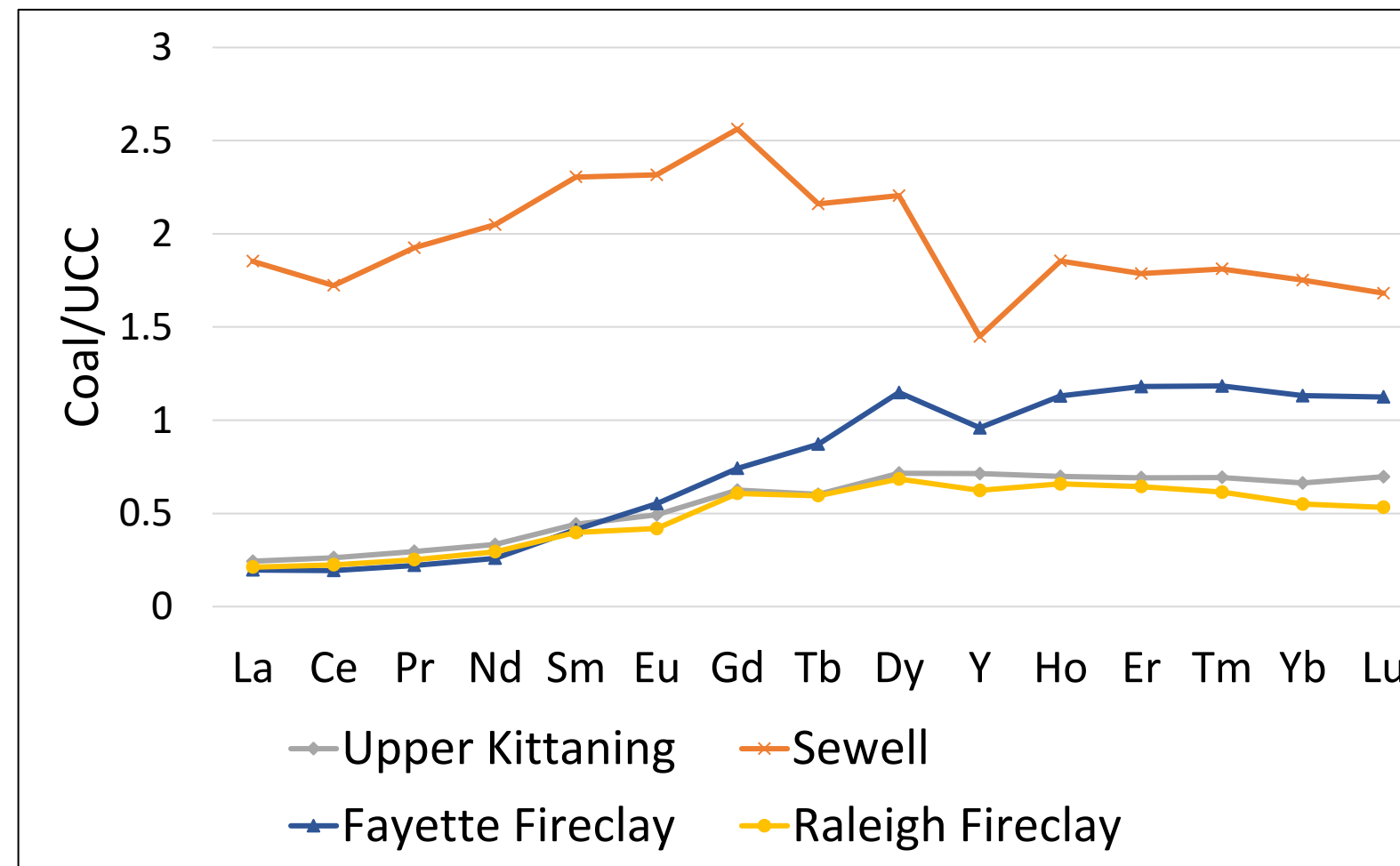


Fig. 2) Sewell is the only sample more enriched than the upper continental crust (UCC) for all REE. This is likely due to the large mineral fraction in the sample. Sewell is also unique in that it has an M-type distribution (enriched in medium REE (MREE)), whereas the remaining samples have H-type distributions (enriched in heavy REE (HREE)). The pH of waters circulating within coal basins can influence REE distribution types, with acidic waters more likely to produce M-type distributions (Seredin & Dai, 2012).

