



Distribution of rare earth elements in coal combustion fly ash, determined by SHRIMP-RG ion microprobe



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A B S T R A C T

During coal combustion for electric power generation, rare earth elements (REE) are strongly retained in the ash fraction leading to significant enrichment compared to the REE content of the respective feed coals. Knowing how the REE are distributed in coal ash is essential to devising effective approaches for REE extraction from this potential resource. To better understand the distribution of REE in coal ash, we used the Stanford-USGS SHRIMP-RG ion microprobe to determine grain-scale REE partitioning in a suite of 19 U.S. and international coal fly ash samples. SHRIMP-RG microanalysis used a nominal spot size of 15 μm and an oxygen negative-ion primary beam. NIST multi-element glass standards SRM 611 and SRM 613 were used for REE calibration. Prior to SHRIMP-RG analysis, samples were characterized by backscattered electron imaging and wavelength-dispersive elemental mapping to delineate constituents of interest for REE microanalysis. Results confirm the occurrence of REE in aluminosilicate glasses consistent with previous results that showed a strong positive correlation between Al and REE content in a larger group of U.S. and international coal fly ash samples. Among these glasses, aluminosilicates consisting of Al and Si and lacking other major constituents tend to have REE contents similar to, or slightly lower than the bulk sample REE content, whereas Ca- and/or Fe-enriched aluminosilicate glasses are similar to, or more REE-enriched than the bulk sample. Co-occurring quartz and/or high-silica glass is almost always the most REE depleted fly ash constituent, having much lower REE contents than the aluminosilicate glasses. Fe-oxide magnetospheres have REE content with relative proportions of light (LREE) to heavy (HREE) rare earths that are more variable than in the aluminosilicate glasses. Results suggest that extraction of REE from the aluminosilicate glass fraction in coal ash will yield a significant portion of the REE present and therefore, this fraction should be targeted in ongoing efforts to recover REE from coal fly ash.

1. Introduction

Rare earth elements (REE) are increasingly needed in a wide range of commercial and military applications, notably, the communications sector, and in wind energy where REE magnets are used in generators (Mayfield and Lewis, 2013; U.S. Geological Survey, 2014). In coal burning for power generation, REE are strongly retained in the solid residue (ash) remaining after coal combustion (Clarke and Sloss, 1992; Ratafia-Brown, 1994) and to a large extent, do not enter the gas phase, as is the case for more volatile elements. This solid fraction, consisting predominantly of fly ash and bottom ash, is derived from non-combustible mineral matter originally present in the coal. In commercial

coals, the ash fraction is relatively small compared to the overall mass of the coal; therefore, during the combustion process, REE are preferentially retained in a much smaller mass fraction. For example, relative to REE concentrations in coal, enrichment by factors of approximately 5 to 10 might be expected for coals having mineral matter contents of 20 to 10%, respectively, assuming total REE retention. Partitioning of rare elements, including REE, into coal ash was recognized early on by Goldschmidt (1935) who proposed their recovery. Subsequently, case studies by Seredin (1991, 1996), Seredin and Dai (2012), and Seredin et al. (2013), among others, gave examples of extreme rare element enrichment in coal and coal ash, and again considered the potential for recovery of non-energy byproducts from these

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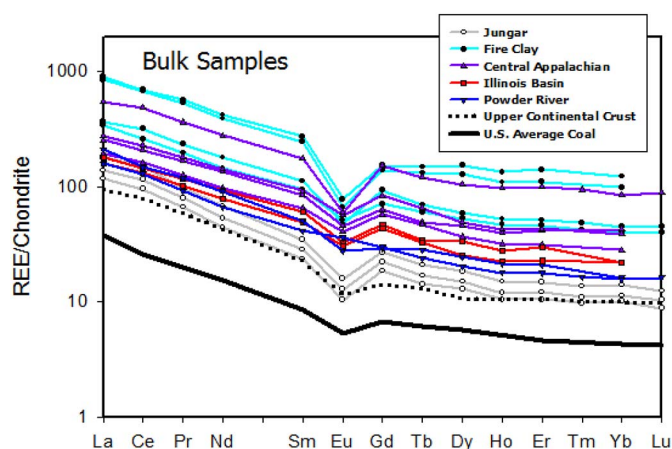


Fig. 1. Chondrite-normalized REE distribution in bulk fly ash samples by region of origin showing REE enrichment relative to upper continental crust (Taylor and McLennan, 1985) and U.S. average coal, compiled from the USGS COALQUAL database (Palmer et al., 2015). Sample data are compiled from sources listed in Table 1. Samples having mixed (77 (A002), 78 (A003)) or unspecified (345, 357) associations, are omitted from the plot. Chondrite normalization is after Korotev (2009). Tm values in Fire Clay samples 92794 and 92803, giving apparent Tm anomalies on a chondrite-normalized plot, are omitted (Supplementary information).

sources. In 2016, approximately 85% of world REE mine production was in China; following closure of the only U.S. mine source in late 2015, there was no domestic U.S. REE production in 2016 (U.S. Geological Survey, 2017). As market conditions for alternative REE sources have become more favorable, recent papers showing the distribution of REE in coal and coal ash, and considering the prospects for recovery of REE from these sources have attracted considerable attention (Blissett et al., 2014; Dai et al., 2016a; Lin et al., 2017; Hower et al., 2016a). Pending shortages of REE in the U.S. and elsewhere have drawn renewed consideration to coal and coal ash as possible REE sources, leading to new research opportunities supported in part by a U.S. Department of Energy effort to develop domestic production of REE from coal and coal ash (U.S. Department of Energy, 2017a).

Concentration ranges of REE in bulk samples of U.S. coal are relatively well known. The USGS COALQUAL database (Palmer et al., 2015) shows that, on average, REE contents of U.S. coals are somewhat lower than those of shales and for the average upper continental crust (Taylor and McLennan, 1985), whereas REE contents of shales and the average upper continental crust are lower than those found in coal fly ash (Fig. 1). Potential recovery of valuable elements from coal and coal ash requires 1) identifying coals and their ashes with the highest rare element concentrations, and 2) devising workable extraction strategies for the REE. Ongoing research is geared towards both goals, but with time, emphasis and support is shifting towards REE recovery. In each case, however, research has primarily been based on bulk sample REE determinations and bulk extraction studies (e.g., Hower et al., 2016a,b; Dai et al., 2016a; Taggart et al., 2016). In the present study we investigate the controls of REE distribution on a grain scale, in order to understand how REE occur in coal fly ash and help predict the capacity for their extraction.

The distribution of REE in coal (and in rocks) is predominantly controlled by REE-bearing trace phases such as monazite ((Ce,La,Nd,Th)PO₄), allanite ((Ce,Ca,Y)₂(Al,Fe³⁺)₃(SiO₄)₃(OH)), zircon (ZrSiO₄), xenotime (YPO₄; Finkelman, 1981), rhabdophane ((Ce,La,Y)PO₄·H₂O) (Dai et al., 2014a), florencite (CeAl₃(PO₄)₂(OH)₆), and Ce-Nd-bearing carbonates (Dai et al., 2016b, 2017; Zhao et al., 2017). Subsidiary fractions of organic-hosted REE also have been suggested, especially for the heavy rare earths (HREE; Eskanazy, 1987a,b, 1999). Scanning electron microscope (SEM) examination of a Kentucky coal and its corresponding ash (Zhang et al., 2015), indicates that REE-bearing trace phases are much more common in the coal than in the ash fraction. Beneficiation of fly ash

and bottom ash from coal with elevated REE contents, using density, magnetic, and hydrophobic approaches to concentrate REE-bearing trace phases, did not result in an increase in REE contents, suggesting that REE trace phases are not the primary mode of REE occurrence (Zhang et al., 2015).

