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# Rare Earth-Bearing Particles in Fly Ash Carbons: Examples from the Combustion of Eastern Kentucky Coals

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Review

# Rare Earth-bearing particles in fly ash carbons: Examples from the combustion of eastern Kentucky coals

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ABSTRACT

Graphitic carbons from the combustion of bituminous coals and, perhaps, other coal ranks, tend to capture iron and a number of hazardous elements, including As, Hg, and Se. Rare earth elements in fly ashes occur in minerals, such as monazite, xenotime, and davidite. They also occur in sub-nm particles, probably in a mineral form, within the Al–Si glass on the investigated fly ashes. Just as graphitic carbons can capture Fe and hazardous elements, the carbons surrounding the fly ash glass and magnetic particles captures or encapsulates a broad suite of rare earth elements.


## 1. Introduction

### 1.1. Rare earth elements and yttrium in coal-combustion fly ash

Rare earth elements, collectively the lanthanides, Y, and Sc following the nomenclature of Connelly et al. (2005), are critical in a number of industrial applications in modern society (Swift et al., 2014; USGS, 2014; Watson, 2018). Coal combustion by-products hold an advantage of being a concentrated, fine-grained source of rare earths (US DOE, 2018).

Fly ash carbons include not only the inertinite, chars, and cokes observable by conventional optical petrology, but also sub-micron-size amorphous and graphitic carbons attached to and binding fly ash particles (Hower et al., 2017a). In this review, following an introduction to the use of electron microscopy techniques in the investigation of non-rare earth elements in fly ashes, studies of micron- and nanometer-scale rare earth minerals in fly ash, the dispersion of sub-nanometer rare earth minerals in fly ash glass, and the occurrence of nanoscale rare earth-rich inclusions in fly ash carbons will be discussed. This work follows the conventions of Seredin and Dai (2012) in their consideration of REE to mean the lanthanides, REY to imply REE + Y, and the division of light versus heavy REE to include La through Sm and Eu through Lu, respectively.

### 1.2. Transmission electron microscopy investigations of metals in fly ash carbons

A number of investigators, including Veranth et al. (2000) and Chen et al. (2004), refined the electron microbeam examination of the carbons (soots) produced in the combustion of coal and residual oils. Chen et al. (2004) described the turbostratic structure of fly ash carbons and noted the presence of V sulfates, oxides, and Ca-, Ni-, and Na-vanadates; Ni sulfates and oxides, including a $NiAl_2O_4$ spinel; Fe sulfates, sulfides, phosphates, and oxides; and lesser occurrences of Ti, Cr, Cu, Zn, Ba, Ca, Cu, and Pb compounds.

Chen et al. (2005a) selected one high volatile bituminous coal from Western Kentucky and subbituminous Powder River Basin coals, one each from Wyoming and Montana, for combustion in a 50-kW, 4.1-m-long, and 20-cm-inside-diameter down-fired furnace. The fly ashes were examined with a 200-keV field emission high-resolution scanning transmission electron microscope (HR-STEM) with the utilization

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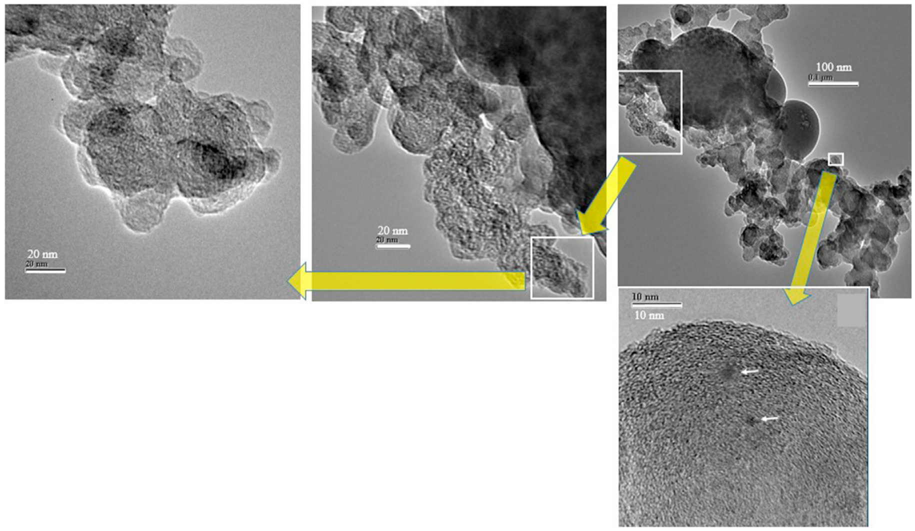


**Fig. 1.** Graphitic carbons (light gray) surrounding Al–Si spheres (dark gray to black) with encased metal particles (white arrows in lower-right figure) (after Hower et al., 2008). Scale bars equal 20 nm on the two left figures, 100 nm on the upper-right figure, and 10 nm on the lower-right figure.

