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Detection of Rare Earth Elements in Appalachian Coal Fly Ash by Cathodoluminescence Spectroscopy

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Cathodoluminescence (CL), the excitation of an inorganic material by energetic electrons that results in photon emission, is one of several mechanisms that occurs as a result of the interaction of an electron beam with an inorganic solid. Photons are emitted as the result of electronic transitions between the conduction and valance bands as well as levels lying with the band gap and can be characterized as being intrinsic (fundamental) or extrinsic (activated). Rare Earth Elements are an extrinsic source that can be detected using CL, with the CL signal being sensitive to the chemical state of the polyvalent elements [1, 2]. CL microscopy and spectroscopy and X-ray Microanalysis/Energy Dispersive Spectroscopy (XRM/EDS) was initiated on a series of coal fly-ash samples collected from the Appalachia region to ascertain the location(s), type(s), and valance states of REE's in the fly-ash samples. XRM/EDS and CL microscopy and spectroscopy was carried out utilizing a Thermo-Electron NS-7 and a Gatan Mono-CL4 interfaced to a JEOL-7600 FESEM. The Gatan CL system is equipped with a PMT and a Princeton Instruments PIXILS 100 CCD camera. Primary analyses were carried out in a wavelength range of approximately 300 nm to 750 nm.

The CL spectroscopic data acquired from the fly-ash samples was compared to the cathodoluminescence spectra obtained from various mineral standards as well as the CSIRO Luminescence Database [3]. EDS was used to identify the host environment as well as REE's such as lanthanum (La^{3+}) and lutetium (Lu^{3+}) that exhibit non-distinctive broad band emissions and whose photon emission wavelengths are outside of the experimentally detectable wavelengths. Of the 17 rare earth elements, 12 were detected in coal fly ash samples by CL, while La was detected by EDS. The REE's identified in the fly-ash samples by CL (Figure 1) were primarily associated with minerals while La which was detected by BSEI and EDS, was associated with clay. The data in Table 1 depicts the cumulative observed spectral lines for each REE according to the type of mineral in which each REE is retained. The observed CL wavelengths correlate well with CSIRO database and mineral standards, indicating that the combustion process and weathering have negligible effect on the REE location, type, and valance state.

References:

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[3] Commonwealth Scientific and Industrial Research Organization (CSIRO) Luminescence Database, www.csiro.au/luminescence (accessed January 31, 2019).

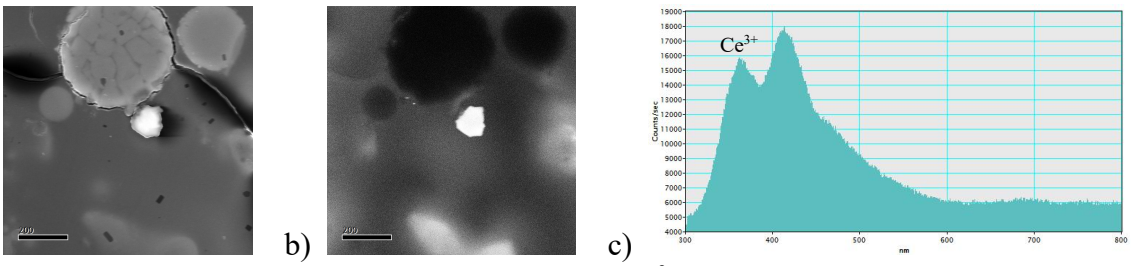

Figure 1. a) SEI; b) CL Image; c) CL spectrum of Ce^{3+} in calcite

Mineral	Activator	Observed Peak	CSIRO Database Peak [3]
Alumina	Eu^{3+}	617, 690	614, 692
Anhydrite	Sm^{3+}	637, 730	640, 732
	Tb^{3+}	438	436
Apatite	Ce^{3+}	361, 457, 458	360, 458
	Dy^{3+}	576 ,579, 580, 667	575, 577, 578, 580, 667
	Eu^{2+}	410, 448	410, 450
	Eu^{3+}	690, 695	690, 695
	Sm^{3+}	654, 690	654, 690
	Tb^{3+}	413, 434, 487	414, 436, 487
	Tm^{3+}	361	363
Barite	Ce^{3+}	330, 333	330
	Eu^{2+}	372, 374, 375	375
Calcite	Ce^{3+}	356	357
Dolomite	Ce^{3+}	362	362
Feldspar	Ce^{3+}	335	335
	Er^{3+}	535	532
	Tb^{3+}	550	550
Lanthanum monophosphate	Eu^{3+}	693	692
Xenotime (Y)	Er^{3+}	518, 525	520, 525, 526
	Dy^{3+}	660, 663, 743, 745	651-669, 735-771
	Ho^{3+}	546, 660, 743, 745	546, 659, 742, 743
	Nd^{3+}	663	656-670
Zircon	Dy^{3+}	472, 474, 475, 484, 487, 578, 665, 758	472, 483, 485, 486, 578, 665, 755
	Er^{3+}	402, 403, 406, 408, 528, 532, 546, 620	405, 530, 545, 548, 620
	Eu^{3+}	578, 638	575, 635
	Ho^{3+}	532, 538, 540, 670	530, 539, 660-670
	Pr^{3+}	528, 532, 546, 620, 745	530, 544, 620, 742
	Sm^{3+}	578	575
	Tb^{3+}	417, 546, 587, 625	417, 546, 590, 625
	Tm^{3+}	458, 758	457, 755

Table 1. Minerals and rare earth activators found in coal fly ash, as determined by cathodoluminescence spectroscopy.

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