



Distribution of rare earth elements in eastern Kentucky coals: Indicators of multiple modes of enrichment?



James C. Hower^{a,*}, Cortland F. Eble^b, Shifeng Dai^c, Harvey E. Belkin^d

^a University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, USA

^b Kentucky Geological Survey, Lexington, KY 40506, USA

^c State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology (Beijing), Beijing 100083, China

^d U.S. Geological Survey ret., 956 National Center, Reston, VA 20192, USA

ARTICLE INFO

Article history:

Received 27 February 2016

Received in revised form 20 April 2016

Accepted 25 April 2016

Available online 29 April 2016

Keywords:

Pennsylvanian

lanthanides

Hydrothermal metamorphism

Volcanic eruptions

Tonstein

ABSTRACT

Four eastern Kentucky Pennsylvanian coals (from oldest to youngest, the Manchester, Pond Creek, Fire Clay, and Hazard coals) were examined for their total rare earth element (REY) concentration and the possible mechanisms for enrichment of the rare earths. Based on previous studies, four possible modes are considered: terrigenous, tuffaceous, infiltrational, and hydrothermal, with the Dean coal, a correlative of the Fire Clay coal, considered to be a typical example of the tuffaceous mode. The Fire Clay owes much of its high REY content to the presence of a volcanic-ash-fall tonstein, with REY-bearing zircon and phosphates in the coal in numerous locations. Some of the original REY elements may have components of the detrital minerals deposited in the peat. Leaching of REY from the tonstein into the surrounding coal and the hydrothermal overprint of mineralizing fluids associated with the northwestwardly movement of the Pine Mountain thrust sheet contributed to the total REY signature in the Fire Clay coal. Not all coals are going to have the complex history of the Fire Clay coal, but it should be considered that the total history of REY enrichment by multiple mechanisms is what gives us both the total REY concentration and the relative distribution of the individual lanthanide elements.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Rare earth elements have come to be of increasing interest given their use in a wide array of modern electronics (Greene, 2012; Hatch, 2012; Hower et al., 2016). Enhanced levels of rare earth elements (REE or REY if yttrium is included in the assessment; for this work, REY > 900 ppm on the ash basis will be considered to be an enhanced concentration) are found in many US coals (data from Bragg et al., 1998), with the Central Appalachian coalfield in eastern Kentucky, central and southern West Virginia, and southwestern Virginia having some of the best prospects. In particular, the Middle Pennsylvanian Fire Clay coal and its correlatives are among the most promising resources owing to the presence of a REY-rich volcanic ash-fall parting (tonstein) (Rice et al., 1994; Hower et al., 1999, 2015a) or the presence of high REY concentrations in the absence of the tonstein (Mardon and Hower, 2004). The available resources of the Fire Clay coal were discussed by Thacker et al. (2000).

The light rare earth elements (LREE) have been considered to include La through Sm and the heavy rare earth elements (HREE) span Eu to Lu (Seredin, 1996a, b; Hower et al., 1999; Mardon and Hower, 2004; Dai et al., 2016b; among others). Seredin and Dai (2012) divided the REY into light, medium, and heavy fractions: LREY (La through Sm), MREY – (Eu through Dy plus Y), and HREY – (Ho through Lu). They also noted L-type ($La_N/Lu_N > 1$), M-type ($La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$), and H-type ($La_N/Lu_N < 1$) enrichment patterns. Further, they emphasized that there were four main genetic modes of REY enrichment in coals, as shown in Table 1. In some cases, the enrichment of REY in coal is attributed to mixed mineralization (e.g., mixed tuffaceous-hydrothermal type; Dai et al., 2016a). Notably, for this evaluation, the Dean coal, a Fire Clay correlative, is considered to be a typical example of the tuffaceous mode of accumulation (Seredin and Dai, 2012).

The Fire Clay tonstein contains kaolinite; sanidine; β -quartz; magnetite and magnetite with ilmenite cores; the TiO_2 polymorphs anatase and brookite; sphene; REE and Y-bearing zircon; Y-bearing Ca-phosphates (crandallite); and Y-, La-, Ce-, Nd-, Dy- and Gd-bearing apatite (Fig. 1) and monazite (Lyons et al., 1992; Hower et al., 1994a, 1999).

* Corresponding author at: University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, USA.

E-mail address: james.hower@uky.edu (J.C. Hower).

Table 1
The main genetic types of high REY accumulation in coals.

Type	REO content in ash, %	Associated elements	Typical example
Terrigenous	0.1–0.4	Al, Ga, Ba, Sr,	Jungar, China (Dai et al., 2006; Dai et al., 2008)
Tuffaceous	0.1–0.5	Zr, Hf, Nb, Ta, Ga	Dean, USA (Mardon and Hower, 2004)
Infiltrational	0.1–1.2	U, Mo, Se, Re	Aduunchulun, Mongolia (Arbuzov and Mashen'kin, 2007)
Hydrothermal	0.1–1.5	As, Sb, Hg, Ag, Au, etc.	Rettikhovka, Russia (Seredin, 2004)

REO, oxides of rare earth elements and yttrium.