Temperatures in coal-fired boilers range from ~1300 °C (fluidized bed boilers) to 1700 °C (cyclones and pulverized-coal fired boilers) (Senior, 2015). Retention of trace phases in coal ash might be predicted by trace phase melting temperatures, which range from 1690 °C for zircon to > 2000 °C for monazite and xenotime (Finch and Hanchar, 2003; Hikichi and Nomura, 1987; Boatner, 2002). Whereas REE-bearing trace phases have been shown to persist in coal ash in some cases (Smolka-Danielowska, 2010; this study), more typically, as shown by Zhang et al. (2015), REE-bearing minerals are much less common in ash than in the corresponding coal, even though the ash is more REE-enriched. This seemingly contradictory result leads to a range of possible alternatives to trace phase retention. One possible alternative involves the breakdown of trace phases with partitioning of REE into the melt formed at boiler temperatures that is now the glass fraction (hereinafter, glass). In this scenario, melting of trace phases in multi-component systems occurs at temperatures below those of the pure phases. This behavior is well known in natural igneous and hydrothermal systems. For example, zircon saturation (and melting) occurs at temperatures well below boiler temperatures, depending on the bulk composition and Zr content of the melt (Watson and Harrison, 1983). Other possible explanations for enrichment of REE in coal ash with disappearance of REE trace phases include 1) persistence of trace phases but with size reduction due to thermal shock (Hood et al., 2017a); 2) localized diffusion of REE from trace phases to the glass; and 3) occurrence of REE as nanoparticles or REE-enriched domains at the nanometer scale (Hood et al., 2017a,b; Hower et al., 2017).

To better understand how REE are distributed in coal ash, in the present study we investigated a suite of coal-ash samples, having a range of bulk REE contents, using trace element microanalysis by SHRIMP-RG ion microprobe (<https://shrimprg.stanford.edu/>). SHRIMP-RG employs Secondary Ion Mass Spectrometry (SIMS), in which a primary beam of incident ions is focused on a region of a solid specimen to sputter secondary ions from the sample (Stern, 2009; Bacon et al., 2012; Ireland, 2014). Characteristic secondary ions are then passed through a large format magnetic sector mass spectrometer with high mass resolution, giving elemental abundances or isotopic compositions on a micrometer scale. We were especially interested in using the SHRIMP-RG to determine REE distributions in fly ash glasses to test the hypothesis that REE are partitioned into the glass. A prior study using electron microprobe wavelength dispersive elemental mapping (Hower et al., 2013a) showed counts for Ce in glassy fractions of the ash, but these are at or near the limits of detection by electron beam methods and so the results are inconclusive. SHRIMP-RG was chosen for this study because: 1) it has appropriate detection limits at the mg kg⁻¹ to sub-mg kg⁻¹ level needed to characterize grain-scale REE distribution in fly ash; 2) compared to laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), which has comparable detection limits, sputtering depths by SHRIMP-RG and other ion microprobes (1–5 μm, depending on the material) are such that an order-of-magnitude less material is needed for quantitative analysis, allowing greater spatial selectivity, especially in the vertical dimension (Stern, 2009; Pisonero et al., 2009; 3) a working spot size of 15 μm is routinely achievable; a larger spot size may be needed for quantification by LA-ICP-MS, especially for the HREE (Horn et al., 1997; Longerich, 2009); 4) mass resolution of the SHRIMP-RG is superior to comparable methods, minimizing the effect of isobaric interferences (Schmidt and Vazquez, 2017); and 5) the staff of the Stanford-USGS SHRIMP-RG lab has considerable experience using the instrument with NIST glasses for calibration, to determine REE distributions in natural volcanic glasses, which are highly analogous to glassy material found in coal ash.

Table 1

Fly ash samples investigated and their bulk REE contents. Samples are derived from U.S. coals except where indicated.

Sample	Coal Bed	Coal Basin	Σ REE	Σ REE + Y	Ce/Yb _N	% Critical ^a	Reference
Jungar 120 +	No. 6	Jungar, Inner Mongolia, China	172.0	192.1	9.4	28.8	Dai et al., 2014b
Jungar 120 × 160	No. 6	Jungar, Inner Mongolia, China	206.0	229.7	10.2	28.7	Dai et al., 2014b
Jungar 160 × 300	No. 6	Jungar, Inner Mongolia, China	263.2	293.5	10.8	28.3	Dai et al., 2014b
77 (A002)	Various	Powder River Basin & Lower Freeport	262.4	313.8	n.d.	39.2	NETL, unpub. data 2016
78 (A003)	Various	Powder River Basin & Lower Freeport	311.0	365.8	n.d.	37.3	NETL, unpub. data 2016
345	Various	Unspecified/mixed	431.2	523.6	5.3	39.7	NETL, unpub. data 2016
357	Various	Unspecified/mixed	482.7	635.2	5.5	44.5	NETL, unpub. data 2016
BS-1	Unspecified	Central Appalachian	429.9	524.5	4.8	39.5	Deonarine, unpub. data, 2012
SP-1	Unspecified	Illinois Basin	300.3	366.5	6.7	39.4	Deonarine, unpub. data, 2012
PRB-1	Unspecified	Powder River Basin	297.8	345.2	9.7	34.5	Deonarine, unpub. data, 2012
92794	Fire Clay	Central Appalachian	1318.3	1534.3	6.8	34.7	Mardon and Hower, 2004
92803	Fire Clay	Central Appalachian	1408.6	1667.6	5.6	36.5	Mardon and Hower, 2004
93,299	Unspecified	Central Appalachian	330.9	401.5	5.7	38.6	Hower et al., 2013b
93310	Unspecified	Illinois Basin	264.5	312.1	6.0	36.2	Hower et al., 2013b
93385	Unspecified	Central Appalachian	468.4	563.6	5.8	38.1	Hower et al., 2013b
93925	Unspecified	Powder River Basin	245.27	283.2	8.2	32.8	Taggart et al., 2016
93932	Fire Clay	Central Appalachian	519.0	626.6	6.5	36.7	Taggart et al., 2016
93953	Fire Clay	Central Appalachian	617.1	723.4	7.1	35.1	Taggart et al., 2016
93962	Unspecified	Central Appalachian	961.3	1175.2	5.8	38.4	Taggart et al., 2016

^a Critical REE include Y, Nd, Eu, Tb, Dy, and Er, as defined by Seredin and Dai, 2012. Ce/Yb_N is expressed on a chondrite-normalized basis.

2. Materials and methods

2.1. Sample materials

A suite of 19 samples of coal fly ash having prior bulk REE determinations was assembled from archival material (Table 1). The samples included fly ash from U.S. power stations burning high volatile bituminous coal from the central Appalachian Basin (BS-1, 92794, 92803, 93299, 93385, 93932, 93953, and 93962) and the Illinois Basin (SP-1, 93310), and subbituminous coal from the Powder River Basin (PRB-1, 93925). In addition, four U.S. fly ash samples having mixed (77 (A002) and 78 (A003)), or unspecified (345, 357) associations were included (Table 1). Archival material also was obtained for one plant burning Chinese high volatile bituminous coal (Jungar). More complete data for the U.S. fly ash samples can be found in Mardon and Hower (2004), Hower et al. (2013b), and Taggart et al. (2016), and for the Jungar samples, in Dai et al. (2014b). The four mixed or unspecified U.S. fly ash samples are part of an extensive database of REE-bearing coal and coal ash maintained by the U.S. Department of Energy, National Energy Technology Laboratory (NETL; U.S. Department of Energy, 2017b); these samples were provided by NETL for this study. Of the central Appalachian Basin coal fly ash samples, four samples from the Fire Clay coal (92794, 92803, 93932, 93953), known for its REE enrichment, are included in the study (Hower et al., 1999; Mardon and Hower, 2004).