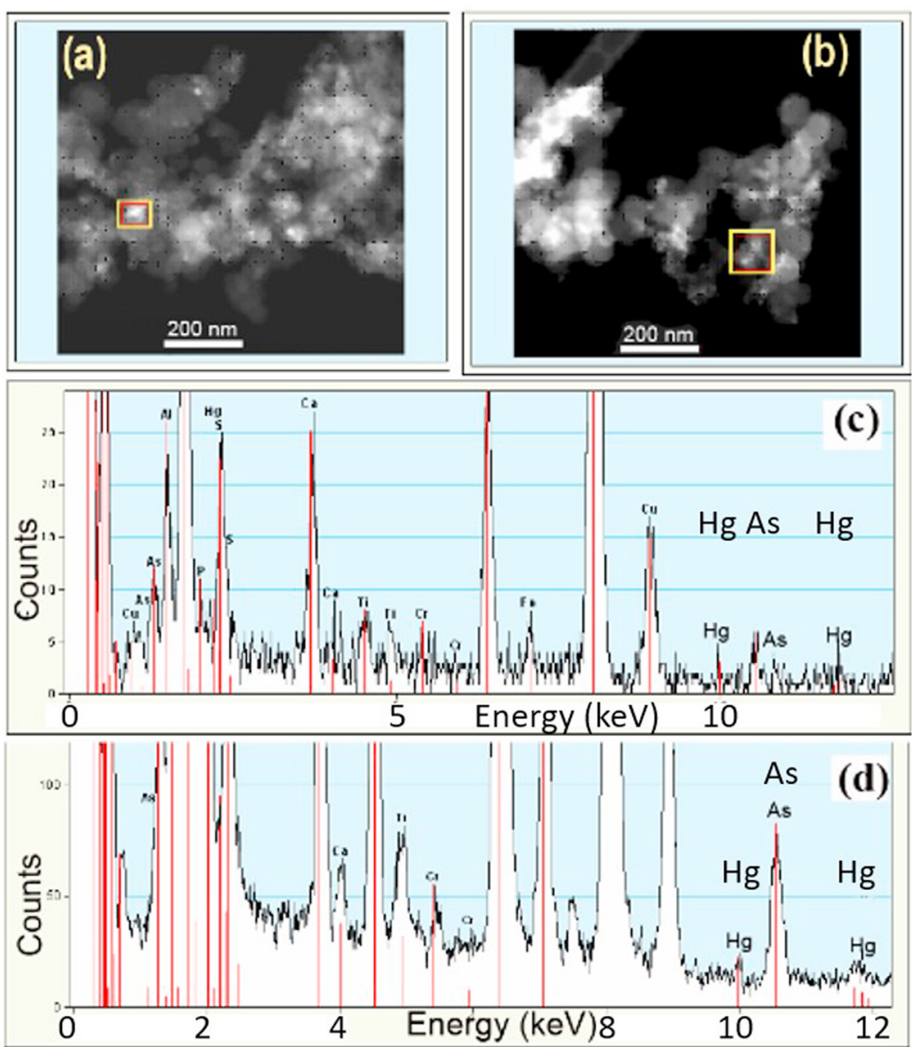


**Fig. 2.** STEM images of graphitic carbon and encased particles (a and b) with EDS spectrum showing As and Hg peaks (c is spectrum for inset on image a; d is spectrum for inset on image b) (after Hower et al., 2008). Scale bars = 200 nm.

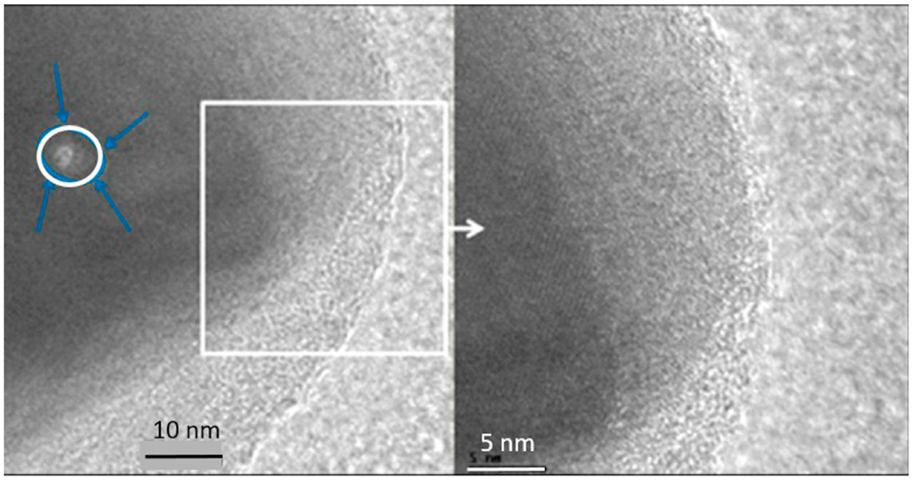


**Fig. 3.** Left: As–Pb–Se–Br–Si–O nanoparticle in circle; Right: Enlarged view of carbon surrounding Al–Si fly ash particle (after Silva et al., 2010). Scale bars equal 10 nm (left) and 5 nm (right).

