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Supporting Information for

Differences in Bulk and Microscale Yttrium Speciation in Coal Combustion Fly Ash

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Table S1. Coal fly ash samples selected for each analysis. Feed coals originated from the Illinois Basin (IL), Appalachian Basin (App), and Powder River Basin (PRB) in the U.S. and the Witbank/Highveld coal fields in South Africa (RSA). The leachable REE in the samples were quantified by selective sequential extraction (SSE) while the solid crystalline phases were characterized by x-ray diffraction (XRD). Element maps were acquired via micro-focus x-ray fluorescence (μ XRF) and yttrium speciation was analyzed using bulk and micro-focus x-ray absorption near edge spectroscopy (XANES). Sample numbers correspond to those used in Taggart et al. (2016)

Sample ID	Sample No.	Ash Type	SSE/XRD^a	Bulk XANES^a	μXRF^b	μXANES^b
App-FA1	93938	Silo	X	X	X	X
App-FA2	93963	ESP		X	X	
App-FA3	93932	ESP		X	X	X
App-PA	93965	Pond		X	X	
IL-FA1	93895	ESP	X	X	X	X
IL-FA3	93964	ESP		X	X	
PRB-FA1	93966	Fly ash	X	X	X	X
PRB-FA2	93973	Fly ash		X	X	X
RSA-FA1	93969	Fly ash		X	X	