Bulk REE data for the samples investigated were compiled from previous ICP-MS determinations (Fig. 1 and Supplementary information). REE results for each sample were plotted on chondrite-normalized plots to insure internal consistency of the results. With the possible exception of Tm in Fire Clay coal fly ash samples 92794 and 92803 (not shown), which is strongly enriched relative to other HREE, in nearly every case, smooth REE patterns with LREE enrichment and negative europium anomalies characteristic of upper crustal materials were obtained. Three samples of Jungar coal fly ash represent a series of size fractions (120 +, 120–160, and 160–300 mesh), with bulk REE content increasing in the finest size fractions. This trend is similar to the trace element distribution seen in electrostatic precipitator hoppers for elements partitioned from the gas phase, such as Hg (Mardon and Hower, 2004), but does not necessarily imply that REE are carried in the flue gas. In other cases, variation in REE content with fly ash grain size was found to be less pronounced (Hower et al., 2013b; Liu et al., 2017).

The proportion of critical REE has been used in past studies as a measure of the economic potential of specific coal and coal ash

resources (e.g., Seredin and Dai, 2012; Seredin et al., 2013). In the present study, the fraction of critical REE (Y + Nd + Eu + Tb + Dy + Er) as defined by Seredin and Dai (2012) was calculated for each bulk fly ash sample investigated (Table 1). As the most abundant REE (La, Ce) are excluded, the proportion of critical REE in light rare earth (LREE)-enriched fly ash is typically < 40%. Variation in the proportion of critical REE is a function of the slope of normalized REE patterns. In Fig. 2, LREE enrichment is calculated as Ce/Yb_N, where bulk sample results are normalized to their respective chondritic Ce and Yb values (Korotev, 2009; Table 1). Samples from the Appalachian and Illinois Basins have slightly flatter (lower Ce/Yb_N) normalized REE slopes and a corresponding higher percentage of critical REE, relative to the average upper continental crust (Taylor and McLennan, 1985), whereas other bulk samples have similar (Powder River Basin) or slightly steeper slopes (higher Ce/Yb_N; e.g., Jungar samples), and a corresponding lesser proportion of critical REE (Fig. 2; Table 1; Supplementary information). Fig. 2B shows that the proportion of critical REE is unchanged as REE + Y increases, because the slopes of the REE patterns remain relatively constant with variation in REE + Y enrichment.

2.2. Electron beam microanalysis

Prior to SHRIMP-RG determinations, the coal ash samples were embedded in epoxy, ground and polished, using silicon carbide and diamond abrasives, at Stanford University by SHRIMP-RG laboratory staff. These mounts then were characterized by backscattered electron (BSE) imaging, using a Hitachi SU5000 field emission SEM, and by wavelength dispersive elemental mapping, using a JEOL JXA 8900R electron microprobe. Both electron beam instruments are located at the USGS in Reston, Virginia. Wavelength dispersive elemental maps were obtained at the K α peak positions for Fe, Ca, Al, Si, and Mg, respectively, using LiF, PETH, TAP, PETJ, and TAP crystal spectrometers. Mapping used a dwell time of 50 ms, at pixel sizes ranging from 0.20 to 1.50 μ m, with a minimum map area of 450 × 450 pixels. BSE images and wavelength dispersive maps showed constituents of the fly ash samples and their major element compositions, which were then used to identify areas of interest to analyze in SHRIMP-RG runs.

2.3. SHRIMP-RG analysis

Trace element microanalyses were determined for the coal ash samples using the Stanford-USGS SHRIMP-RG ion microprobe at Stanford University. Secondary ions were sputtered from Au-coated

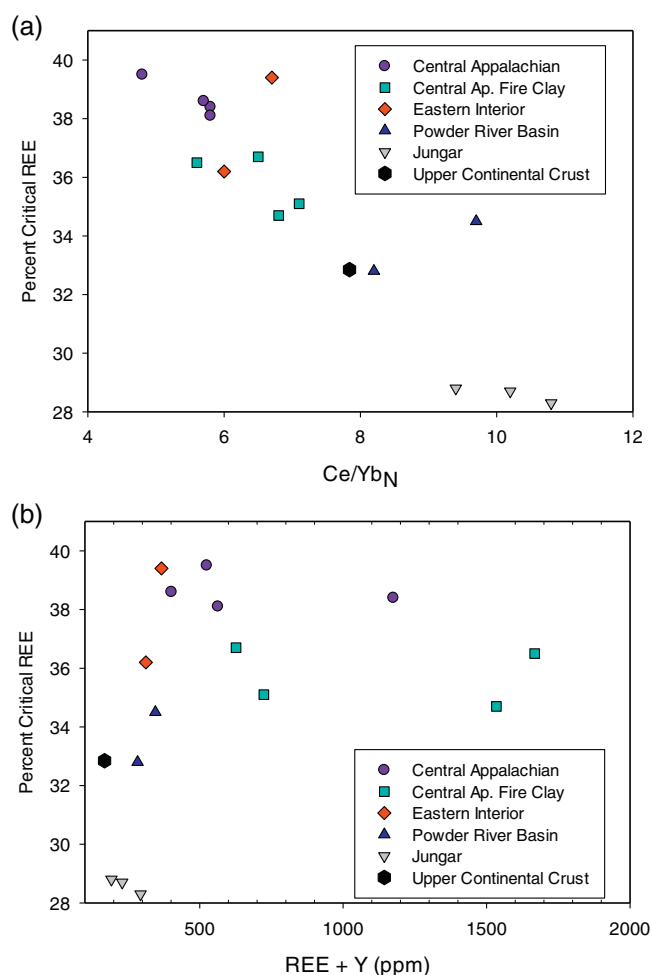


Fig. 2. (A) Plot showing variation in LREE enrichment (Ce/Yb_N) vs. percent critical REE ($Y + Nd + Eu + Tb + Dy + Er$) for bulk fly ash samples investigated. Data are from sources listed in Table 1. Appalachian Basin and Eastern Interior samples are less LREE-enriched than average upper continental crust (Taylor and McLennan, 1985), and therefore have a higher proportion of critical REE (Seredin and Dai, 2012); whereas, the Powder River Basin and Jungar samples are similar to, or more LREE-enriched, than average upper crust. Samples having mixed associations (77 (A002), 78 (A003)) lack Yb values and cannot be plotted. Samples with unspecified associations (345, 357) are omitted from the plot. (B) Plot showing variation in REE + Y vs. percent critical REE ($Y + Nd + Eu + Tb + Dy + Er$) for bulk fly ash samples investigated. Data are from sources listed in Table 1. Plot shows REE + Y enrichment of samples vs. upper continental crust and lack of correspondence between REE + Y abundance and the proportion of critical REE. Samples having mixed (77 (A002), 78 (A003)) or unspecified (345, 357) associations are omitted from the plot. Upper continental crust value is from Taylor and McLennan (1985).