of Gatan parallel electron energy loss spectroscopy (PEELS), energy dispersive spectroscopy (EDS), selected area electron diffraction (SAED), and microbeam diffraction (MBD) techniques. The Western Kentucky-derived fly ash contained spherical-to irregular-shaped cokes and chars and 100-nm to 1-μm soot aggregates. The primary particles in the 20-50-nm aggregates consisted of concentrically-stacked graphitic layers. Several inorganic associations (Fe, Ti, Ca, Al–Ti, Ti–Al–Fe, Fe–Si–Al, Ti–Si–Al, and Al–Mg–Fe) were detected along with the carbons; with magnetite, rutile, lime, various non-magnetite spinels (Chen et al., 2005a), and maghemite ($\gamma$-$Fe_2O_3$) (Chen et al., 2005b) being the major minerals. Yang et al. (2017) further examined the nature of Ti-oxides in coal-derived fly ash, determining that many of the T-bearing minerals were actually Ti-suboxides, specifically Magnéli phases, with a $Ti_xO_{2x-1}$ formula with $4 \le x \le 9$, with the most abundant Magnéli phase being $Ti_6O_{11}$. Toxicity studies indicated an impact on the viability of zebrafish embryos (Yang et al., 2017).

Linak et al. (2007) produced fly ash from subbituminous Montana coal and high volatile bituminous Utah and Illinois coals. Ultrafine particles were enriched in S, Cl, Na, K, V, and P; with a depletion in Si, Al, Ca, Ti, and Mg; and inconsistent trends for Fe. Soot contained Fe particles and thiophenic S. Toxicology studies on mice showed that the Montana coal caused the highest levels of lung endema with the Illinois and Utah coals have little to no effect. Iron oxides, possibly associated with Cr, caused oxidative stresses on tissues. In a toxicology study of a laboratory-produced fly ash from an Illinois coal, Cho et al. (2009) found that Fe-bearing soot was associated with increased pulmonary inflammation.

Hower et al. (2008) examined fly ash from electrostatic precipitator (ESP) hoppers at a southeastern Kentucky wall-fired 220-MW unit. At the time of the ash collection, the unit was burning a single-seam, single-mine coal from Knox County, Kentucky (Mardon and Hower, 2004). Using the same instruments as Chen et al. (2005a, b), they noted Al–Si fly ash particles with attached graphitic carbon with encased few-nm metal particles (Fig. 1). The EELS FeL3 peak at 715 keV compared to the FeL2 peak at 720 keV suggests that both ferric and ferrous Fe are present in the particles, indicating that it is a magnetite or similar spinel mineral. STEM imaging accompanied by EDS indicates that As and Hg are present within the graphitic carbon (Fig. 2).

Wilcox et al. (2015) examined two Illinois Basin bituminous-derived fly ashes and one 70:30 blend of Illinois Basin coal (the same coal as for one of the latter units) and Powder River Basin subbituminous coal. The Illinois Basin-derived fly ashes contained Cr–As–V–Mn-bearing spinel; Ni–Zn-bearing spinel; and Fe spinels with Cd, Se, and Co. They did not observe metals within the graphitic carbon seen in the Illinois Basin-derived ashes. Similarly, Saikia et al. (2015) noted nanotubes, but no metals, in fly ash from coals of Assam, India.

Silva et al. (2010) examined an Eastern Kentucky coal-sourced stoker ash, finding abundant fullerenes and metallofullerenes in the fine baghouse ash. The ash, originally investigated by Mardon et al. (2008) with a later study by Fu et al. (2018), has high levels of As, exceeding 9000 ppm in a size fraction of the baghouse ash (Fu et al., 2018). Concentrations of both As and Se are controlled by the concentrations of Fe oxides in the ash (Fu et al., 2018). Silva et al. (2010) noted carbonaceous As–Pb–Se–Br–Si–O- (Fig. 3) and Hg- and Se-bearing nanoparticles within the graphitic carbon (Fig. 4).

Silva et al. (2012) investigated anthracite-derived fly ash carbons

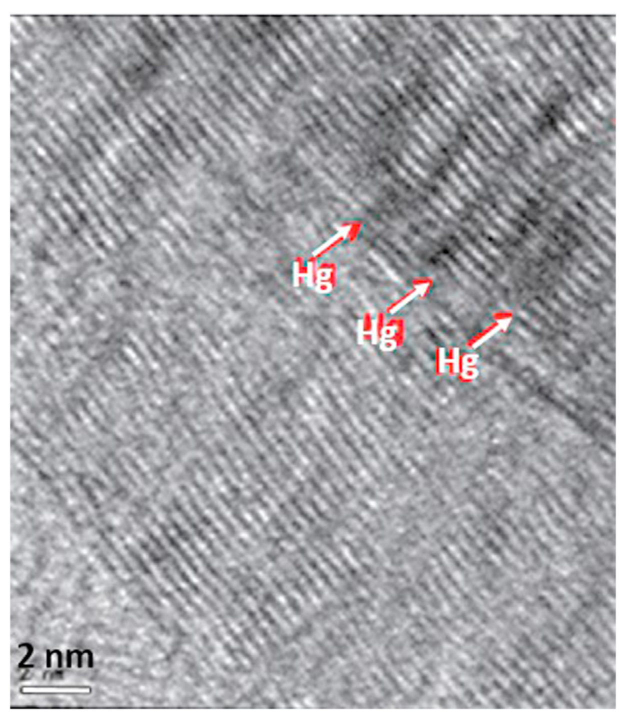


**Fig. 4.** Mercury-bearing nanoparticles in well-developed graphitic carbon from a stoker-fired steam plant burning eastern Kentucky coal (after Silva et al., 2010). Scale bar = 2 nm.