^a bulk ash

^b thin sections mounted on quartz slides

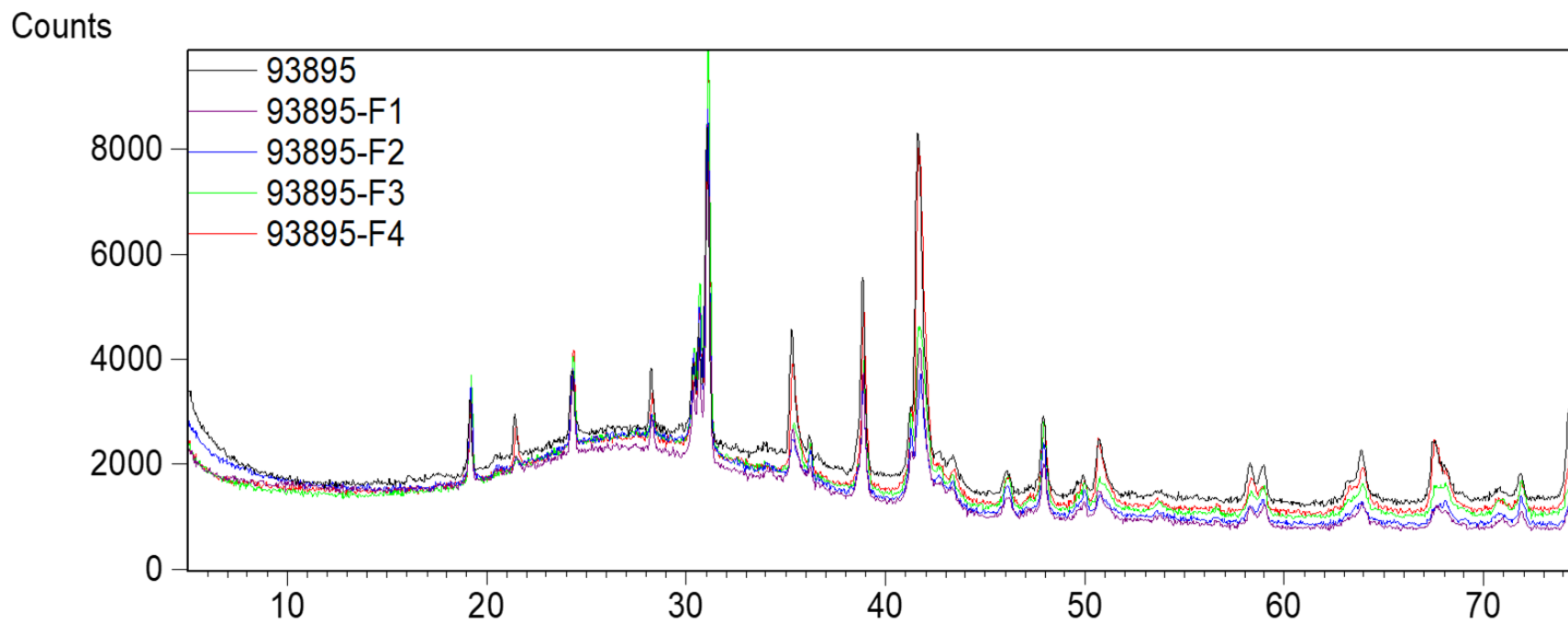


Figure S1. XRD spectra with background for IL-FA1. The target fractions were: water soluble (F1), acid soluble (F2), reducible (F3), and oxidizable (F4). The leaching solutions were distilled water (F1), 0.11 M CH_3COOH (F2), pH 2 $\text{NH}_2\text{OH}\cdot\text{HCl}$ (F3), and $\text{H}_2\text{O}_2/\text{CH}_3\text{COONH}_4$ (F4).

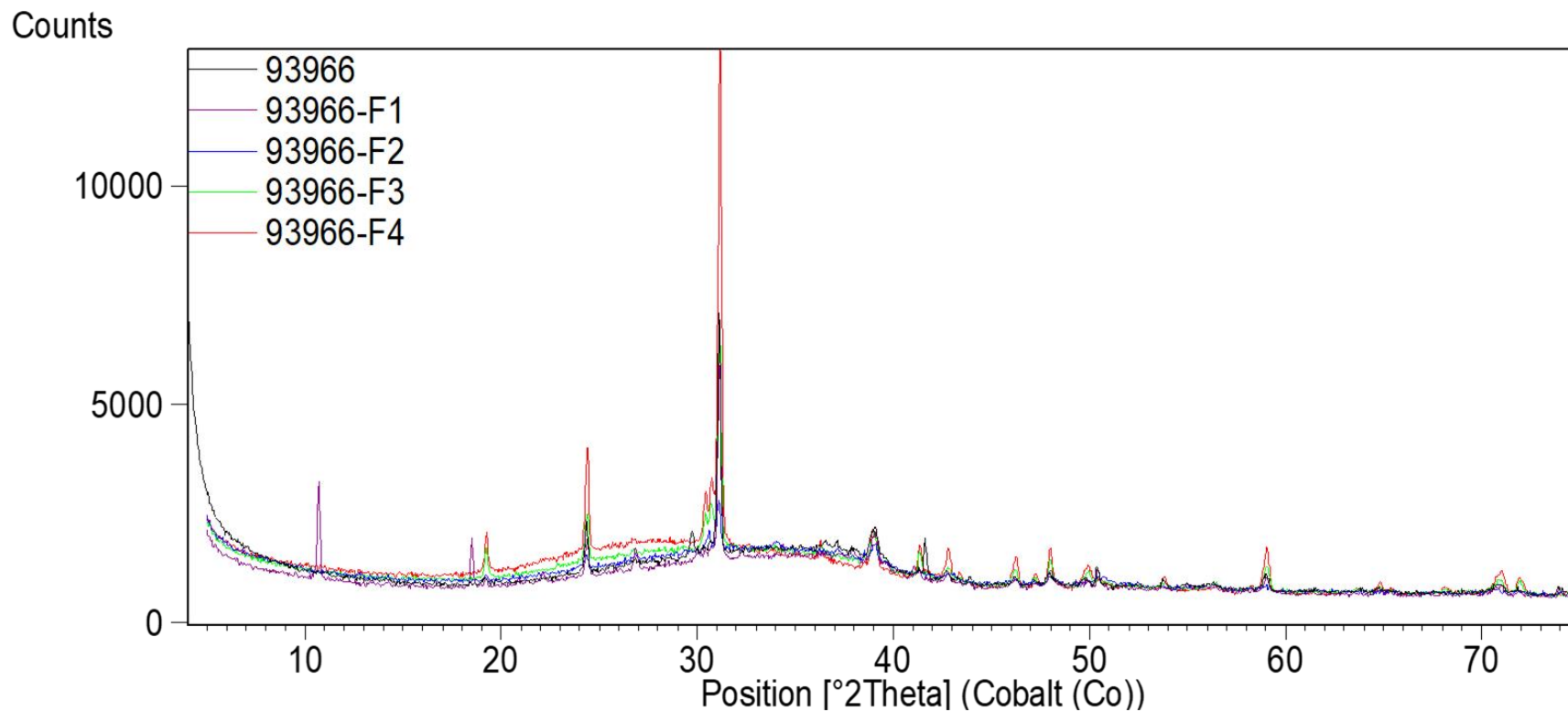


Figure S2. XRD spectra with background for PRB-FA1. The target fractions were: water soluble (F1), acid soluble (F2), reducible (F3), and oxidizable (F4). The leaching solutions were distilled water (F1), 0.11 M CH_3COOH (F2), pH 2 $\text{NH}_2\text{OH}\cdot\text{HCl}$ (F3), and $\text{H}_2\text{O}_2/\text{CH}_3\text{COONH}_4$ (F4).