sample material using an approximately 1 nA O_2^- primary ion beam with Kohler illumination and focused to a spot size of 15 μm . REE were determined from measurements of positive secondary ions of elements ($^{139}La^+$, $^{140}Ce^+$, $^{146}Nd^+$, $^{147}Sm^+$, and $^{151}Eu^+$), or, to obtain sufficient yield for the HREE, as oxides ($^{158}Gd^{16}O^+$, $^{159}Tb^{16}O^+$, $^{159}Dy^{16}O^+$, $^{166}Er^{16}O^+$, $^{172}Yb^{16}O^+$, and $^{175}Lu^{16}O^+$). Pr, the least abundant LREE, and two odd numbered HREE, Tm and Ho, were omitted to expedite the analyses. Count times were 10 s. for LREE and 20 s. for HREE. In addition to REEs, two other elements of interest, $^{89}Y^+$ and $^{93}Nb^+$, were determined. Elemental concentrations were calculated based on element/ ^{30}Si ratios determined for NIST silicate glass standards SRM 611 and SRM 613 calibrated to mean values for these standards given in Jochum et al. (2011). Reported errors were calculated from the counting statistics of these same ratios. The NIST glass standards contain a wide range of elements, including REE, at nominal concentrations of approximately 400 mg kg $^{-1}$ (NIST SRM 611), and 40 mg kg $^{-1}$ (NIST

SRM 613), respectively (NIST, 2012a,b). Certified REE values are not available for REE in either standard, but informational values for NIST SRM 613 range from 35 mg kg $^{-1}$ (Dy) to 42 mg kg $^{-1}$ (Yb). Multiple in-run REE determinations for the NIST standards are within the uncertainty of available informational values (Supplementary information). Overall analytical uncertainty for REE in aluminosilicate glasses reported here is ± 10 –20% or better (see Criteria for data acceptance). This is comparable to what is achievable by alternate methods of trace element microanalysis of glasses, such as LA-ICP-MS.

2.3.1. Grain nomenclature

Sample materials in SHRIMP-RG analysis were identified either by matching sample grains observed in reflected light viewed in the SHRIMP-RG optics with pre-mapped areas covered by BSE/wavelength dispersive elemental mapping, and/or by using four major element monitors – $^{57}Fe^+$, $^{30}Si^+$, $^{43}Ca^+$ and $^{27}Al^{16}O^+$ acquired simultaneously with SHRIMP-RG REE determinations. The isobars ^{43}Ca and $^{27}Al^{16}O$ were completely resolved from each other by tuning the mass spectrometer to a mass resolution ($M/\Delta M$) of 10,000. Whereas the Al/Si of the aluminosilicate glasses varies widely, for descriptive purposes, where the measured $^{27}Al^{16}O/^{30}Si$ (Al/Si) was 0.5 or greater, aluminosilicates were designated (Al–Si), and where this ratio was < 0.5 , these regions were designated (Si–Al). Where $^{27}Al^{16}O/^{30}Si$ was < 0.1 these areas were designated quartz/ SiO_2 , which was also distinguishable by an angular outline compared to the round aluminosilicate cenospheres and a lack of other major constituents. The presence of Ca and Fe in the glasses was noted where $^{43}Ca/^{30}Si$ (Ca/Si) was ≥ 0.1 , and where the $^{57}Fe/^{30}Si$ (Fe/Si) was ≥ 0.2 , respectively. Fe-oxide spheres were distinguished by a $^{57}Fe/^{30}Si$ ratio of 1.0 or greater. The presence of zircon, where not previously recognized, was indicated by a monitor for $^{90}Zr^{16}O^+$, in which counts for all other materials were negligible, and also by its morphology.

In most cases, where possible, comparison of grain nomenclature determined from major element monitors confirmed the observed selections, based on matching the SHRIMP-RG reflected light image with our elemental maps. In some cases, the major element monitors showed that the anticipated target was missed or that the maps were misinterpreted. In addition, where we were unable to locate pre-mapped areas in reflected light or where grains outside of the mapped areas were selected for analysis, we relied entirely on the SHRIMP-RG major element monitors to identify the analyzed grains. Locations of all points determined were captured in reflected light digital images acquired in the course of the SHRIMP-RG runs.

2.3.2. Criteria for data acceptance

Data obtained in our SHRIMP-RG runs were reviewed to identify analyses with low count rates for major elements, and/or corresponding high ($\geq 20\%$) errors in results for the REE. These conditions may have resulted from penetration of hollow grains by the primary beam, overlap of grains selected for analysis with epoxy, or other issues potentially affecting determinations by microanalysis in a point mode. SHRIMP-RG analysis of our aluminosilicate glasses generally gave count rates in the 10^5 to 10^6 range for ^{30}Si ; where count rates for ^{30}Si in the glasses were 10^4 or lower, the corresponding analyses were rejected and the entire analysis was excluded from the reported results. Errors are based on 1/the square root of the counts per second ($1/\sqrt{cps}$); low count rates result in unacceptably high errors, especially for the HREE, where the count rate may be only 1 cps or less. In addition to exclusion of data on the basis of count rate for ^{30}Si , individual REE values for aluminosilicate analyses were rejected where the calculated analysis error exceeded 20%. This usually affected the HREE due to their low abundance. Where two or more elements in order of atomic number had errors that exceeded 20%, the entire lanthanide analysis was rejected. The same tolerance was applied for Fe-oxides ($> 20\%$ for any REE). For these, a greater uncertainty may have resulted from mismatch of sample matrix with the NIST glass standards used for calibration. For

quartz/SiO₂, the presence of low REE concentrations resulted in large analytical uncertainties for the REE despite acceptable count rates for ³⁰Si. These data were retained where errors for the REE were within 20% or better. Where errors exceeded 20% as detection limits were approached, results for the SiO₂ fraction were expressed as d.l. (detection limit) to demonstrate that these grains were analyzed and found to be devoid of REE. Application of all of these criteria resulted in acceptance of REE results for 302 (75%) of 400 points determined, for an average of 16 points per sample. This eliminated many analyses that did not define a smooth REE distribution on a chondrite-normalized plot, and some that did. No attempt was made to estimate bulk REE contents by averaging the accepted points. Usable bulk REE analyses were available already and estimates of bulk composition based on a small number of microanalysis points are not statistically valid.

3. Results

Bulk REE data for the samples investigated and grain scale SHRIMP-RG results passing acceptance criteria are compiled as Supplementary material. In the following sections, REE partitioning characteristics of specific fly ash constituents are described, together with selected comparisons by sample location.

3.1. Aluminosilicates

Backscattered electron imaging (Fig. 3), wavelength dispersive elemental mapping (Fig. 4), and energy dispersive spectra from the SEM and electron microprobe analyzers (not shown) indicated that glassy aluminosilicate cenospheres consisting almost entirely of Al and Si in varying proportions were the most common constituent of each sample investigated. This variability also is shown by the range in ²⁷Al/³⁰Si (Al/Si) determined by the SHRIMP-RG major element monitors, with an arbitrary division of Al/Si of 0.50 used to distinguish Al-rich aluminosilicates (Al–Si) from Si-rich aluminosilicates (Si–Al) (Supplementary information).