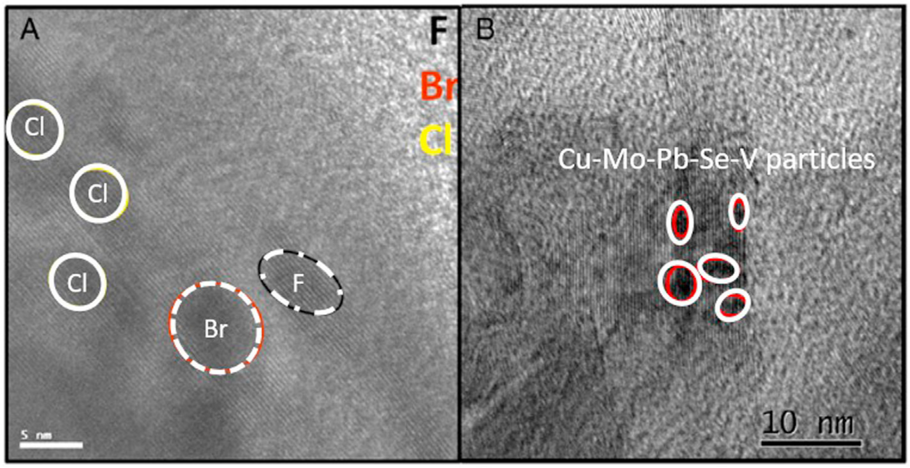


**Fig. 5.** Halogen-bearing nanoparticles (A) and Cu–Mo–Pb–Se–V nanoparticles (B) (after Silva et al., 2012). Scale bars equal 5 nm (A) and 10 nm (B).

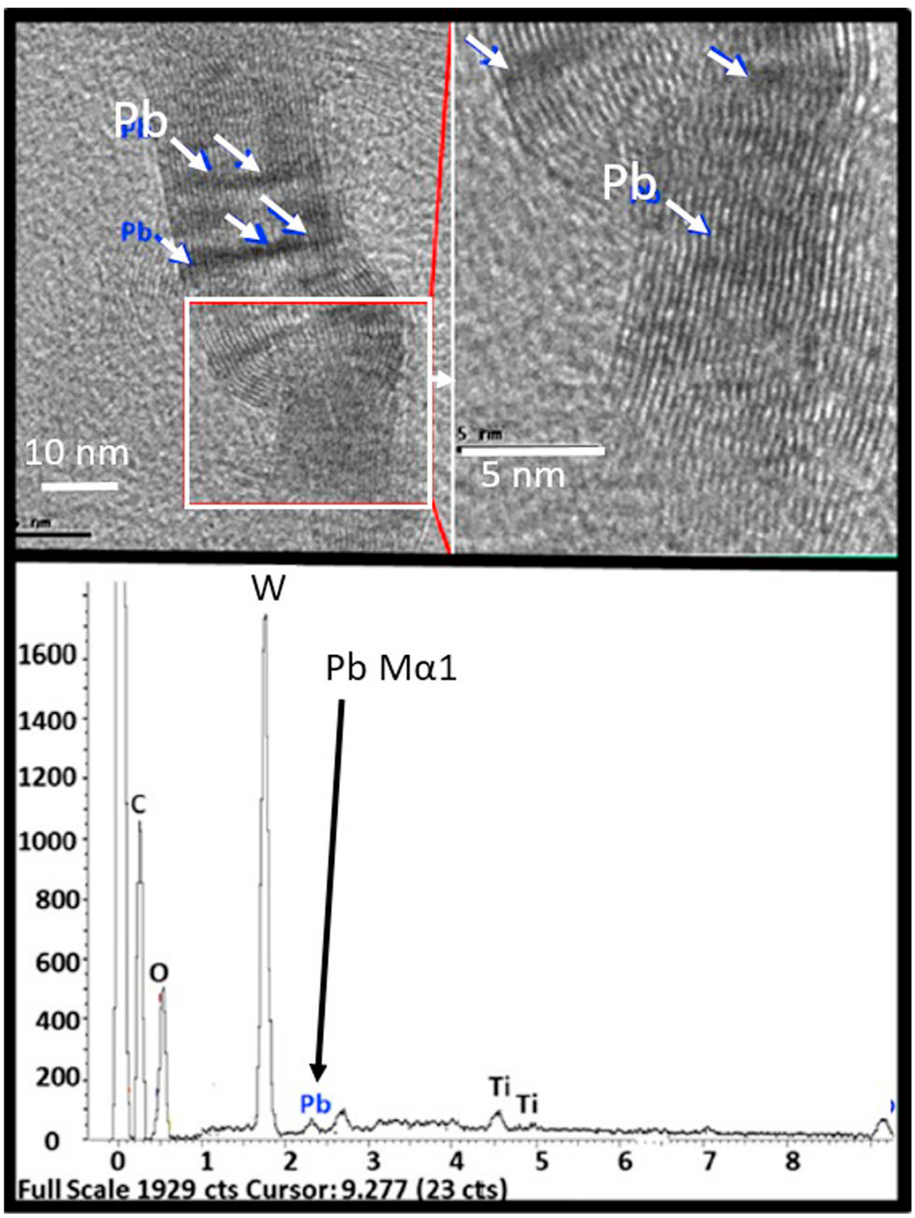


**Fig. 6.** HRTEM (top) and EDS (bottom) indications of Pb- and Ti-bearing particles in nanotubes from Portuguese anthracite-derived fly ash (modified after Ribeiro et al., 2013). The W peak is an artefact of the tungsten filament in the TEM. Scale bars equal 10 nm (upper left) and 5 nm (upper right).