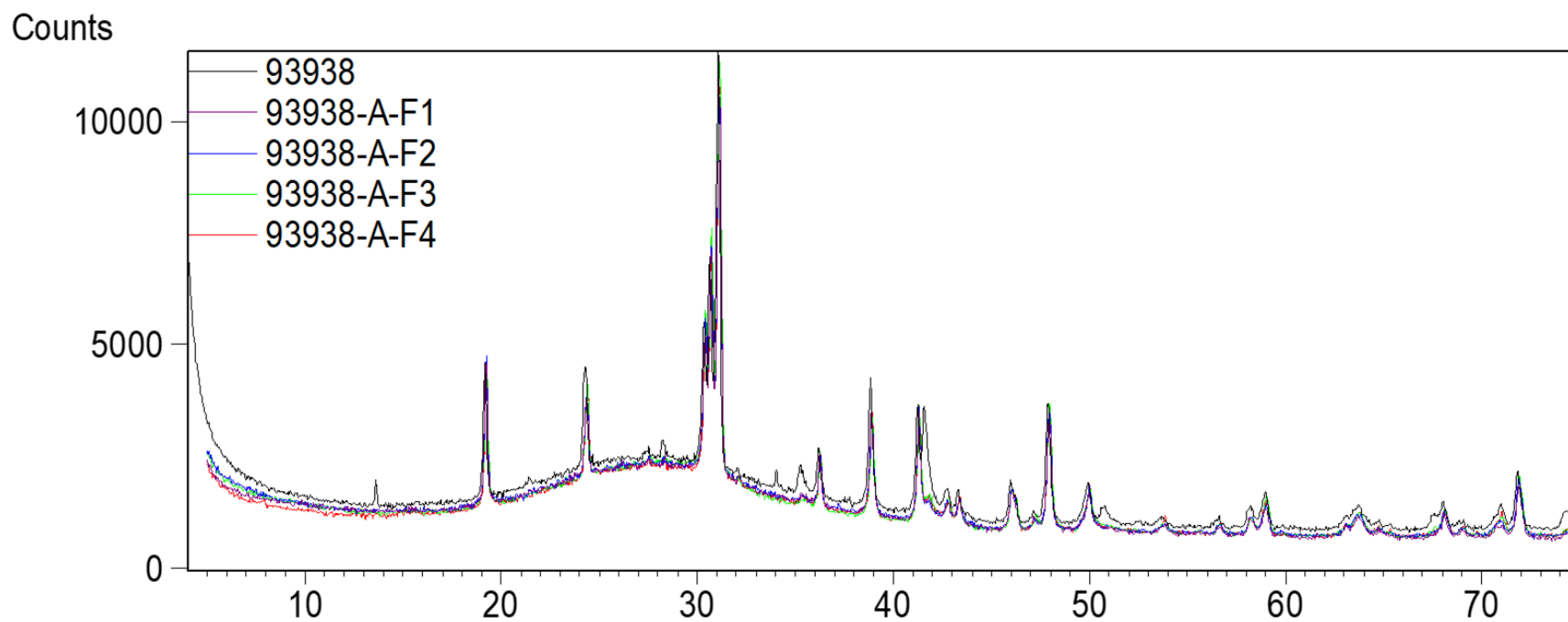


Figure S3. XRD spectra with background for App-FA1 extracted with acetic acid in F2. The target fractions were: water soluble (F1), acid soluble (F2), reducible (F3), and oxidizable (F4). The leaching solutions were distilled water (F1), 0.11 M CH_3COOH (F2), pH 2 $\text{NH}_2\text{OH}\cdot\text{HCl}$ (F3), and $\text{H}_2\text{O}_2/\text{CH}_3\text{COONH}_4$ (F4).

