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# Chemical Studies of Stack Fly Ash from a Coal-Fired Power Plant

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■ Concentrations of 42 minor and trace elements in four size fractions of stack fly ash from a large Western coal-fired power plant are reported. Mass median diameters of the four size fractions were 2.4, 3.7, 6.0, and 18.5  $\mu\text{m}$ . Based on the enrichments relative to coal as a function of fly-ash particle size, the elements are grouped into three classes: Group I, elements that show little or no enrichment in the small particle fraction (Al, Ca, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, Sc, Ta, Th, Ti, and the rare earths: Ce, Dy, Eu, La, Nd, Sm, Tb, and Yb); Group II, elements whose enrichments increase with decreasing particle size (As, Cd, Ga, Mo, Pb, Sb, Se, W, and Zn); and Group III, elements whose behavior is intermediate to that of elements in Groups I and II (Ba, Be, Co, Cr, Cu, Ni, Sr, U, and V). The elements in Groups I and II are described in terms of their lithophilic and chalcophilic geochemical behavior, respectively. The chemical behavior of individual elements in Group III is discussed.

Coal combustion contributes significantly to the total pollutant burden in the United States. In 1973 coal use for electric power generation in the U.S. produced 3.6 million tons of fly ash, 22.6% of the total U.S. particulate emissions (1). With the addition of 241 new coal-fired power plants, coal consumption by U.S. electric utilities is expected to expand from 446 million tons in 1976 to more than 840 million tons in 1985 (2), further increasing the amount of fly ash emitted to the atmosphere. The most significant portion of the fly ash is in the respirable size range, i.e., aerodynamic diameters  $<10 \mu\text{m}$ , because it constitutes the greatest potential hazard for human inhalation. This fine-particle fraction has the highest particulate concentrations of some potentially toxic chemical species (3-13).

In view of the predicted increases in coal usage, an understanding of the behavior of chemical species during combustion, emission, and environmental transport is of critical importance. We have performed a detailed characterization of the physical and chemical properties of size-classified fly ash collected downstream from a cold-side electrostatic precipitator (ESP) in the stack breaching of a large Western U.S. power plant burning low-sulfur, high-ash coal. The physical and morphological properties of the four fly-ash fractions were reported previously (14). Preliminary chemical analyses of the four fractions by atomic absorption spectroscopy (AAS) and instrumental neutron activation analysis (INAA) were presented (15). This report presents the concentrations of 42 minor and trace elements in these four size fractions and discusses their geochemical behavior.

## Experimental

**Sample Collection.** Samples of aerodynamically sized stack fly ash were obtained from a large Western coal-fired power plant that burns low sulfur (0.46%), high ash (23%) coal. Kilogram quantities of four size fractions of fly ash were collected at 30 cubic feet per minute (cfm) and at 100  $^{\circ}\text{C}$  by a specially designed fractionator mounted at the outlet of a cold-side ESP. The details of this device are reported by McFarland et al. (16). For each fraction as determined by Stokes' law of settling (14), the mass median diameters (mmd) were 18.5, 6.0, 3.7, and 2.4  $\mu\text{m}$ . Geometric standard deviations

of the fractions were 2.3, 2.0, 1.7, and 1.8  $\mu\text{m}$ , respectively. Pulverized coal samples were collected daily during the 30-day period that the fractionator was operating.

**Analytical Techniques.** Up to 39 elements in both the size-classified stack fly-ash and input-coal samples were analyzed by INAA as described previously (15, 17). Samples were irradiated simultaneously with standard elemental flux monitors in the 3-MW Livermore pool-type reactor. The  $\gamma$ -ray spectra of the radioactive species were measured with large volume, high-resolution Ge(Li) spectrometer systems. The spectral data were analyzed on a CDC-7600 computer with the GAMANAL code (18, 19), which fits the peaks with Gaussian and exponential functions and a smoothed background function. Validation of the data was ensured by analysis of NBS standard reference materials 1632 and 1633 (20) and by comparison with AAS analysis of the size-classified fly ash (15).

The size-classified fly ash was analyzed for 18 elements by AAS at the Radiobiology Laboratory, University of California at Davis (21). The concentrations of Be and Cd in the coal were measured by AAS, and Cu, Ni, and Pb concentrations by X-ray fluorescence (XRF) (22).