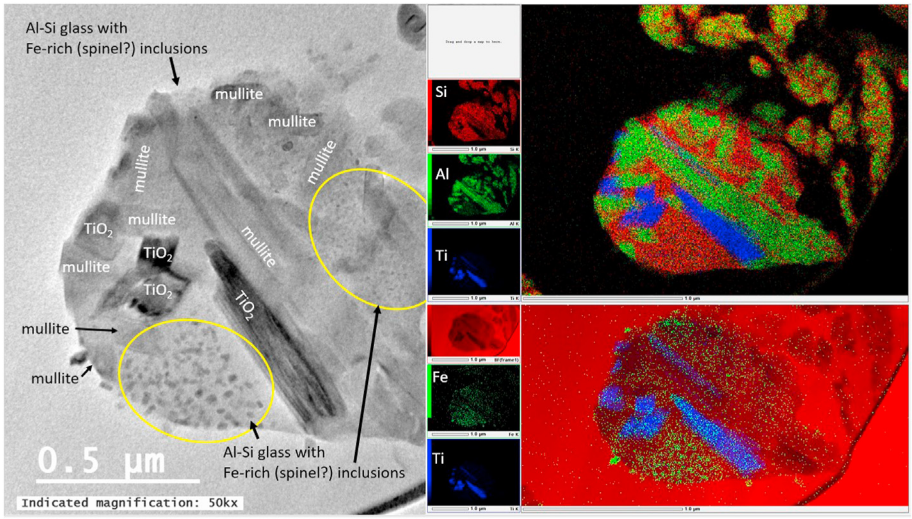


**Fig. 7.** Complex fly ash grain with included $TiO_2$ minerals, mullite, and Al–Si glass with Fe-rich inclusions. Insets on the right show the element overlays for Si, Al, and Ti and for Fe and Ti. Modified after Hood et al. (2017). Scale bar on bright-field TEM image (left) equals 500 nm (0.5 μm).

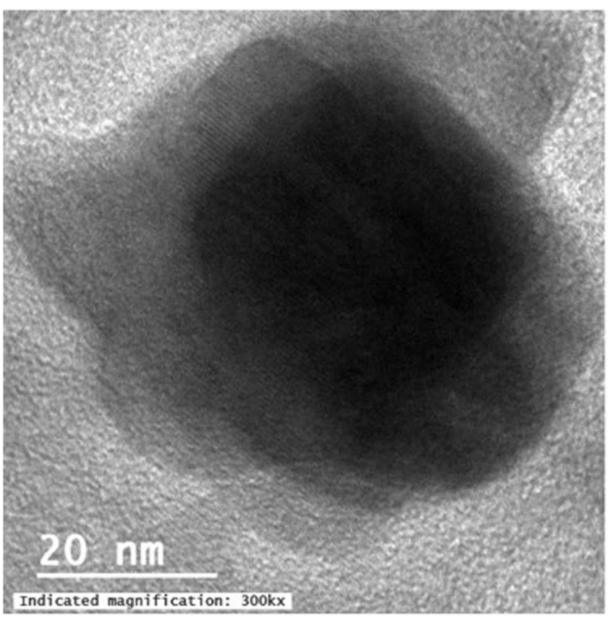


**Fig. 8.** Yttrium-bearing zircon from fly ash sample 91,953. Unpublished from Hood et al. (2017) study. Scale = 20 nm.

from two power plants in Yunnan, China. They noted Br and other halogens encapsulated as 3- to 8-nm particles within multi-walled carbon nanotubes (MWCNT) (Fig. 5A). All MWCNT contain complex heterogeneous Cu–Mo–Pb–Se–V nanoparticles (Fig. 5B) and all carbon nanotubes contain Cu–Mo–Pb–V nanoparticles. Ribeiro et al. (2013) found Hg-, Se-, Co-, Ti-, and Pb-bearing nanotubes in a Portuguese anthracite-derived fly ash (Fig. 6).

The co-combustion of coal and other materials, such as petroleum coke and waste tires, poses special challenges for determining the source of the metals in fly ashes. Silva et al. (2013) found V–Fe–Al–Cd- and Ni-bearing particles in MWCNT from the fly ash of a coal- and petroleum coke-fired unit in Western Kentucky. High concentrations of V and Ni are found in the fly ash, largely owing to the petroleum coke in the fuel blend. The fly ash from a cyclone unit burning 2–3% waste tires with an Illinois Basin coal blend had nano-size sphalerite but no apparent fullerenes (Silva et al., 2011). Aside from the Zn in the coal, Zn is in both the coatings of the steel belts and also in the rubber in the shredded tires (Hower et al., 2001).