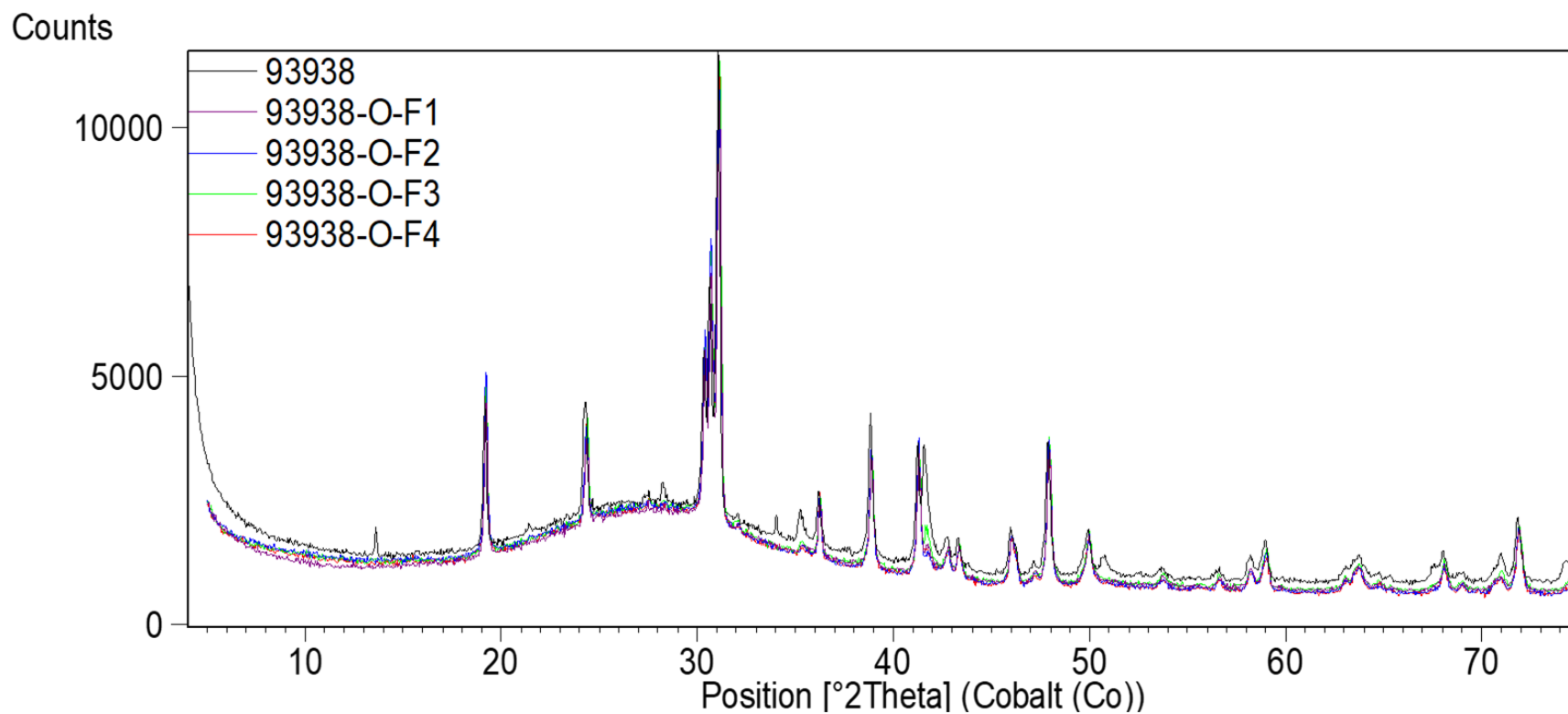


Figure S4. XRD spectra with background for App-FA1 extracted with oxalic acid in F2. The target fractions were: water soluble (F1), acid soluble (F2), reducible (F3), and oxidizable (F4). The leaching solutions were distilled water (F1), 0.11 M HOCCOOH (F2), pH 2 NH₂OH·HCl (F3), and H₂O₂/CH₃COONH₄ (F4).