## Results

Results of the analyses of 44 elements in input coal by INAA, XRF, and AAS are listed in Table I. Table II lists concentrations of 42 elements in the four fractions of the size-classified stack fly ash. Forty elements are common in the two sample types. Silicon was not measured in the samples of input coal. Table II consists of concentrations of 24 elements measured by INAA only, 6 elements measured by AAS only,

Table I. Concentrations of Elements in the Input Coal

INAA measurements Elements	Concentration, $\mu\text{g/g} \pm \sigma$	Elements	Concentration, $\mu\text{g/g} \pm \sigma$
Al	$29500 \pm 2390$ (7)	Sb	$0.61 \pm 0.09$ (7)
As	$2.8 \pm 0.8$ (6)	Sc	$3.0 \pm 0.2$ (7)
Ba	$420 \pm 170$ (7)	Se	$1.7 \pm 0.2$
Ca	$5620 \pm 860$ (7)	Sm	$1.8 \pm 0.2$ (7)
Ce	$27 \pm 2$ (7)	Sr	$98 \pm 8$ (7)
Cl	$48 \pm 17$ (1)	Ta	$0.51 \pm 0.06$ (7)
Co	$2.1 \pm 0.2$ (7)	Tb	$0.22 \pm 0.02$ (7)
Cr	$7 \pm 1$ (7)	Th	$6.2 \pm 0.7$ (7)
Cu	$0.72 \pm 0.16$ (7)	Ti	$1230 \pm 180$ (6)
Dy	$1.6 \pm 0.1$ (7)	U	$2.1 \pm 0.2$ (7)
Eu	$0.26 \pm 0.02$ (7)	V	$25 \pm 3$ (4)
Fe	$6470 \pm 570$ (7)	W	$0.9 \pm 0.4$ (7)
Ga	$8 \pm 1$ (7)	Yb	$0.84 \pm 0.06$ (7)
Hf	$2.4 \pm 0.1$ (7)	Zn	$16 \pm 3$ (7)
In	$0.039 \pm 0.006$ (5)	Zr	$67 \pm 10$ (7)
K	$1730 \pm 260$ (7)		
La	$13.4 \pm 0.8$ (7)	AAS measurements	
Li	$0.23 \pm 0.03$ (6)	Be	$1.2 \pm 0.6$ (7)
Mg	$2240 \pm 750$ (6)	Cd	$0.22 \pm 0.02$ (7)
Mo	$2.7 \pm 0.3$ (6)		
Mn	$60 \pm 20$ (7)	XRF measurements	
Na	$2930 \pm 250$ (7)	Cu	$12.7 \pm 0.6$ (7)
Nd	$11 \pm 1$ (7)	Ni	$4 \pm 1$ (7)
Rb	$12 \pm 2$ (7)	Pb	$12.1 \pm 0.7$ (7)

\* Errors are  $1\sigma$  deviation from the mean of the replicates.

**Table II. Comparison of Elemental Concentrations in Size-Classified Fly-Ash Fractions**

Element	Concentration, $\mu\text{g/g}$ (unless $\Sigma$ indicated)			
	Fraction 1, 18.5 $\mu\text{m}^b$	Fraction 2, 6.0 $\mu\text{m}^b$	Fraction 3, 3.7 $\mu\text{m}^b$	Fraction 4, 2.4 $\mu\text{m}^b$
Al ( $\Sigma$ )	13.8 $\pm$ 0.1	14.4 $\pm$ 0.1	13.3 $\pm$ 0.6	13.9 $\pm$ 0.3
Ba ( $\Sigma$ )	0.168 $\pm$ 0.001	0.245 $\pm$ 0.002	0.31 $\pm$ 0.01	0.41 $\pm$ 0.02
Ca ( $\Sigma$ )	2.1 $\pm$ 0.1	2.23 $\pm$ 0.08	2.30 $\pm$ 0.14	2.36 $\pm$ 0.09
Co	8.9 $\pm$ 0.2	17.7 $\pm$ 0.4	20.3 $\pm$ 0.7	21.8 $\pm$ 0.4
Cr	28 $\pm$ 3	53 $\pm$ 3	64 $\pm$ 3	68 $\pm$ 3
Fe ( $\Sigma$ )	2.51 $\pm$ 0.09	3.09 $\pm$ 0.02	3.04 $\pm$ 0.08	3.2 $\pm$ 0.1
K ( $\Sigma$ )	0.74 $\pm$ 0.01	0.80 $\pm$ 0.07	0.82 $\pm$ 0.08	0.81 $\pm$ 0.03
Mn	208 $\pm$ 5	231 $\pm$ 5	269 $\pm$ 6	309 $\pm$ 3
Na ( $\Sigma$ )	1.22 $\pm$ 0.03	1.75 $\pm$ 0.05	1.81 $\pm$ 0.06	1.85 $\pm$ 0.03
Ni	25 $\pm$ 3	37 $\pm$ 1	43 $\pm$ 4	40 $\pm$ 2
Ti ( $\Sigma$ )	0.62 $\pm$ 0.05	0.74 $\pm$ 0.05	0.73 $\pm$ 0.1	0.77 $\pm$ 0.05
Zn	68 $\pm$ 1	189 $\pm$ 4	301 $\pm$ 9	590 $\pm$ 98