Variation in REE content of the fly ash aluminosilicates is shown in

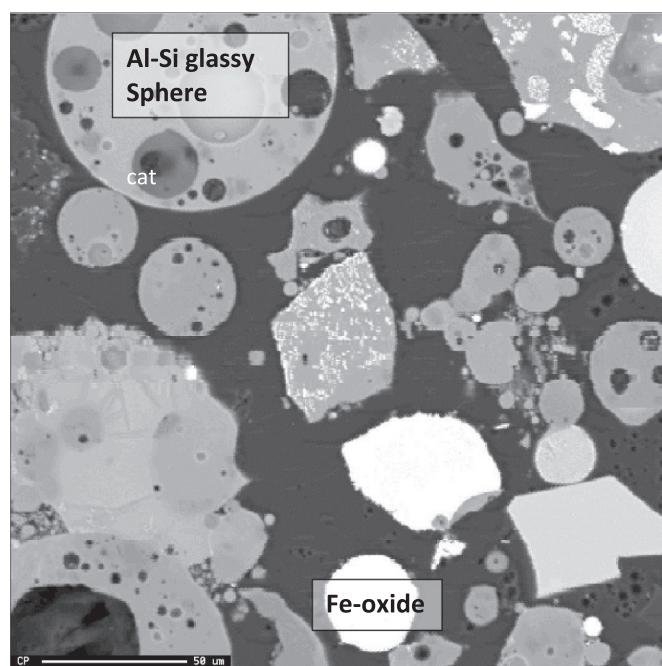


Fig. 3. Backscattered electron image of representative area in sample 357 showing variation in fly ash constituents determined selectively by SHRIMP-RG, including glassy cenospheres (upper left) and Fe-oxide magnetospheres (bottom center). Width of field of view is 225 μm.

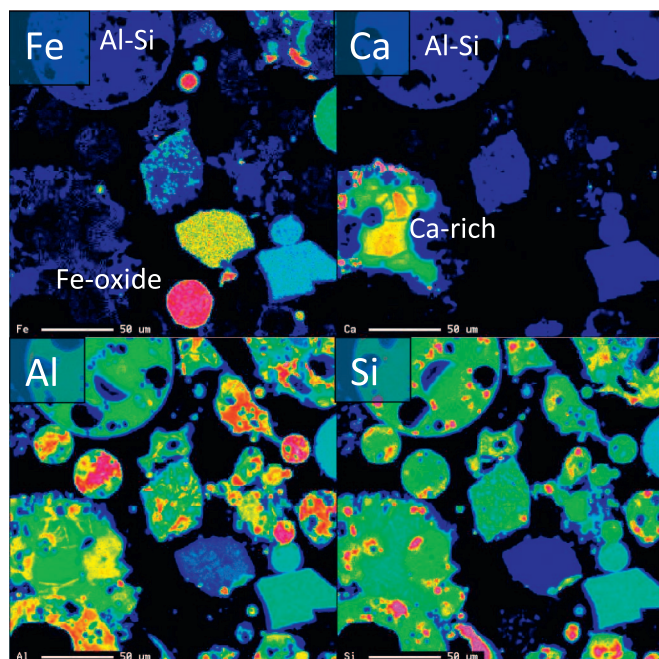


Fig. 4. Wavelength-dispersive electron microprobe elemental maps for Fe, Al, Ca, and Si of the area shown in Fig. 3. Width of field of view in each map is 225 μm. Images show Ca-enriched aluminosilicate at center left whose composition is less apparent in the back-scattered electron image (Fig. 3).

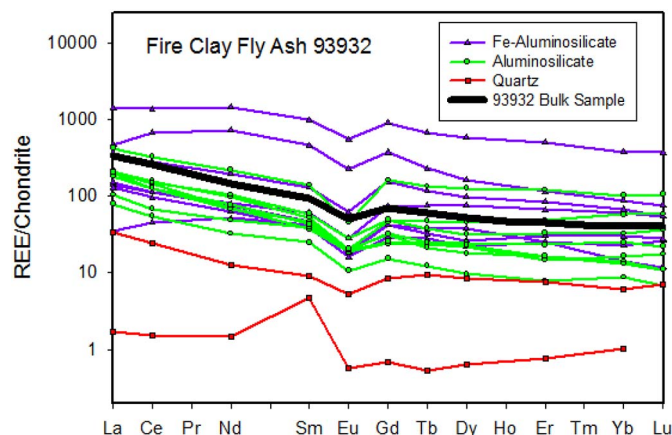


Fig. 5. Chondrite-normalized plot showing SHRIMP-RG results for sample 93932, coal fly ash derived from Fire Clay Appalachian Basin coal. Bulk REE distribution is from Taggart et al. (2016). Plot shows relative REE enrichment in Fe-bearing aluminosilicate glass relative to Fe-poor glasses, which are further distinguished by Al/Si in Supplementary information. Quartz shows relative REE depletion or is below detection. One quartz analysis, having REE contents below detection, is excluded.

Figs. 5–9 as chondrite-normalized plots. In general, chondrite-normalized REE distributions for these aluminosilicates are similar to or slightly lower than that of the bulk composition for a given sample. Where Al–Si and Si–Al compositions are distinguished (Fig. 6; Supplementary information), the more SiO₂-rich glasses appear to trend towards lower REE contents, consistent with pronounced REE depletion in quartz, here defined as having an Al/Si of < 0.1. Within the uncertainty of the SHRIMP-RG determinations, REE patterns for individual aluminosilicate cenospheres resemble patterns of their corresponding bulk samples. This appears to confirm partitioning of REE into the glass during coal combustion, but also provides an independent check on the REE bulk determinations compiled from various sources

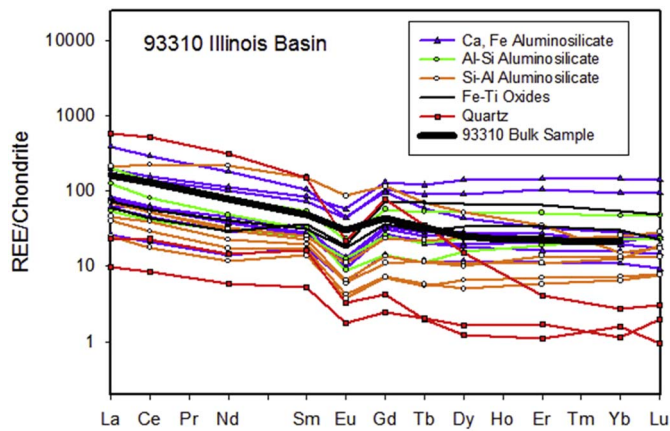


Fig. 6. Chondrite-normalized plot showing SHRIMP-RG results for sample 93310, coal fly ash derived from Illinois Basin coal. Bulk REE distribution is from Hower et al. (2013b). Fe, Ca aluminosilicate grouping includes analyses that show enrichment in Fe, Ca, or both, as defined in the text. Here Al–Si and Si–Al aluminosilicates are distinguished. Glasses with $^{27}\text{Al}^{16}\text{O}/^{30}\text{Si}$ of 0.5 or greater (Al–Si) tend to parallel the bulk composition whereas glasses with $^{27}\text{Al}^{16}\text{O}/^{30}\text{Si}$ of < 0.5 (Si–Al) trend towards lower abundances. Quartz has the lowest REE content, with the exception of one point having an SiO_2 -rich bulk composition that is strongly LREE-enriched, possibly due to included monazite (see text). Three quartz analyses having REE contents below detection are excluded from the plot.