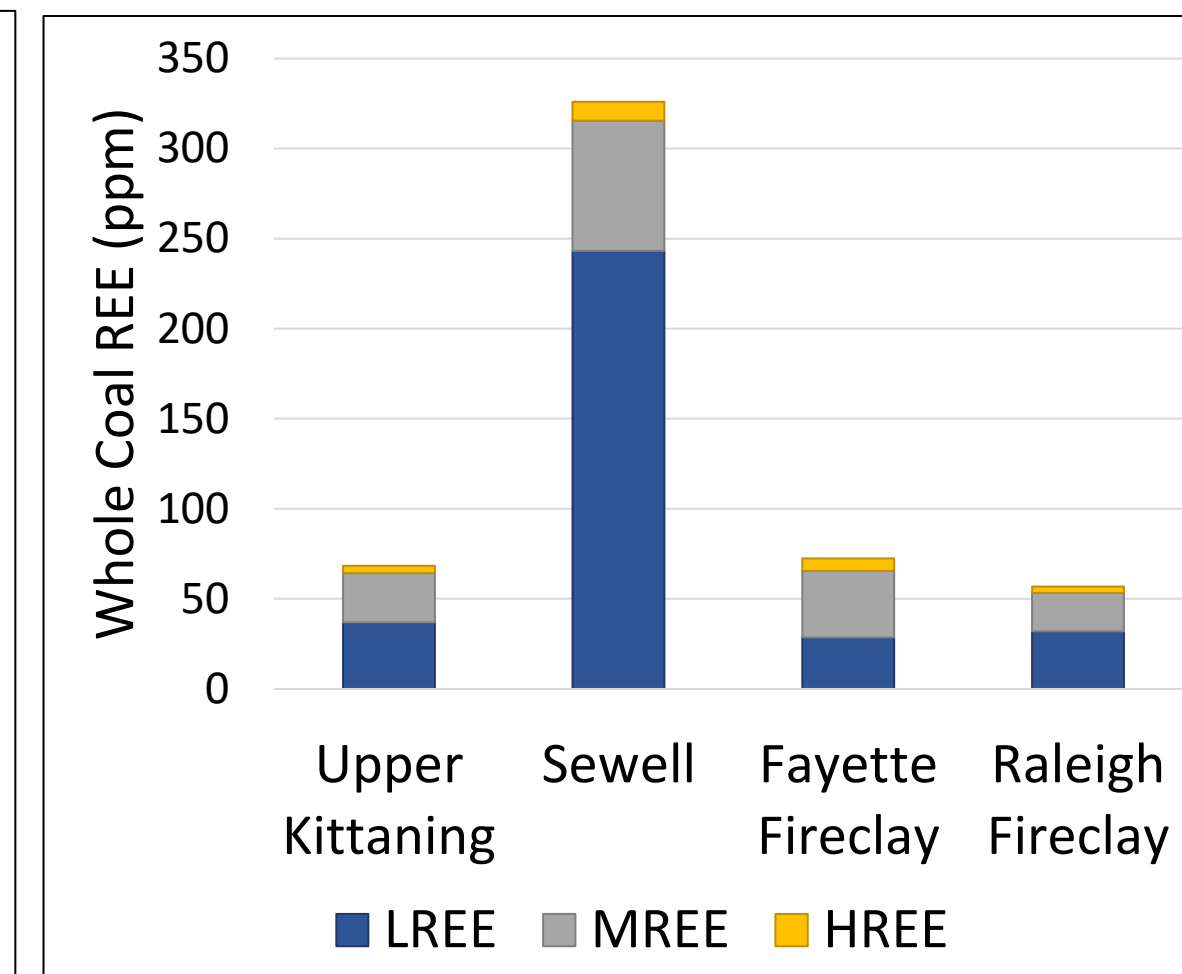


Fig. 3) Light rare earth elements (LREE) account for almost 75% of the TREE concentration in the Sewell sample, slightly more than 50% in the Upper Kittanning and Raleigh Fireclay samples, and only 39% in the Fayette Fireclay. Heavy REE account for less than 10% of the TREE content in all samples.