Element	Concentration, $\mu\text{g/g}$ (unless $\Sigma$ indicated)			
	Fraction 1, 18.5 $\mu\text{m}^b$	Fraction 2, 6.0 $\mu\text{m}^b$	Fraction 3, 3.7 $\mu\text{m}^b$	Fraction 4, 2.4 $\mu\text{m}^b$
Be	6.3 (0.2)	8.5 (0.2)	9.5 (0.3)	10.3 (0.5)
Cu	56 (1)	89 (1)	107 (4)	137 (1)
Cd	0.4 (0.2)	1.6 (0.3)	2.8 (0.4)	4.6 (0.2)
Hg ( $\Sigma$ )	0.47 (0.01)	0.56 (0.01)	0.60 (0.02)	0.63 (0.01)
Pb	73 (3)	169 (2)	226 (4)	278 (3)
Si ( $\Sigma$ )	29.6 (0.7)	28.0 (0.1)	27.5 (0.3)	26.8 (0.1)

Element	Concentration, $\mu\text{g/g}$ (unless $\Sigma$ indicated)			
	Fraction 1, 18.5 $\mu\text{m}^b$	Fraction 2, 6.0 $\mu\text{m}^b$	Fraction 3, 3.7 $\mu\text{m}^b$	Fraction 4, 2.4 $\mu\text{m}^b$
As	13.7 $\pm$ 1.3	56 $\pm$ 14	87 $\pm$ 9	132 $\pm$ 22
Ce	113 $\pm$ 4	122 $\pm$ 5	123 $\pm$ 6	120 $\pm$ 5
Cs	3.2 $\pm$ 0.1	3.7 $\pm$ 0.2	3.7 $\pm$ 0.2	3.7 $\pm$ 0.2
Dy	6.9 $\pm$ 0.3	8.5 $\pm$ 0.9	8.1 $\pm$ 0.3	8.5 $\pm$ 0.8
Eu	1.0 $\pm$ 0.1	1.2 $\pm$ 0.2	1.2 $\pm$ 0.2	1.3 $\pm$ 0.4
Ga	43 $\pm$ 12	116 $\pm$ 52	140 $\pm$ 23	178 $\pm$ 90
Hf	9.7 $\pm$ 0.4	10.3 $\pm$ 0.3	10.5 $\pm$ 0.3	10.3 $\pm$ 0.5
La	62 $\pm$ 3	68 $\pm$ 4	67 $\pm$ 11	69 $\pm$ 3
Mo	9 $\pm$ 2	28 $\pm$ 1.4	40 $\pm$ 5	50 $\pm$ 9
Nd	45 $\pm$ 4	47 $\pm$ 4	49 $\pm$ 7	52 $\pm$ 6
Rb	51 $\pm$ 3	56 $\pm$ 4	57 $\pm$ 3	57 $\pm$ 8
Sb	2.6 $\pm$ 0.1	8.3 $\pm$ 0.4	13.0 $\pm$ 0.7	20.6 $\pm$ 0.7
Sc	12.6 $\pm$ 0.5	15.3 $\pm$ 0.6	15.8 $\pm$ 0.6	16.0 $\pm$ 0.2
Se	19 $\pm$ 2	59 $\pm$ 2	78 $\pm$ 2	198 $\pm$ 20
Sm	8.2 $\pm$ 0.3	9.1 $\pm$ 0.4	9.2 $\pm$ 0.4	9.7 $\pm$ 0.4
Sr	410 $\pm$ 60	540 $\pm$ 140	590 $\pm$ 140	700 $\pm$ 210
Ta	2.06 $\pm$ 0.09	2.3 $\pm$ 0.2	2.5 $\pm$ 0.3	2.7 $\pm$ 0.1
Tb	0.90 $\pm$ 0.05	1.06 $\pm$ 0.06	1.10 $\pm$ 0.07	1.13 $\pm$ 0.06
Th	25.8 $\pm$ 0.6	28.3 $\pm$ 0.6	29 $\pm$ 1	30 $\pm$ 2
U	8.8 $\pm$ 1.9	16. $\pm$ 3	22 $\pm$ 4	29 $\pm$ 4
V	86 $\pm$ 44	178 $\pm$ 17	244 $\pm$ 18	327 $\pm$ 40
W	3.4 $\pm$ 0.2	9 $\pm$ 2	16 $\pm$ 2	24 $\pm$ 2
Yb	3.4 $\pm$ 0.4	4.1 $\pm$ 0.4	4 $\pm$ 0.2	4.2 $\pm$ 0.3
$\Sigma$ ( $\Sigma$ )	0.101	0.304	0.425	0.711