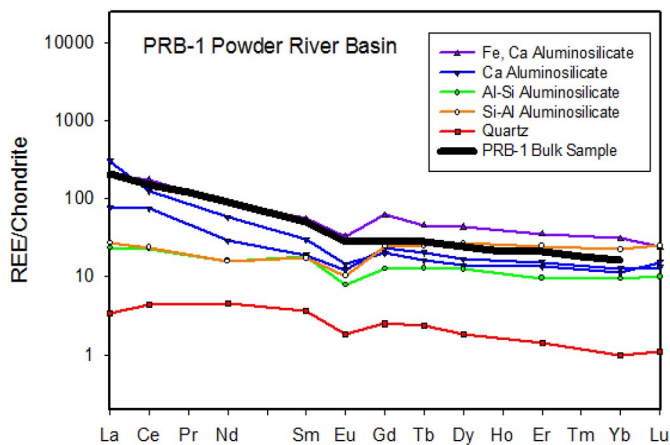


Fig. 7. Chondrite-normalized plot showing SHRIMP-RG results for sample PRB-1, coal fly ash derived from Powder River Basin coal. Bulk REE distribution is from Deonarine (unpublished data, 2012). Plot shows range of REE enrichment in 6 point analyses encompassing the major constituents observed. Aluminosilicates overlap the bulk composition with Fe and Ca-enriched glasses showing slightly greater enrichment than pure aluminosilicate glasses. Quartz has the lowest REE content. Six quartz analyses having REE contents below detection are excluded.

(Table 1; Supplementary information).

3.2. Ca-, Fe-rich aluminosilicates

In many fly ash samples, notably, 93925 and PRB-1 (Powder River Basin), 93932 (Appalachian Basin-Fire Clay), 93310 and SP-1 (Illinois Basin), 77 (A002) and 78 (A003) (mixed Appalachian Basin and Powder River Basin), and in each of the Jungar samples, a subset of Ca, Fe, or Ca–Fe enriched aluminosilicates was found to co-occur with glassy cenospheres consisting predominantly of Al and Si (Supplementary information). Selective analysis by SHRIMP-RG confirmed our hypothesis that these constituents were REE-enriched compared to the more abundant Ca- and Fe-poor cenospheres. Unlike Al- or Si-enriched glasses, REE patterns for the Ca- and/or Fe-bearing glasses are generally similar to or above the sample bulk composition on chondrite-normalized plots, while retaining the overall shape of the REE distribution

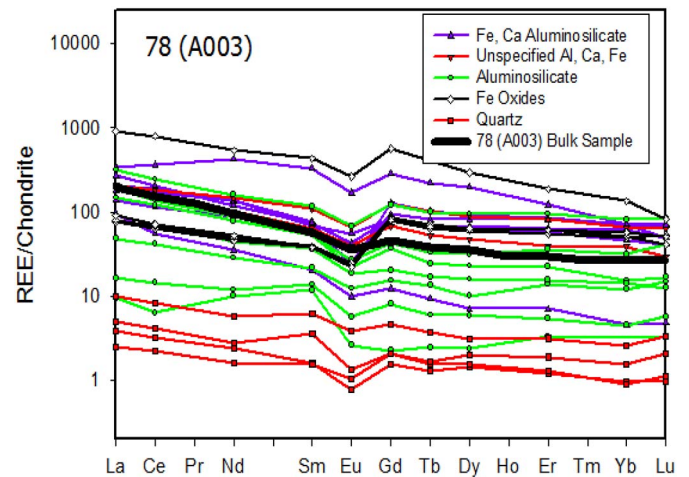


Fig. 8. Chondrite-normalized plot showing SHRIMP-RG results for sample 78 (A003), coal fly ash derived from mixed Powder River Basin and Appalachian Basin coal. Bulk REE distribution is from NETL, 2016 (unpublished data). Fe, Ca aluminosilicate grouping includes analyses that show enrichment in Fe, Ca, or both, as defined in the text. Plot includes two analyses of unspecified Si-rich, Al-poor Ca, Fe-bearing silicate glass with similar REE distribution to Fe, Ca aluminosilicate. Plot excludes Fe-aluminosilicate analysis 1.7, which has a random REE distribution pattern despite application of data acceptance criteria (Supplementary information). One quartz, and one aluminosilicate analysis, each having REE contents below detection, are also excluded.

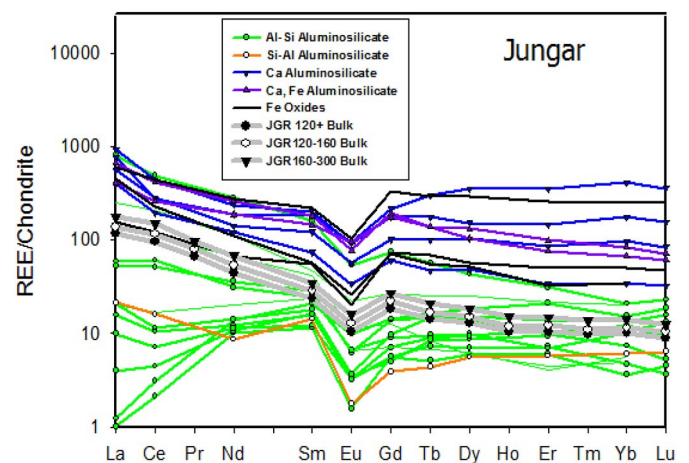


Fig. 9. Chondrite-normalized plot showing SHRIMP-RG REE results in Jungar, China bulk fly ash samples (Dai et al., 2014b) and SHRIMP-RG results for Jungar fly ash constituents as defined in text. Plot includes SHRIMP-RG results for all three Jungar size splits combined. Results show preferential REE concentration in Ca- and Fe-bearing aluminosilicates. Eleven analyses having REE contents below detection (6 Al-Si; 2 Si-Al; 3 SiO_2) are omitted from the plot. Results for bulk data show relative REE enrichment in the finer size fractions, as noted by Dai et al. (2014).

seen in the bulk samples (Figs. 5–9). Some Ca-enriched zones also may contain Ca-oxides, for which REE were not determined. Taggart et al. (2016) found that REE in fly ash derived from Ca-enriched Powder River Basin coal were more readily leachable than fly ash derived from more REE-enriched Appalachian Basin coal. If the Ca-Fe-enriched constituents prove to be more readily extractable, they could explain the greater extractability of REE from ash derived from Powder River Basin coals despite their lower overall REE contents (see Discussion). Where Ca- and Ca-Fe-enriched spheres are present and these are distinguished, as in the Jungar samples, their relative REE contents are similar (Fig. 9).

3.3. Fe-oxides

During coal combustion, Fe may be incorporated into

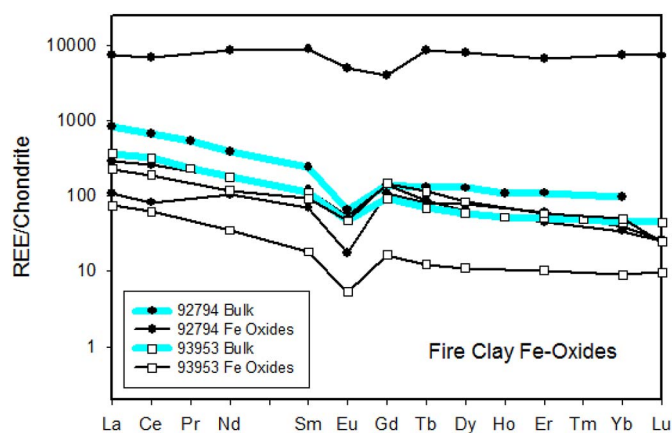


Fig. 10. Chondrite-normalized plot showing SHRIMP-RG results for Fe-oxides in Fire Clay coal ash samples 92794 and 93953, together with bulk REE results for these samples from Mardon and Hower (2004), and Taggart et al. (2016), respectively. Plot shows variability in Fe-oxide REE distributions.

aluminosilicate glasses, from which skeletally-textured Fe-oxides rapidly nucleate (Waanders et al., 2003; Zeng et al., 2009; Yang et al., 2014). The resulting fine intergrowths of Fe-oxide in a matrix of interstitial glass are characteristic of Fe-oxide magnetospheres (Yang et al., 2014). The proportions of Fe-oxides and glass in these intergrowths are highly variable. In the SHRIMP-RG major element monitors, a minimum $^{57}\text{Fe}/^{30}\text{Si}$ of 1.0 was set in order to designate Fe-oxides, based on $^{57}\text{Fe}/^{30}\text{Si}$ ratios obtained for known Fe-oxides observed in electron beam images.

