

SHRIMP-RG Determination of Rare Earth Element Distribution in Coal Fly Ash

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Rare earth elements (REE) are strongly retained in solids remaining after coal combustion, leading to present day consideration of coal ash for REE recovery, as Goldschmidt initially proposed [1]. Relative to crustal averages, REE enrichments of 2-10 times in fly ash are typical, but much less is known about how REE occur in fly ash. In the present study, the Stanford-USGS SHRIMP-RG ion microprobe was used to investigate grain scale REE distribution in U.S. and international coal fly ash samples, with a nominal spot size of 15 micrometers and an oxygen negative-ion primary beam.

Results show that REE are partitioned into the melt/glass phase at peak boiler temperatures (1500 to 1700 °C). Aluminosilicate glasses are typically the most abundant constituent of fly ash. Chondrite-normalized REE distribution of Al-Si glasses resemble whole ash distributions at concentrations above or below the bulk. Aluminosilicates enriched in components other than Al-Si, such as Ca and Fe, tend to have REE abundances similar to or higher than the bulk sample. Fe-oxide magnetospheres are also REE-bearing, with greater variability in their REE patterns. Co-occurring quartz and/or high-silica glasses are mostly REE-depleted. In a few samples, zircon (MP = 1690 °C), with characteristic HREE enrichment, was found to survive the combustion process. REE partitioning into aluminosilicates is consistent with results for bulk samples of mainly U.S. coal fly ash showing a strong positive correlation ($r^2 = 0.71$) between Al₂O₃ percent and Σ REE [2]. Understanding the distribution of REE in fly ash on a grain scale potentially helps inform selective extraction strategies.

[1] Goldschmidt, V.M., 1935, Rare elements in coal ashes, *Ind. and Eng. Chem.*, 27 (9), p. 1100–1102.

[2] Taggart, R.K., et al., 2016, *Environ. Sci. Technol.*, 50 (11), 5919–5926, DOI: 10.1021/acs.est.6b00085.

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