Unextracted vs. Extracted Bulk XANES Fits

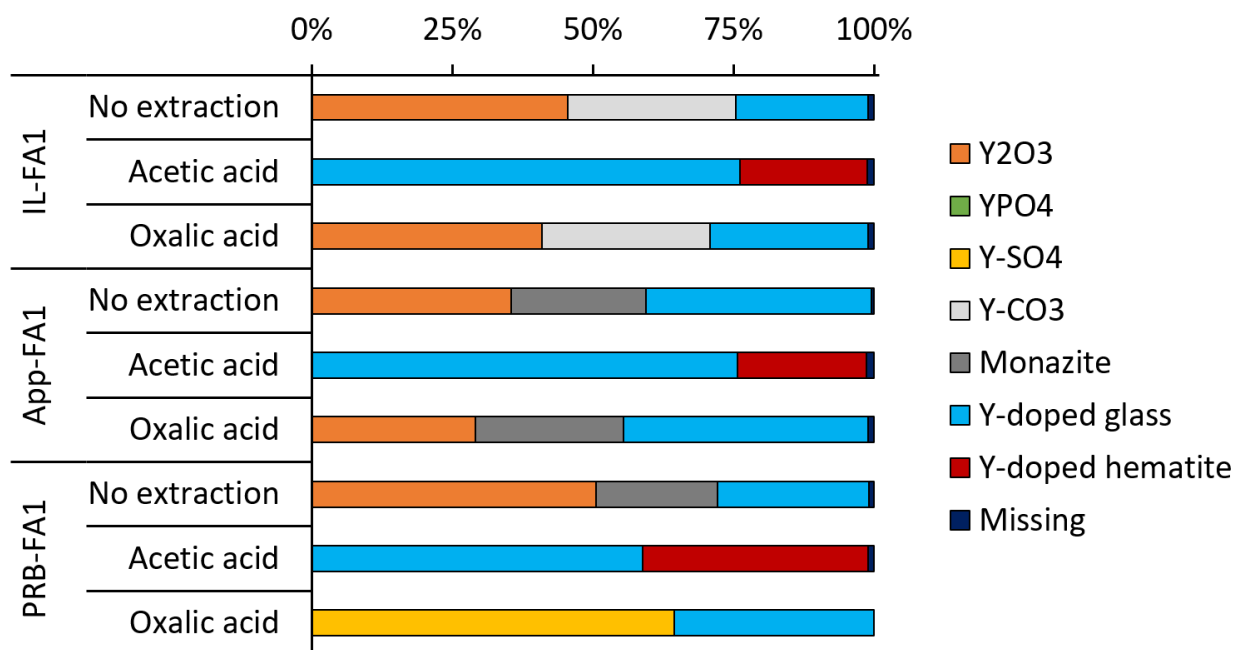


Figure S5. Linear combination fits for unextracted and extracted fly ash samples. For the acetic acid and oxalic acid extractions, ash samples were leached overnight in 0.11 mol/L acetic acid or 0.11 mol/L oxalic acid, rinsed with MilliQ water, and dried prior to XANES sample preparation. The fitting region was 17,008 eV to 17,158 eV.