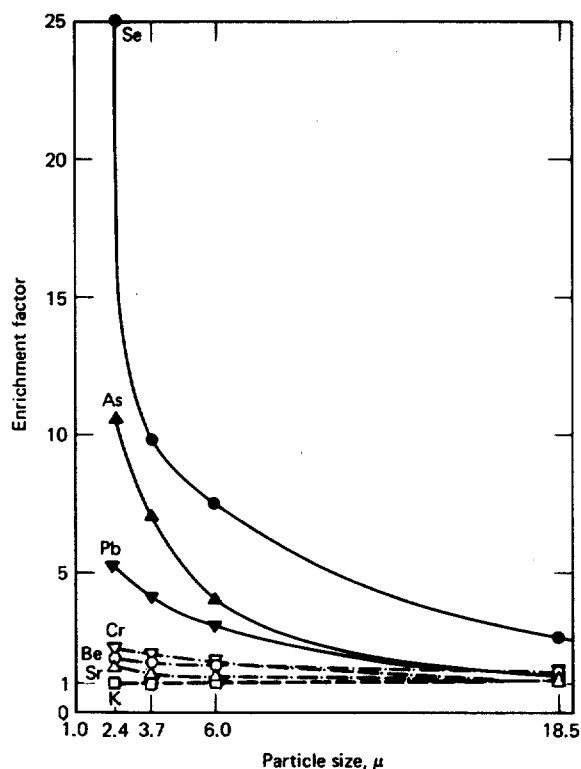
<sup>a</sup> Weighted average for all determinations, both techniques. <sup>b</sup> Mass median diameters (mmd) determined by centrifugal sedimentation. <sup>c</sup> Errors in parentheses are the range for duplicate determinations. <sup>d</sup> INAA values are the weighted averages of three determinations. Uncertainties are the largest of twice the weighted standard deviation, the range, or our estimate of the accuracy.

and 12 elements measured by both methods.

The enrichment factor (EF) of each element in the four size fractions of fly ash was calculated (see Table II). This EF is the ratio of the concentration of an element [X] to that of Ce in the fly-ash fraction divided by the corresponding ratio in the input coal:

$$EF = \frac{([X]/[Ce])_{\text{fly-ash fraction}}}{([X]/[Ce])_{\text{coal}}}$$

The data are normalized to a rare earth element, because concentrations of rare earths are constant in all of the sized fly-ash samples and can therefore be used as tracers for the aluminosilicate-dominated ash matrix. Cerium was chosen



**Figure 1.** Enrichment factors of selected elements vs. particle size in stack fly ash collected downstream from an electrostatic precipitator (ESP). Errors in data are given in Table III. Group I elements (---), Group II elements (—), and Group III elements (· · ·)

because of the higher precision in its replicate analysis over other rare earths. Normalization compensates for the apparent enrichment from loss of carbon during combustion.

The EFs of the 40 elements in the coal and fly ash are given in Table III. The EFs of Mg are nearly constant in all four fly-ash fractions and are between 0.5 and 0.6. These anomalously low values result from poor INAA measurements of Mg in coal because of the large corrections required for Al interference (20). Copper, Ni, and Pb in fly ash were measured by AAS, and Cu, Ni, Pb in coal by XRF. Beryllium and Cd were measured by AAS in both fly-ash and coal samples. The weighted average of all measurements by both INAA and AAS is given for Al, Ba, Ca, Co, Cr, Fe, K, Mn, Na, Ni, Ti, and Zn. In all other cases, only INAA coal data are compared to INAA fly-ash data to avoid possible systematic differences in absolute concentrations resulting from the different analytical techniques.