## 2. Current study methods

Fly ashes were collected from several locations in the United States, including the ash pond at a central Kentucky power plant (Hower et al., 2017b), a fly ash generated in the combustion of the REE-rich Fire Clay coal at a southeastern Kentucky power plant (Hood et al., 2017), a university-based stoker-fired steam plant (Hower et al., 2018), a southeastern US power plant burning REE-rich Fire Clay coal (Hower et al., 2019a), and a distillery-based stoker-fired steam plant (Hower et al., 2019b). Hower et al. (2020) discussed the pilot-scale beneficiation of later collections of fly ashes from the plants discussed by Hower et al. (2017b) and Hood et al. (2017). All of the coal sources were from central eastern Kentucky mines.

Scanning electron microscopy (SEM) and EDS was conducted using a Helios NanoLab 660 DualBeam focused ion beam (FIB)/SEM and TEM was run on a JEOL 2010F instrument at the University of Kentucky Electron Microscopy Center. Further TEM studies were conducted on a JEOL 2100 analytical TEM with a large window EDS detector at the Virginia Tech National Center for Earth and Environmental Nanotechnology Infrastructure (NanoEarth), Blacksburg, VA. HR-TEM was also conducted on an FEI Tecnai TF20 TEM operating at 200 keV at the National Institute for Occupational Safety and Health in Cincinnati, OH.

## 3. Rare earth elements associated with fly ash

Aside from associations with carbons, a number of REY-bearing and other minerals were found in the fly ashes studied by Hood et al. (2017) and Hower et al. (2017b). As an example of the other, non-REY-bearing mineral assemblages is a complex grain with $TiO_2$ (and/or $Ti_xO_{2x-1}$; Magnéli phases after Yang et al., 2017), mullite, and Al–Si glass with Fe-rich (spinel) inclusions (Fig. 7). Yttrium-bearing zircons (Hood et al., 2017; Hower et al., 2020) (Fig. 8), monazite (Hower et al., 2019b), monazite with included xenotime (Hower et al., 2017b), cerium orthophosphate (possibly Ce-rich monazite) (Hower et al., 2018), and davidite (Hower et al., 2019b) are among the REY-bearing minerals detected in fly ashes and stoker ashes. REY can also be finely (sub-nm) distributed within the Al–Si glass; diffraction studies indicate that minerals are present, but their size and random

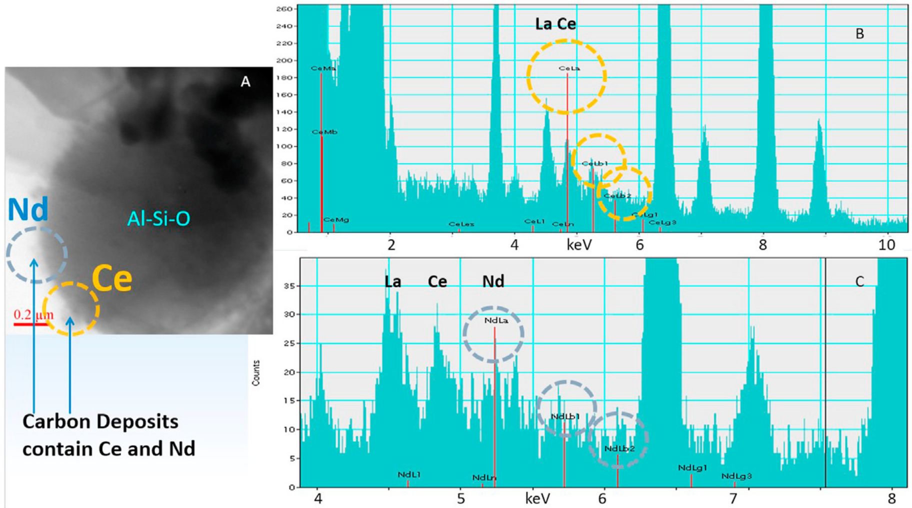


**Fig. 9.** La–Ce- and La–Ce-Nd-bearing particles (B and C) in carbon surrounding Al–Si glass fly ash particle (A) (unpublished from Hower et al., 2017b). Scale bar in (A) is 200 nm (0.2 μm).