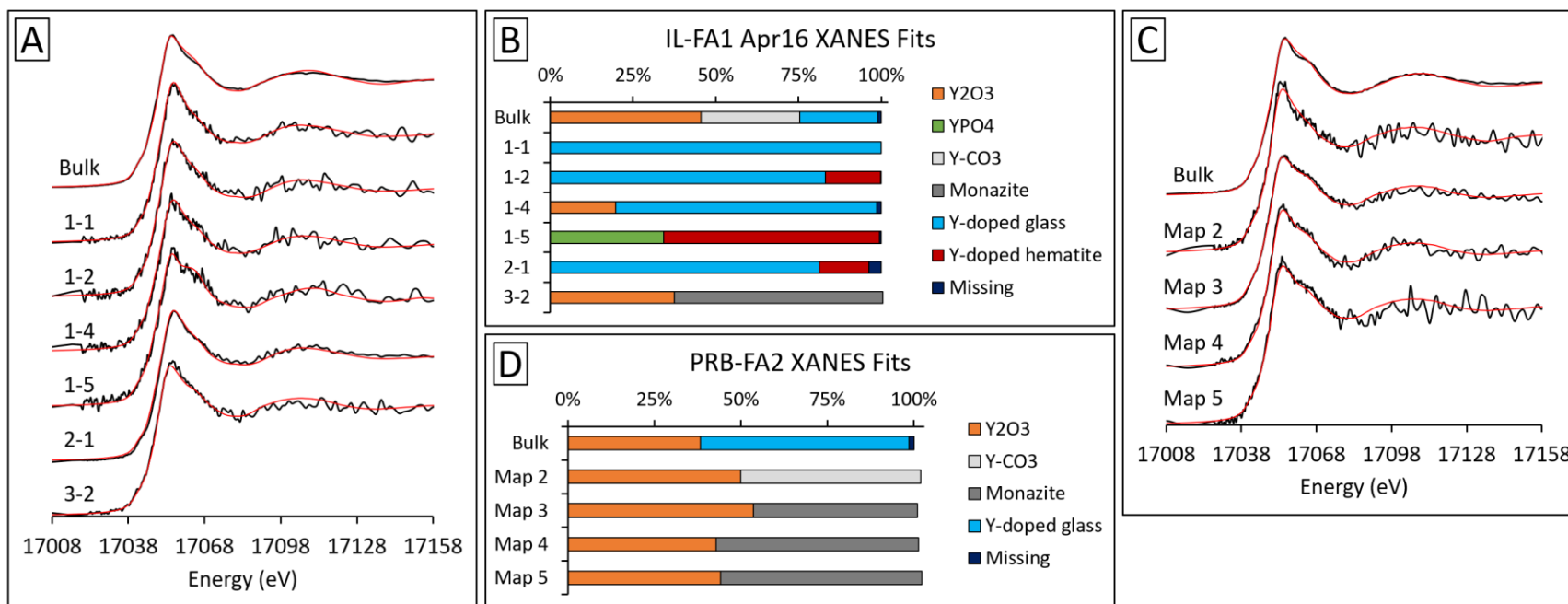


Figure S6. April 2016 Synchrotron x-ray spectroscopy analysis for Illinois Basin coal fly ash IL-FA1 and Powder River Basin fly ash PRB-FA2, including: (A)(C) Y K-edge bulk and micro-focus XANES spectra with linear combination fits indicated in red and (B)(D) fit weights. The fitting region was 17,008 eV to 17,158 eV. Multiple points (e.g. P1, P2, P4) were analyzed for several maps (e.g. M1, M2, M3) in IL-FA1.

Table S2. Linear combination fits for bulk fly ash samples analyzed using Y K-edge XANES. The fitting region was 17,008 eV to 17,158 eV. “Glass” and “Hematite” denote Y-doped glass and Y-doped hematite standards synthesized in lab. The monazite standard was a geological sample.

Sample ID	R-factor ^a	Standard Weights							
		Y ₂ O ₃	Y ₂ (SO ₄) ₃	Y ₂ (CO ₃) ₃	YPO ₄	Monazite	Glass	Hematite	Sum
App-FA1	0.0006481	35.5%				23.9%	40.1%		99.5%
App-FA2	0.0003731	17.7%			17.9%		63.4%		99.0%
App-FA3	0.0006782	38.7%				30.8%	30.2%		99.7%
App-PA	0.0007522	45.7%		31.6%			21.7%		99.0%
IL-FA1	0.0007502	45.5%		29.9%			23.6%		99.0%
IL-FA3	0.0006524	34.4%				28.0%	36.3%		98.7%
PRB-FA1	0.0007507	50.6%				21.6%	26.9%		99.1%
PRB-FA2	0.0007968	38.3%					60.3%		98.6%
RSA-FA1	0.0003568	23.1%					76.0%		99.1%

^a R-factor is a measure of the mean square sum of the misfit of each data point, calculated as

$$\frac{\sum_i (y_{data,i} - y_{fit,i})^2}{\sum_i (y_{data,i})^2}$$

where the sums are over the data points in the fitting region.

Table S3. Linear combination fits for bulk fly ash samples extracted with oxalic acid or acetic acid and analyzed using Y K-edge XANES. The fitting region was 17,008 eV to 17,158 eV. Ash samples were leached overnight in 0.11 mol/L oxalic acid or 0.11 mol/L acetic acid, rinsed with MilliQ water, and dried prior to XANES sample preparation. “Glass” and “Hematite” denote Y-doped glass and Y-doped hematite standards synthesized in lab. The monazite standard was a geological sample.