The elements are grouped in Table III according to their EFs. Changes in the EFs with particle size of representative elements of each group are shown in Figure 1. Group I elements have EFs near unity in all four size fractions, thus indicating their association with the fly-ash matrix, i.e., their lithophilic behavior. The EFs of Group II elements increase greatly from fraction 1 to 4. The range of values in the finest fraction, fraction 4, is 4.2 to 25. This small particle association is interpreted as chalcophilic (sulfur-associated) behavior. Group III elements behave in a manner intermediate between Groups I and II and are arbitrarily defined as those elements with EFs in fraction 4 between 1.6 and 3.0.

Other studies (3, 5, 8, 9, 23–25) show similar groupings of elements; however, our results agree most closely with those of Klein et al. (23).

Klein et al. (23) and Block and Dams (8) placed Na and Cs in Group III (we placed them in Group I) and included Ba, Co, and Sr in Group I (we placed them in Group III). Our data on Cs clearly indicates that its place is in Group I because of the

Table III. Enrichment Factors for Size-Classified Stack Fly Ash<sup>a</sup>

	Element	Enrichment factor			
		Fraction 1 18.5 $\mu\text{m}^b$	Fraction 2 6.0 $\mu\text{m}^b$	Fraction 3 3.7 $\mu\text{m}^b$	Fraction 4 2.4 $\mu\text{m}^b$
Group I  (Matrix elements)  Lithophilic behavior	Al	1.1 $\pm$ 0.1	1.1 $\pm$ 0.1	1.0 $\pm$ 0.1	1.1 $\pm$ 0.1
	Ca	0.9 $\pm$ 0.2	0.9 $\pm$ 0.2	0.9 $\pm$ 0.2	0.9 $\pm$ 0.2
	Ce	1.0 $\pm$ -	1.0 $\pm$ -	1.0 $\pm$ -	1.0 $\pm$ -
	Cs	1.1 $\pm$ 0.2	1.1 $\pm$ 0.3	1.1 $\pm$ 0.3	1.2 $\pm$ 0.3
	Dy	1.0 $\pm$ 0.1	1.2 $\pm$ 0.2	1.1 $\pm$ 0.1	1.2 $\pm$ 0.2
	Eu	0.9 $\pm$ 0.1	1.0 $\pm$ 0.2	1.0 $\pm$ 0.2	1.1 $\pm$ 0.4
	Fe	0.9 $\pm$ 0.1	1.1 $\pm$ 0.1	1.0 $\pm$ 0.1	1.1 $\pm$ 0.1
	Hf	1.0 $\pm$ 0.1	1.0 $\pm$ 0.1	1.0 $\pm$ 0.1	1.0 $\pm$ 0.1
	K	1.0 $\pm$ 0.2	1.0 $\pm$ 0.2	1.0 $\pm$ 0.2	1.0 $\pm$ 0.2
	La	1.1 $\pm$ 0.1	1.1 $\pm$ 0.1	1.1 $\pm$ 0.2	1.2 $\pm$ 0.1