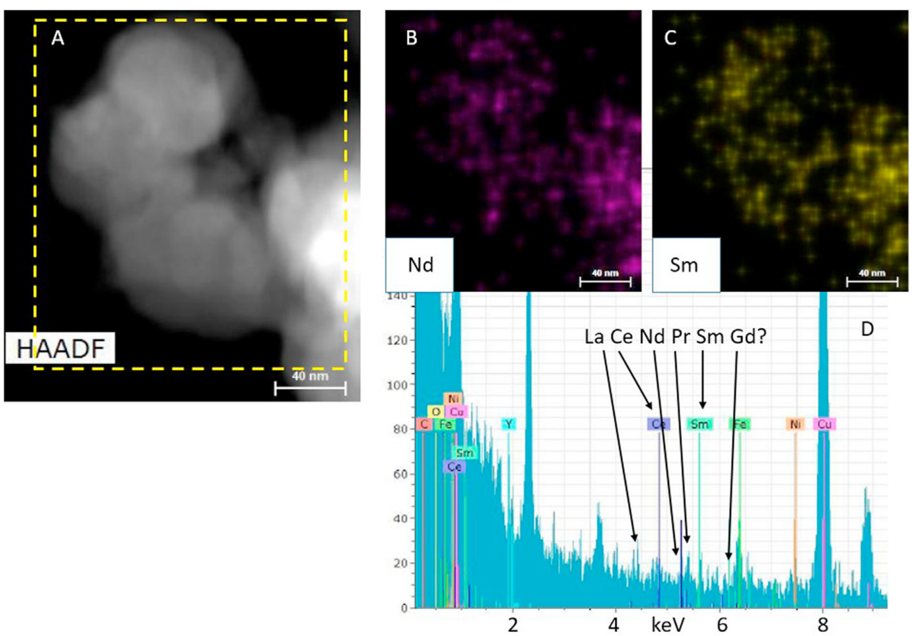


**Fig. 10.** High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Al–Si glass fly ash particles surrounded by carbon (A) with element overlays of Nd (B) and Sm (C) and the EDS spectrum for the area indicated by the dashed yellow box (D) (unpublished from Hower et al., 2017b). Scale = 40 nm.

orientation defies quantification at the HRTEM scales used in our studies (Hower et al., 2019a). In the latter study, La, Ce, Pr, Nd, and Sm (with L$\alpha$ peaks possibly attributable to Gd and Dy) were identified within an Al–Si glass sphere (their Fig. 2). Hood et al. (2017, their Fig. 6) identified a Ce–La-Nd-bearing glass.

In line with the established association of metals with the carbons surrounding Al–Si glass fly ash particles, Hood et al. (2017) and Hower et al. (2017b) noted examples of rare earth associations with fly ash carbons. In Fig. 9A, a thin, seemingly less than 100-nm thick, carbon shell surrounds an Al–Si glass sphere. The carbon, in turn, contains Ce and Nd (Fig. 9B and C). Similarly, Fig. 10 shows La, Ce, Nd, Pr, Sm, and Gd (?) associations with the carbon surrounding Al–Si glass spheres. The resolution is not fine enough to determine if the individual REE are in the same particles or occur individually or in varying concentrations. A detailed view of graphitic carbon from the C-rich froth flotation product of fly ash beneficiation shows few-nm-size Ce- and Fe-rich particles (Fig. 11). While the TEM-EDS software identified the lesser Ce peaks (meaning the Lß, etc., peaks), the locations are close to those of the La, Pr, Sm, and Gd peaks, suggesting that these lanthanides may also be present in the particles. Note that while the software identified Ce Ma peaks, their locations are obscured by the carbon and other light element peaks.

Carbon does not just surround the glassy fly ash particles, it also encases the Fe-spinels (magnetite). A Fe-spinel with a carbon coating is shown in Fig. 12. In this case, Ce and Sm (illustrated on Fig. 12B) were detected within the carbon. As above, a broader suite of REE is possible but they cannot be detected at this relative scale. The magnetite-rich fraction of a beneficiated fly ash (Hower et al., 2017b) shows a REE enrichment in the carbon binding together several spinel grains (Fig. 13A). Among the REY, Nd is illustrated in

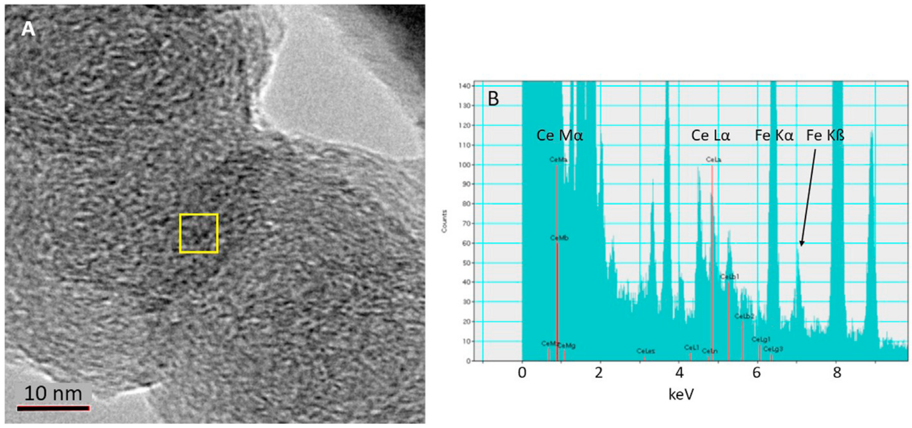


**Fig. 11.** Particles (within yellow box) in graphitic carbon (A) and shown to contain Ce and Fe (B) (unpublished from Hower et al., 2017b). Scale = 10 nm.