Like the aluminosilicate glasses, the Fe-oxides were found to be REE-bearing, but unlike the glasses, the slopes of the REE patterns and their overall REE contents were found to be much more variable (Fig. 10). To some extent this variability may be due to differences in the proportions of Fe-oxides and interstitial glass. Some Fe-oxides appear to be less LREE-enriched than their corresponding bulk samples (Figs. 6, 8; Supplementary information).

3.4. Quartz/ SiO_2

The REE contents for fly ash constituents having Al/Si monitors < 0.10 are consistently REE-depleted relative to the bulk REE contents and other fly ash constituents determined by SHRIMP-RG (Figs. 5–8). This is to be expected, given the known lack of minor element substitution in the quartz structure (Deer et al., 1963). In many cases, the REE contents of quartz grains determined were below detection by SHRIMP-RG (Figs. 5–9). The only exception to the observed REE depletion in quartz/ SiO_2 is a single point in sample 93310 (Illinois Basin) that is strongly LREE-enriched (Fig. 6). This finding is suggestive of monazite that may be included in quartz or otherwise present at a scale finer than the width of the incident ion beam. Although monazite was not observed, evidence for its presence includes: 1) the LREE-rich bulk composition of monazite; 2) direct determinations of single monazites in previous studies using trace-element microanalysis, showing strongly LREE-enriched chondrite-normalized REE patterns with negative europium anomalies (Rubatto et al., 2006; Buick et al., 2006); and 3) evidence from TEM studies that REE minerals may in some cases survive the combustion process with a reduction in size to the nanometer scale range (Hower et al., 2017; Hood et al., 2017a,b).

3.5. Trace phases

Samples in this study represent ashes obtained from pulverized-coal fired boilers operating at a normal range of temperatures (1300–1600 °C). For boilers operating at lower temperatures, such as stoker boilers, REE-bearing trace phases may be more likely to persist in

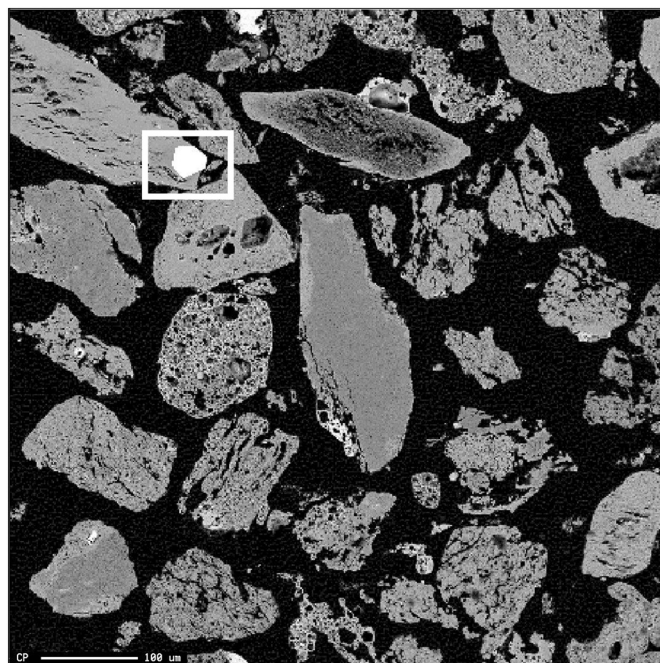


Fig. 11. Backscattered electron image of zircon (at upper left) in Jungar 120 + fly ash sample, shown in Fig. 12. Width of field of view is 640 μm.

coal combustion products because operating temperatures are well below the melting temperatures of these phases. With the possible exception of monazite contributing to the REE distribution of one quartz grain in one sample of ash from Illinois Basin coal (previous section), of the range of REE-bearing trace phases present in coal, only zircon was found in the fly ashes investigated, such as in samples 93385 and 93962 (Appalachian Basin) and the Jungar 120 + size fraction (Figs. 11, 12). These zircons show characteristic HREE enrichment (Fig. 12; Hanson, 1980). Where HREE enrichment is less pronounced, as in sample 93962, the determination likely reflects overlap between zircon and its aluminosilicate host.

4. Discussion

Comparison of REE data for whole coals with those for their bulk ash samples shows that REE are strongly retained as a group with little or no fractionation (Ratafia-Brown, 1994). As a result, characteristics of the whole coal REE patterns such as LREE enrichment and negative europium anomalies are preserved in the bulk ash (Fig. 1). Aluminosilicates, including glass and neoformed minerals such as mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), are the most abundant components of bulk fly ash, especially in ASTM Class F ash (ASTM, 2015). Grain-scale determinations of coal ash aluminosilicates in the present study confirm that REE were partitioned into the glass during coal combustion, likely at the expense of trace phases present in feed coal, which are reduced in the ash. Taggart et al. (2016) investigated > 100 primarily U.S. bulk fly ash samples, and among other findings, showed a positive correlation ($r^2 = 0.711$) between total REE in the ash and bulk Al_2O_3 content. With the exception of Powder River Basin ashes, Taggart et al. (2016) also showed poor REE recovery ($\leq 50\%$ of the amount present) in bulk leaching experiments using heated concentrated nitric acid. Together, these findings led Taggart et al. (2016) to suggest that REE are likely contained within fly ash glassy particles. Our findings confirm that the REE primarily reside in glassy aluminosilicates, consistent with the observations of Taggart et al. (2016), based on bulk determinations, and Hower et al. (2013a) based on electron beam microanalysis. Taggart et al. (2016) also noted an enhanced fraction of acid extractable REE in Ca-rich ashes, such as those from the Powder River Basin, and