	Mg <sup>c</sup>	0.5 $\pm$ 0.4	0.6 $\pm$ 0.4	0.6 $\pm$ 0.4	0.6 $\pm$ 0.4
	Mn	0.8 $\pm$ 0.3	0.8 $\pm$ 0.3	1.0 $\pm$ 0.3	1.2 $\pm$ 0.3
	Na	1.0 $\pm$ 0.1	1.3 $\pm$ 0.1	1.4 $\pm$ 0.1	1.4 $\pm$ 0.1
	Nd	1.0 $\pm$ 0.2	1.0 $\pm$ 0.2	1.0 $\pm$ 0.2	1.1 $\pm$ 0.2
	Rb	1.0 $\pm$ 0.2	1.0 $\pm$ 0.2	1.0 $\pm$ 0.2	1.1 $\pm$ 0.2
	Sc	1.0 $\pm$ 0.1	1.1 $\pm$ 0.1	1.2 $\pm$ 0.1	1.2 $\pm$ 0.1
	Sm	1.1 $\pm$ 0.1	1.1 $\pm$ 0.1	1.1 $\pm$ 0.1	1.2 $\pm$ 0.1
	Ta	1.0 $\pm$ 0.1	1.0 $\pm$ 0.2	1.1 $\pm$ 0.2	1.2 $\pm$ 0.1
	Tb	1.0 $\pm$ 0.1	1.1 $\pm$ 0.1	1.1 $\pm$ 0.1	1.2 $\pm$ 0.1
	Th	1.0 $\pm$ 0.1	1.0 $\pm$ 0.1	1.0 $\pm$ 0.1	1.1 $\pm$ 0.2
	Ti	1.2 $\pm$ 0.2	1.3 $\pm$ 0.2	1.3 $\pm$ 0.2	1.4 $\pm$ 0.2
	Yb	1.0 $\pm$ 0.2	1.1 $\pm$ 0.2	1.0 $\pm$ 0.1	1.1 $\pm$ 0.1
Group II  (Strong small particle association)  Chalcophilic behavior	As	1.2 $\pm$ 0.4	4.0 $\pm$ 2.0	7.0 $\pm$ 2.0	10.5 $\pm$ 4.0
	Cd	0.4 $\pm$ 0.2	1.6 $\pm$ 0.4	2.8 $\pm$ 0.6	4.7 $\pm$ 0.7
	Ga	1.2 $\pm$ 0.4	3.0 $\pm$ 1.5	3.6 $\pm$ 0.9	4.7 $\pm$ 2.5
	Mo	0.8 $\pm$ 0.2	2.3 $\pm$ 0.3	3.3 $\pm$ 0.6	4.2 $\pm$ 0.9
	Pb <sup>d</sup>	1.4 $\pm$ 0.1	3.1 $\pm$ 0.1	4.1 $\pm$ 0.1	5.2 $\pm$ 1.0
	Sb	1.0 $\pm$ 0.2	3.0 $\pm$ 0.5	4.7 $\pm$ 0.8	7.6 $\pm$ 1.4
	Se	2.6 $\pm$ 0.5	7.5 $\pm$ 1.3	9.8 $\pm$ 1.7	25.0 $\pm$ 5.0
	W	0.9 $\pm$ 0.3	2.1 $\pm$ 0.9	3.9 $\pm$ 1.5	6.0 $\pm$ 2.2
	Zn	1.0 $\pm$ 0.2	2.6 $\pm$ 0.6	4.0 $\pm$ 0.9	8.1 $\pm$ 2.2
Group III  Intermediate behavior	Ba	1.0 $\pm$ 0.4	1.3 $\pm$ 0.5	1.6 $\pm$ 0.6	2.2 $\pm$ 0.9
	Be	1.3 $\pm$ 0.6	1.6 $\pm$ 0.8	1.7 $\pm$ 0.8	1.9 $\pm$ 0.9
	Co	1.0 $\pm$ 0.1	1.9 $\pm$ 0.2	2.1 $\pm$ 0.3	2.4 $\pm$ 0.3
	Cr	1.0 $\pm$ 0.2	1.7 $\pm$ 0.3	2.0 $\pm$ 0.4	2.2 $\pm$ 0.4
	Cu <sup>d</sup>	1.1 $\pm$ 0.1	1.6 $\pm$ 0.2	1.8 $\pm$ 0.2	2.4 $\pm$ 0.2
	Ni <sup>d</sup>	1.4 $\pm$ 0.4	1.9 $\pm$ 0.5	2.2 $\pm$ 0.6	2.1 $\pm$ 0.5
	Sr	1.0 $\pm$ 0.2	1.2 $\pm$ 0.3	1.3 $\pm$ 0.3	1.6 $\pm$ 0.5
	V	1.0 $\pm$ 0.3	1.7 $\pm$ 0.4	2.3 $\pm$ 0.5	3.1 $\pm$ 0.6
		0.8 $\pm$ 0.4	1.6 $\pm$ 0.3	2.2 $\pm$ 0.4	3.0 $\pm$ 0.6