Oxalic Acid Extraction		Standard Weights							
Sample ID	R-factor	Y₂O₃	Y₂(SO₄)₃	Y₂(CO₃)₃	YPO₄	Monazite	Glass	Hematite	Sum
App-FA1	0.0004329	29.1%		16.8%		26.3%	43.5%		98.9%
App-FA2	0.0001332	14.1%					85.6%		99.7%
App-FA3	0.0001407					11.0%	70.5%	18.1%	99.6%
App-PA	0.0001059						100.0%		100.0%
IL-FA1	0.0006454	41.0%		29.9%			28.1%		99.0%
IL-FA3	0.0001699	22.9%				12.7%	63.9%		99.5%
PRB-FA1	0.0009672		64.5%				35.5%		100.0%
PRB-FA2	0.0014494		46.5%				53.4%		99.9%
RSA-FA1	0.0001786	13.0%	19.6%				67.4%		100.0%

Acetic Acid Extraction		Standard Weights							
Sample ID	R-factor	Y₂O₃	Y₂(SO₄)₃	Y₂(CO₃)₃	YPO₄	Monazite	Glass	Hematite	Sum
App-FA1	0.0005174						75.8%	22.9%	98.7%
IL-FA1	0.0005494						76.1%	22.7%	98.8%
PRB-FA1	0.001715						58.9%	40.0%	98.9%

Table S4. Linear combination fits for μ XANES spectra of high Y points in fly ash thin sections collected in February 2017. The fitting region was 17,008 eV to 17,158 eV. “Glass” and “Hematite” denote Y-doped glass and Y-doped hematite standards synthesized in lab. The monazite standard was a geological sample.

Sample ID	Point	R-factor	Standard Weights							Sum
			Y ₂ O ₃	Y ₂ (SO ₄) ₃	Y ₂ (CO ₃) ₃	YPO ₄	Monazite	Glass	Hematite	
IL-FA1	A1	0.0017791	41.7%			59.2%				100.9%
IL-FA1	A2	0.0018068	60.4%		41.4%					101.8%
IL-FA1	A3	0.0032064	53.5%		49.1%					102.6%
IL-FA1	B1	0.0024086	62.7%		40.2%					102.9%
IL-FA1	B2	0.0036639	54.8%		48.7%					103.5%
IL-FA1	B3	0.0011916	36.1%		34.5%	31.7%				102.3%
IL-FA1	B4	0.0023576	59.8%		42.1%					101.9%
IL-FA1	B5	0.0036352	57.8%		44.9%					102.7%
App-FA1	1a	0.0065006				50.2%		45.7%		95.9%
App-FA1	1b	0.005767				69.4%		32.3%		101.7%
App-FA1	2	0.0023778				73.8%			27.9%	101.7%
App-FA1	3	0.0032745	46.2%				55.2%			101.4%
PRB-FA1	1a	0.0008112				20.9%	23.0%		56.1%	100.0%
PRB-FA1	1b	0.0008479				19.7%	24.2%		55.5%	99.4%
PRB-FA1	2	0.003727	27.2%					73.1%		100.3%
PRB-FA1	3	0.0062067				57.1%			44.1%	101.2%
PRB-FA1	4	0.0038275				34.7%			66.2%	100.9%

Table S5. Linear combination fits of μ XANES spectra for high Y points in fly ash thin sections collected in April 2016. The fitting region was 17,008 eV to 17,158 eV. “Glass” and “Hematite” denote Y-doped glass and Y-doped hematite standards synthesized in lab. The monazite standard was a geological sample.

Sample ID	Point	R-factor	Standard Weights							
			Y ₂ O ₃	Y ₂ (SO ₄) ₃	Y ₂ (CO ₃) ₃	YPO ₄	Monazite	Glass	Hematite	Sum
IL-FA1	1-1	0.0008895						100.0%		100.0%
IL-FA1	1-2	0.0070887						83.1%	16.7%	99.8%
IL-FA1	1-4	0.0080282	19.8%					78.9%		98.7%
IL-FA1	1-5	0.010105				34.3%			65.2%	99.5%
IL-FA1	2-1	0.0025297						81.3%	15.0%	96.3%
IL-FA1	3-2	0.0048296	37.5%				62.9%			100.0%
App-FA3	Map 4	0.0014660				100.0%				100.0%
App-FA3	Map 6	0.0042225	35.9%					64.1%		100.0%
PRB-FA2	Map 2	0.01067	49.9%		52.1%					102.0%
PRB-FA2	Map 3	0.0029029	53.7%				47.4%			101.1%
PRB-FA2	Map 4	0.0058908	42.8%				58.6%			101.4%
PRB-FA2	Map 5	0.012571	44.1%				58.2%			102.3%