Recent investigations by Belkin (this paper) found that the LREE-enriched, Ce-bearing monazite contained 60.8 wt.% total rare earth oxides, 4.2 wt.% ThO₂, and 2.1 wt.% Y₂O₃. Zoning in the monazite is due to variations in the Th content. The apatite tends to have a fluorapatite composition and is LREE enriched with about 1 wt.% total rare earth oxides. Zoned HREE-enriched zircons were found to have 0.33 wt.% total rare earth oxides and 0.23 wt.% Y₂O₃.

The coal lithotype underlying the Fire Clay tonstein has 4200 ppm REY and 5700 ppm Zr (both on ash basis) (Andrews et al., 1994; Hower et al., 1999). REY enrichment below tonsteins was also noted by Zielinski (1985); Triplehorn and Bohor (1983); Crowley et al. (1989, 1993), and Ruppert and Moore (1993), as well as cases in other areas (Dai et al., 2016a).

Crowley et al. (1989) noted that secondary enrichment can be a function of (1) ground water leaching of volcanic ash followed by

uptake of the REY by organic matter, (2) ground water leaching of the volcanic ash followed by incorporation into minerals, and (3) incorporation of volcanic minerals in the peat. Zielinski (1985) and Crowley et al. (1989), in studies of Wyoming and Utah coals, respectively, noted enrichments of REE in lithotypes immediately below tonsteins. REY in coal are commonly found in clays and phosphates (Eskenazy, 1995); loosely bound REYs may become mobile when associated, in particular, with clays (Eskenazy, 1999). Acidic waters tend to preferentially desorb the heavier REY from the clays. There tends to be an enrichment of HREE in peats and low-rank coals due to the stronger HREE (versus the LREE) affinity for organics and the greater strength of HREE-organic complexes (Eskenazy, 1978, 1987a, b, c, 2015; Eskenazy et al., 1986; Seredin et al., 1999; Pédrot et al., 2010; Davranche et al., 2011; Aide and Aide, 2012). In contrast, for Pennsylvanian coal from Inner Mongolia, China, Dai et al. (2008) found that the LREEs had a

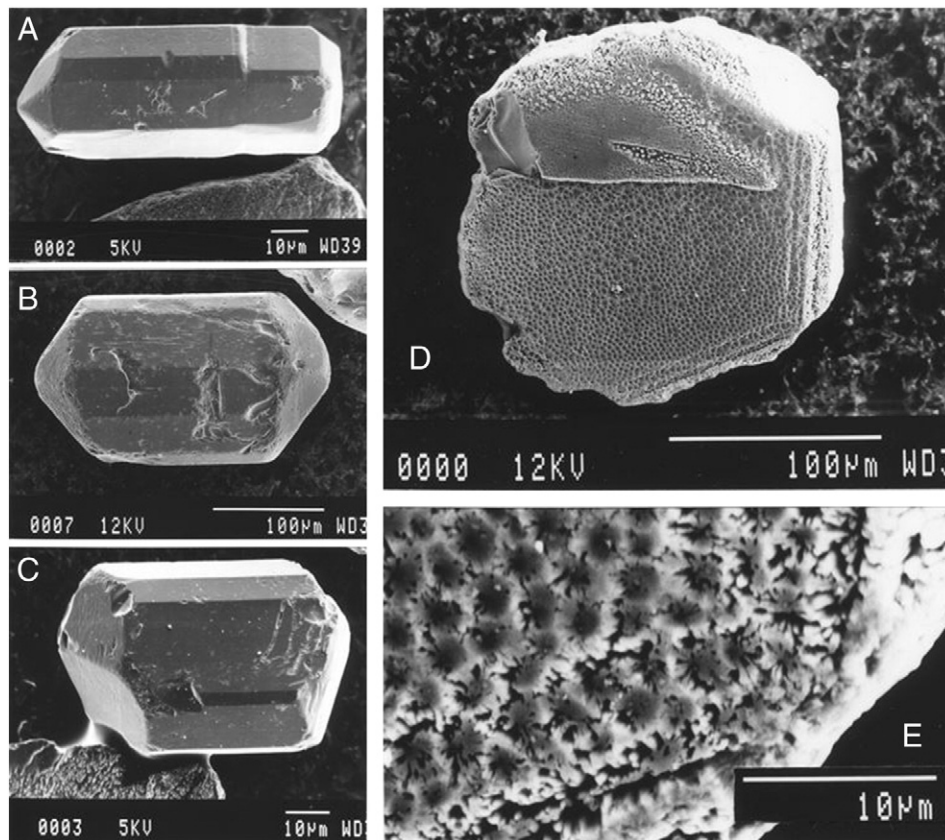


Fig. 1. SEM backscattered electron images of unaltered apatite (A–C) and altered apatite (D–E) from the Fire Clay tonstein in eastern Kentucky. The apatite contains 0.08% La₂O₃, 0.51% Ce₂O₃, 0.36% Nd₂O₃, 0.12% Dy₂O₃, and 0.36% Y₂O₃. Quadrangle (7 ½-minute) locations: A & C/Ivydell, Tennessee; B/Hoskinston, Kentucky; and D & E/Sylvester, West Virginia. Specimens and analyses from studies by Harvey Belkin.

Download English Version:

<https://daneshyari.com/en/article/1752758>

Download Persian Version:

<https://daneshyari.com/article/1752758>

[Daneshyari.com](https://daneshyari.com)