<sup>a</sup> With 1 $\sigma$  propagated error (deviation from the mean or counting statistics, whichever was larger). <sup>b</sup> Mass median diameter (mmd) determined by centrifugal sedimentation. <sup>c</sup> Coal data from INAA, ash data from AAS (data low due to systematic error in INAA analysis). <sup>d</sup> Coal data from XRF, ash data from AAS.

lack of significant enrichment in the smaller-sized particle fraction. The placement of Na is more tentative because of its slight enrichment in the smaller-sized particle fraction, although the analytical error leaves this enrichment uncertain. However, the concentration of Na is not as dependent upon particle size as that of other elements, and this could explain the anomalously low EF in fraction 1. Our placement of Ba, Co, and Sr in Group III is based on the increasing EFs from fraction 1 to 4. Of these elements, Co shows the strongest increase in EF and has the smallest analytical error. The EF of Sr increases the least and has a substantial analytical error.

We also disagree with the work of Klein et al. (23) in the placement of Cu in Group II, which we place in Group III. Other studies disagree on the behavior of Cu; Davison et al. (3) place it in Dams' Group I, whereas Block and Dams (8) consider it a Group II element. The moderate increase in the EF of Cu does not warrant its placement in Group II.

Although our groupings of the remaining elements agree with those of Klein et al. (23), notable differences exist in the work of others. Davison et al. (3) place Al, Fe, Mg, Mn, and Si in Group III. Block and Dams (8) place Cd, Ga, Mn, Mo, and K in Group III. Davison et al. (3) place Cr in Group II, and

Block and Dams (8) place it in Group I. The elemental grouping by Gladney et al. (9) is difficult to compare with that of other studies because they do not distinguish between the lithophilic elements and those we define as displaying intermediate behavior. They also showed the concentrations of Fe and Ce decreased rapidly with decreasing particle size.

### Discussion

To discuss the postcombustion distribution of elements, an understanding of the coal mineralogy of each element and its association with inorganic or organic phases is useful. Mackowsky (26) describes the mineral character and Nicholls (27) the geochemistry of coal beds. Gluskoter (28) discusses the affinity of various elements in coals with organic and inorganic components.

Some western coals, including the coal in this study, were deposited as recently as the Paleocene Epoch (~70 million years ago). Since then these beds have remained basically undisturbed except for coal metamorphism, varying degrees of diastrophism, and groundwater interaction. The associated trace elements are probably in equilibrium with the prevailing geological environment. The drastic alteration of the chemical and physical properties of the coal that occurs when it is exhumed, pulverized, and burned at temperatures of 1500 to 1600 °C may render the otherwise contained toxic elements into *mobile* and consequently more hazardous forms. The geochemical behavior of the elements during coal formation as well as their chemical behavior during combustion explain in part the elemental groupings we propose.

**Group I Elements.** Twenty-two elements, Al, Ca, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, rare earth elements (Ce, Dy, Eu, La, Nd, Sm, Tb, and Yb), Sc, Ta, Th, and Ti, showed little or no enrichment on the smaller fly-ash particles. Mason (29) classifies these elements as lithophiles. Because lithophilic elements are associated with aluminosilicate minerals, we would expect them to be volume distributed in the aluminosilicate ash matrix of the fly ash. However, subsequent interaction with surface-formed  $H_2SO_4$  may lead to surface-associated sulfate crystals, predominantly  $CaSO_4$  (30).

**Group II Elements.** The EFs of nine elements, As, Cd, Ga, Mo, Pb, Sb, Se, W, and Zn, increased with decreasing particle size. Mason (29) classifies these as chalcophiles. Because of their association with sulfide minerals, they are mostly volatilized during combustion and later condense onto the smaller fly-ash particles (4). Selenium shows the greatest enrichment on the smaller sized fly-ash particles. Andren et al. (31) claim that 68% of the Se from the Allen Steam Plant (Memphis) was on the fly ash and 32% in the vapor phase. Although Mason classifies W as a chalcophile, Krauskoff (32) considers it to be a lithophilic element. The behavior of W during coal combustion is open to speculation. Eskenazy (33) suggests that W is associated with the organic phase of coal as a covalently bound organometallic complex. This is consistent with our observation of W enrichment on small particles.

**Group III Elements.** Nine elements, Ba, Be, Co, Cr, Cu, Ni, Sr, U, and V, showed behavior intermediate to that of elements in Groups I and II. All of these elements had higher EFs on smaller particles. However, their EFs did not increase as dramatically as those of the Group II elements. Because the behavior of these nine elements is not as easily understood as that of elements in Groups I and II, we will discuss them individually.

**Barium.** Barium oxide forms the volatile species  $Ba(OH)_2$  in steam at temperatures between 1155 and 1626 °C (34). Because the coal in our study contains 6.8% water and combustion temperatures at the plant range from 1500 to 1600 °C, the formation of volatile  $Ba(OH)_2$  is possible. Subsequent condensation on the fly ash could occur as flue temperatures drop below 1155 °C.

**Beryllium.** Mason (29) considers this element as a lithophile. However, Zubovic et al. (35) assumed Be association with the organic residue of coals, and Jedwab (36) found a higher content in low-ash coals than in high-ash coals. The mobility of Be may be inferred from its common occurrence in pegmatites (37) as beryllium aluminosilicates (beryl), which are crystallized residual melts related to nonvolcanic igneous crystallization. These residual melts are rich in water and volatile species (38). Hormann (39) states that fluorine is important in the transport of Be during metasomatism because of the formation of soluble fluoroberyllates. This may also occur during coal combustion. The affinity to organic matter that may restrict incorporation of Be into the aluminosilicate matrix and the mobility implied by pegmatite association might explain a moderate enrichment of Be on small particles. The exact combustion chemistry cannot be determined from our data.