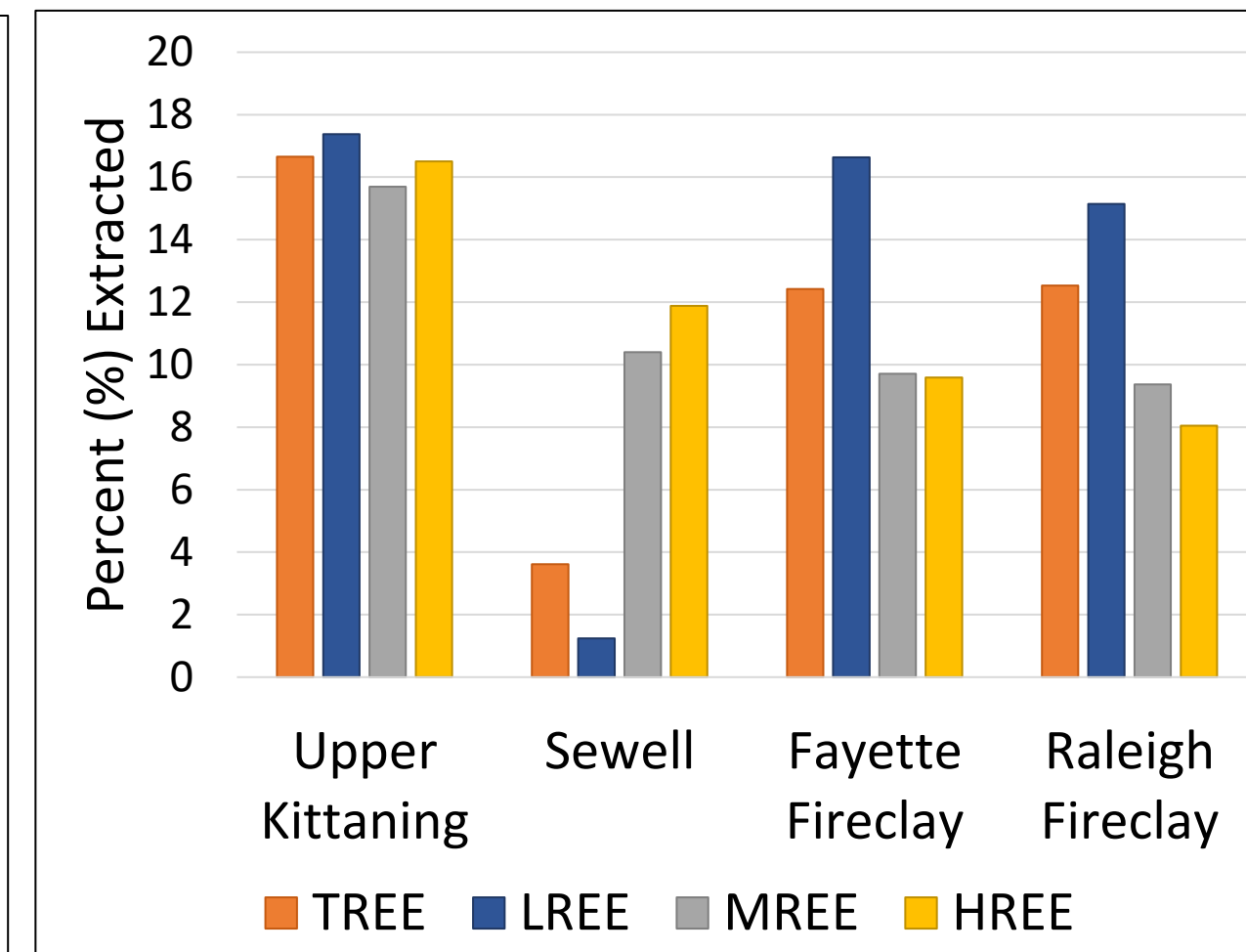


Fig. 4) Total REE recovery from sequential extractions was highest for the Upper Kittanning sample and recoveries for LREE, MREE, and HREE were similar. Total REE recovery in the Fayette and Raleigh Fireclay samples was similar, with LREE recovery significantly higher than MREE and HREE in both samples. Sewell had the lowest TREE recovery and, unlike the other samples, LREE had the poorest recovery.

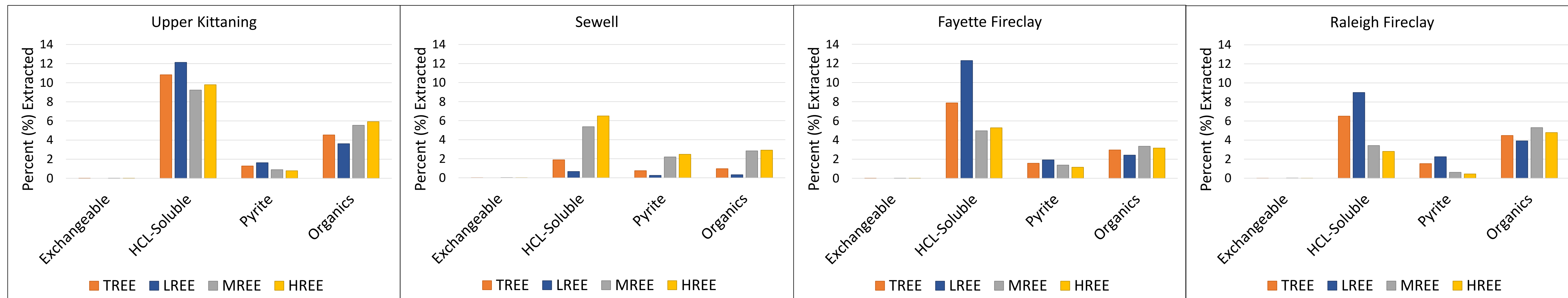


Fig. 5) In all samples, the majority of recoverable REE were extracted from the HCL-soluble phase, suggesting an association with carbonates, oxides, and possibly monosulfides. Less than 0.1% of TREE were extracted during the ion-exchange step. The organic fraction contributed a larger proportion of MREE and HREE, which are more likely than LREE to be sorbed or bonded to humic matter in coal (Seredin & Dai, 2012; Dai et al., 2021). In the Sewell sample, MREE and HREE had higher recovery than LREE in all of the extracted coal fractions. With the highest ash yield, Sewell would contain the largest fraction of aluminosilicate minerals. A majority of REE in this sample are assumed to be associated with or shielded by aluminosilicates or may be present in other resistant mineral phases, including detrital and authigenic phosphates.

Conclusions & Future Work

- Overall, total REE recovery from sequential extractions was low, ranging from about 4% (Sewell) to 17% (Upper Kittanning).
- More than half of recoverable REE were extracted from the HCL-soluble phase, suggesting an association with carbonates, oxides, and possibly monosulfides.
- Medium and heavy REE had better recovery than light REE in the organic fraction because they are more likely to be sorbed or bonded to humic matter in coal.
- Poor REE recovery suggests that the majority of REE are associated with or shielded by aluminosilicate minerals, or are present in other resistant mineral phases.
- Results of pending X-ray diffraction for extracted residues will provide additional insight into REE phase associations.
- Future experiments will utilize alkaline additives and high-temperature roasting to enhance recovery of REE from WV coals by targeting aluminosilicate phases.

References

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