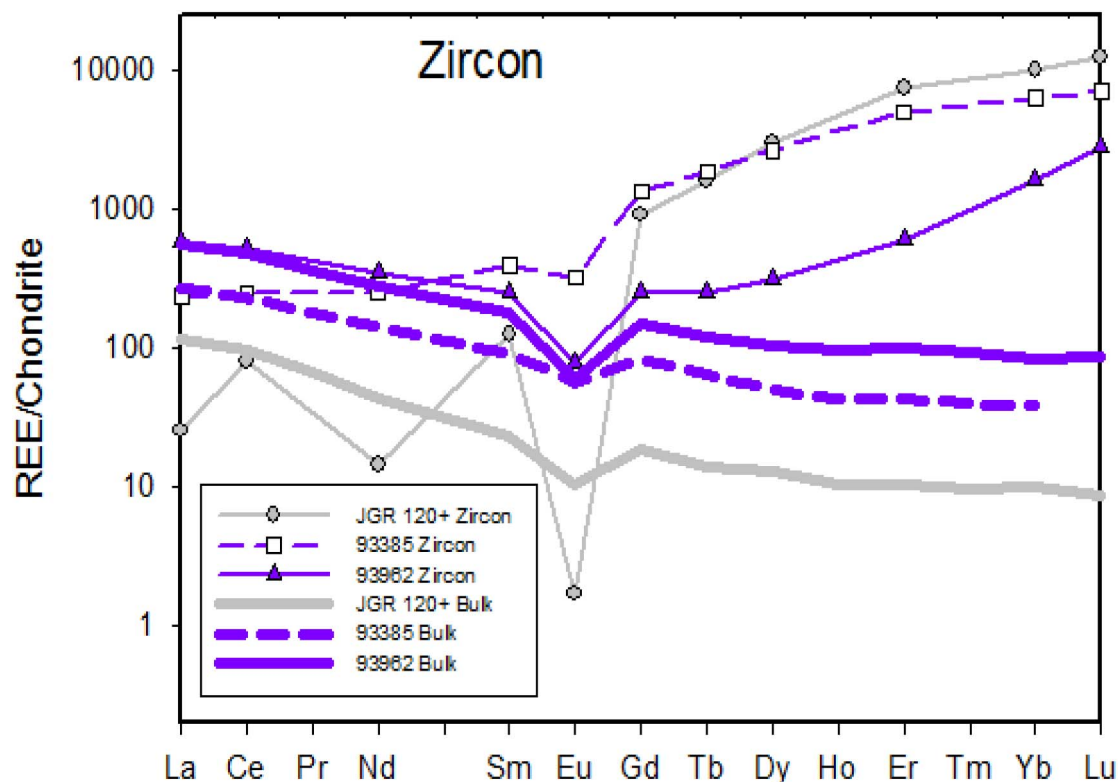


Fig. 12. Chondrite normalized REE plot showing SHRIMP-RG results for individual trace phase zircon determined in fly ash samples Jungar 120 + from Inner Mongolia, China, and samples 93385 and 93962 from the U.S. Central Appalachian Basin, and their respective bulk samples. The zircons show characteristic HREE enrichment. Similarity of LREE in sample 93962 zircon with bulk distribution suggests partial overlap with glassy host.

suggested that this may be due to enhanced solubility of Ca-bearing particles, such as calcium oxides, in the leachate. While Ca and Mg oxide phases are known to occur, especially in Class C fly ash, micro-analysis in the present study shows that Ca is incorporated in aluminosilicate glasses to varying degrees, and this is characteristic of ash derived from Powder River Basin and Jungar coals, among coals from other locations. Ca- and Fe-bearing aluminosilicates in ash from these coals are comparatively REE-enriched, perhaps due to the similarities in ionic radii between divalent Ca and trivalent LREE, and between divalent Fe and trivalent HREE. If Ca-(Fe)-rich glasses also are more soluble than pure Al–Si glasses, it would explain the greater extractability of REE from ashes of U.S. western coals. As suggested by Taggart et al. (2016), the enhanced extractability of REE from Powder River Basin ashes may offset their lower concentrations overall, in providing a potential resource for REE recovery.

Uniformity of REE partitioning into the glass phase argues against alternative modes of REE occurrence, such as persistence of trace phases with size reduction, which would otherwise result in REE micro-scale hotspots. Using transmission electron microscopy, Hood et al. (2017a,b) and Hower et al. (2017) showed the existence of nanometer-scale REE-enriched domains in fly ash from Kentucky coals and this mode may complement glass-phase bulk REE substitution. However, the presence of REE as nanoparticles does not explain the uniformity of REE distributions in the glass phase and the similarity of glass REE distributions to sample REE bulk compositions. Another possible explanation for REE enrichment of coal ash, diffusion of REE from trace phases to the glass, is an important process in natural igneous systems where, potentially, time scales in the millions of years are available for diffusion of REE from trace phases to the melt (Brady and Cherniak, 2010). But in combustion systems with thermal maxima lasting on the order of 1–2 s (Senior, 2015), diffusion beyond the immediate surface of trace phases is extremely unlikely.

Whereas aluminosilicates are the primary REE host, we also

demonstrate partitioning of REE into Fe-oxide magnetospheres consisting of Fe-oxides nucleating from within an iron-rich glass phase (Yang et al., 2014). Overall, Yang et al. (2014) found that REE contents in bulk separates of Fe-oxide magnetospheres were slightly lower than those for the whole ash. Our results suggest that REE contents in Fe-oxides and the proportions of LREE to HREE are much more variable than those in the glasses, possibly due to varying extents of overlap between skeletal Fe-oxides and host Fe-rich glasses in point analyses. REE variability in Fe-oxide magnetospheres may have advantages as a source of middle and heavy “critical” REE's, and further investigation is warranted. In contrast, quartz, also a minor fly ash constituent, was consistently found to be strongly REE-depleted compared to bulk concentrations, suggesting that limited REE pre-concentration may be possible with its removal from the bulk ash.

4.1. Implications for REE recovery

Currently, just over 50% of U.S. coal ash is beneficially reused (ACAA, 2016). While this is a milestone for the industry, it suggests that a large fraction of unused material produced in electric power generation remains available as a potential REE resource. Material available for REE recovery is increased if legacy ash in ponds and impoundments is considered (Hower et al., 2017). Research on recovery of REE from coal ash is actively ongoing, and whether or not this will be possible on a commercial scale remains to be determined. Confirmation of REE partitioning into the glass phase in the present study and the inability to extract a high fraction of REE in nitric acid alone, shown by Taggart et al. (2016), suggest that more aggressive approaches are needed to extract REE on a commercial scale. In the laboratory, REE extraction from aluminosilicates is accomplished using concentrated acids, including HF (Lichte et al., 1987), or by fusing the sample together with sodium peroxide prior to acid digestion (Meier and Slowik, 2002). Neither process, but especially digestion using concentrated

acids, is likely to be viable on a commercial scale, leading to a range of alternatives currently in development.

Promising approaches include pre-treatment of fly ash to improve REE extractability (Roth et al., 2017), membrane-based REE separation approaches (Hendren et al., 2017), REE extraction by ion exchange (Rozelle et al., 2016), and selective chelation for capture of REE from solution on solid substrates (Karamalidis et al., 2017). Most approaches have the near-term goal of concentrating REE to a minimum of two weight percent, a goal set by DOE in sponsorship of these projects (U.S. Department of Energy, 2017b). DOE suggests a threshold of 300 mg kg⁻¹ REE + Y as a minimum interest level for potential REY feedstock. With the exception of the three Jungar fly ash samples and one Powder River Basin fly ash (93925), all of the samples investigated in the present study meet this threshold.

5. Conclusions

Using SHRIMP-RG, we quantified REE substitution in fly ash aluminosilicate glasses, indicated indirectly in previous studies by counts for Ce at or near the detection limit using electron beam instruments, and by bulk analyses showing a correlation between REE content and Al₂O₃. Chondrite-normalized REE patterns for fly ash constituents resemble those of the corresponding bulk samples, arguing against REE occurrence as randomly distributed sub-micron domains, including REE nanoparticles and trace phase fragments persisting from the coal. Skeletal Fe-oxides also were found to be REE-bearing, whereas quartz is consistently REE-depleted relative to bulk sample REE contents. Laboratory-scale digestion approaches, while suitable for bulk REE determinations, are unlikely to be scalable, leading to the range of alternative approaches to REE recovery currently under development. Whatever process is successful, the present study shows that REE in the glass phase, the most abundant constituent of coal fly ash, should be targeted for extraction and concentration.

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Appendix A. Supplementary information

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.coal.2017.10.002>.

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