**Cobalt.** Mason (29) considers Co in the earth's crust to have both lithophilic and chalcophilic character. Nicholls (27) suggests co-precipitation of Co with FeS during organic material deposition. This hypothesis indicates that Co behaves more as a chalcophile than a lithophile during coal formation, which could account for the moderate EF. However, Fe does not show a significant enrichment on the finer fly-ash particles. Iron is either less mobile upon combustion or inorganic Fe from the equipment in the plant overwhelms any Fe enrichment.

**Chromium.** Chromium is classified as a lithophile by Mason (29); however, it does show a moderate enrichment on small particles. Natural chromium sulfide has only been found in meteorites as the mineral daubréelite ( $FeCr_2S_4$ ) and breznaita ( $Cr_3S_4$ ) (40). It cannot, therefore, be classified in the earth's crust as a chalcophile. Nicholls (27) suggests that Cr is sorbed onto very finely divided clays that are distributed throughout the organic matter. Upon combustion the highly dispersed clays may form small fly-ash particles that incorporate the sorbed Cr, thereby causing its size dependence and consequently a moderate EF. The actual mechanism cannot be determined from our data.

**Copper.** Copper is regarded as a chalcophile by Mason (29). It exists in coal predominantly as chalcopyrite ( $CuFeS_2$ ) (26, 27). Because this mineral will fuse (37) at about 800 °C, it should become molten during coal combustion. Its moderate EF most likely results from subsequent condensation upon the surface of fly-ash particles.

**Nickel.** Nickel is classified as either a chalcophile or lithophile by Mason (29). Nicholls (27) found Ni in coal as the sulfide mineral millerite ( $NiS$ ), but its occurrence is not correlated with the location of other sulfide minerals. He suggests that much of it could be deposited separately as a primary sulfide. Later postburial enrichment by circulating groundwaters probably contributes to the total Ni content of the coal. If Ni does exist as millerite, it can fuse (37) at less than 800 °C and probably behaves like Cu during coal combustion.

**Strontium.** Strontium shows the least small particle enrichment of the Group III elements. Mason (29) considers it as a lithophile. Nicholls (27) states that Sr is predominantly associated with clays and other inorganic minerals. Its slight enrichment in the finer fly-ash particles is less easily understood, but it probably behaves in a manner similar to Ba.

**Uranium.** Uranium shows the greatest small particle enrichment in Group III. Coles et al. (7) suggest that its small particle enrichment is the result of a bimodal residence in the coal (both organic and inorganic associations) with subsequent formation of the volatile species  $UO_3$  from the uraninite ( $UO_2$ ) in the organic fraction.

**Vanadium.** In spite of Mason's (29) classification of V as a lithophile, it shows a definite small particle enrichment in the sized fly ash. Nicholls (27) states that most of the V is

sorbed on clays similarly to Cr. Its postcombustion behavior may also be similar to that proposed for Cr.

## Conclusion

Group I elements, Al, Ca, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, Sc, Ta, Th, Ti, and rare earth elements, showed no particle-size dependence. Group II elements, As, Cd, Ga, Mo, Pb, Sb, Se, W, and Zn, showed a large increase in enrichment with decreasing particle size. Group III elements, Ba, Be, Co, Cr, Cu, Ni, Sr, U, and V, behaved in a manner intermediate between that of Groups I and II.

Group I elements are considered as lithophiles and are assumed to have been homogeneously incorporated into the aluminosilicate-dominated fly-ash matrix. Group II elements are considered chalcophiles, which form volatile species upon combustion. The volatile species presumably then condense onto the surface of the fly-ash particle somewhere along the flue line. The greater surface area to volume ratio of smaller particles would account for the enrichment on small particles. Group III elements showed definite enrichment on small particles, but not nearly as strongly as Group II elements. They are a mixture of lithophiles and chalcophiles, and each possesses unique characteristics that account for its intermediate behavior.

We conclude that certain elements in coal are more concentrated on the finer fly-ash particles that escape the emission control systems and are emitted into the atmosphere. The public is more likely to be exposed to these fine particles because of their longer atmospheric residence times (compared to larger particles) and their eventual deep lung deposition. Consequently, further studies on the biological availability of the associated and potentially toxic elements are warranted.

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