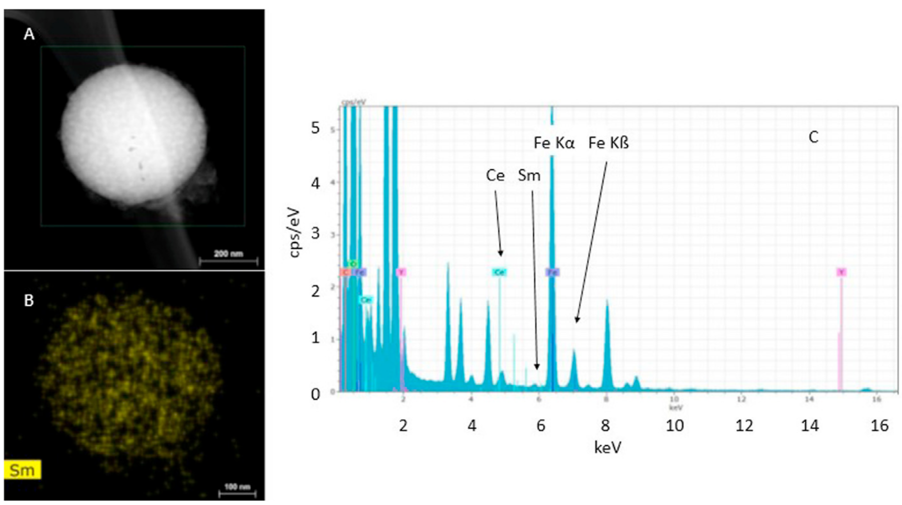


**Fig. 12.** Fe-spinel (A) with Ce and Sm in the carbon surrounding the spinel (B). The Ce, Sm, and Fe Kα and Fe Kß EDS peaks are shown in (C) (unpublished from Hower et al., 2017b). Scale bar is 200 nm for (A) and 100 nm for (B).

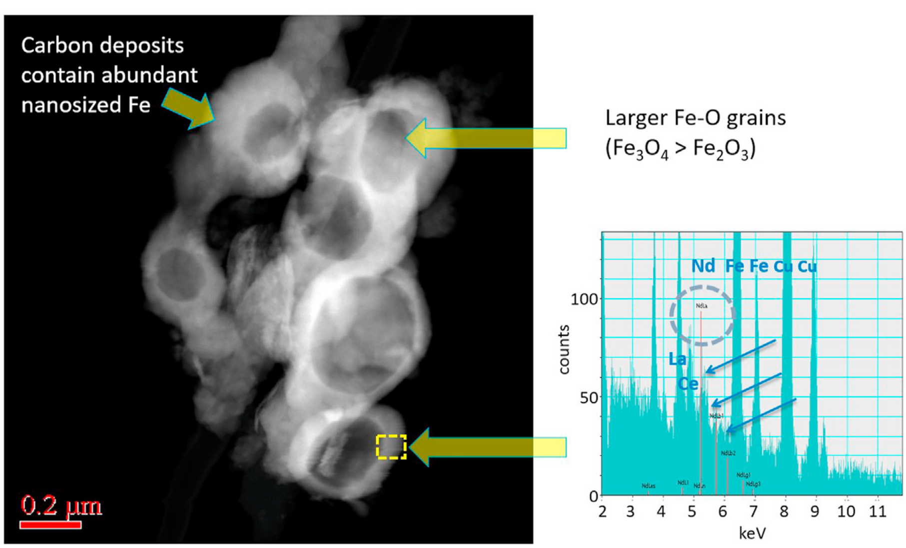


**Fig. 13.** Carbon deposits surrounding magnetite and hematite in the magnetics concentrate from the beneficiation of a fly ash (modified from Hower et al., 2017b). Scale bar is 0.2 µm or 200 nm.

Fig. 13B, but Y, La, Ce, and Sm are also present.

Hower et al. (2017b, 2020) noted the enrichment of Gd in the magnetic fractions of some beneficiated fly ashes. While the overall REY content of the magnetic fraction is somewhat lower than other fractions (327-ppm REY for the magnetic fraction versus 485-ppm REY for the <200-mesh clean product (Hower et al., 2020)), the Gd concentrations are 55 ppm and 18 ppm for the same two fractions, respectively. Praseodymium is the only other REY element with a significantly increased concentration in the magnetic fraction (35 ppm versus 19 ppm). Terbium also has an increased concentration, but, as an odd-numbered heavy REE, the baseline is low and a comparison of 2 ppm versus 5 ppm is not highly significant. At this time, an electron microbeam investigation has not yet been conducted.

## 4. Summary

Chen et al. (2005a, b), Linak et al. (2007), Hower et al. (2008), Silva et al. (2010, 2011, and 2012), Ribeiro et al. (2013), and Wilcox et al. (2015) noted metal- and halogen-bearing amorphous, graphitic, and fullerene carbons in the fly ashes from the combustion of bituminous- and anthracite-rank coals. Nano-scale Fe is a common constituent in the carbons and its combination with the soot may be a factor in pulmonary inflammation (Cho et al., 2009). Yang et al. (2017) suggested that Magnéli phases ($Ti_xO_{2x-1}$) are potentially hazardous. Aside from the Fe- and Ti-bearing particles, As, Se, Pb, and Hg are common elements in the fine carbons.

Lanthanides and Y occur in plus-micron, sub-micron, and nano-scale particles in fly ash. Among the occurrences noted are Y-bearing zircons (Hood et al., 2017; Hower et al., 2020), monazite (Hower et al., 2019b), monazite with included xenotime (Hower et al., 2017b), cerium-rich monazite (Hower et al., 2018), and davidite (Hower et al., 2019b). Nano-scale grains containing La, Ce, Nd, Pr, Sm, and/or Gd were found in amorphous and graphitic carbons surrounding and binding both Al–Si glass and Fe-spinel (magnetite) fly ash particles.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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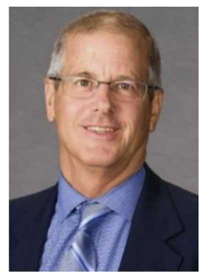

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