FACTORS INFLUENCING TRACE ELEMENT
VARIATIONS IN U.S. COALS

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INTRODUCTION

Although trace element data exist for thousands of coal samples, more will be required to better elucidate trace element trends within coal basins and to help decipher the geological and geochemical controls on trace element distribution and mode of occurrence. However, increased numbers of analyses will not necessarily provide all the answers. We run the risk of ending up information rich but knowledge poor.

The purpose of this paper is to give our analysis of coal trace element data in the literature. Several valuable compilations of trace element data exist for U.S. coal (1-4). We have borrowed freely from these compilations to illustrate their value in elucidating just one aspect of coal geochemistry: the factors influencing trace element variations.

Trace elements are generally defined as those elements with concentrations below 0.1 wt. % (1000 ppm). Despite concentrations in the parts-per-million range, certain trace elements can have a significant impact on coal utilization. For example, the chalcophile elements As, Cd, Hg, Pb, and Se, which are released during coal combustion or leached from coal waste products, can present significant environmental hazards; halogens such as Cl and F can cause severe boiler corrosion, and volatilized Ni or V can cause corrosion and pitting of metal surfaces. Moreover, although not strictly a trace element, sodium, even in small concentrations, can contribute to boiler fouling or to agglomeration of fluidized-bed reactors. On the positive side, some trace elements (e.g., Ge, Zn, U, Au) may eventually prove to be economic by-products, and others may be useful in helping to understand depositional environments (e.g., B) and to correlate coal seams (5,6).

In early studies of trace elements in coal (7-11), coal ash was analyzed using emission spectroscopy. Recent studies (3,4,12,13) have employed quantitative multi-element instrumental methods. Because a particular analytical technique is better suited for certain elements than for others, a combination of methods is usually necessary to determine all elements of interest. Methods for determining trace elements in coal must be accurate and precise. In addition, if possible, they should determine a large number of elements of interest simultaneously, require relatively little sample preparation, be capable of automation, produce an output compatible with computerized data processing, and be rapid.

Trace element concentrations in coal show variations from a microscopic to a worldwide scale. From a resource evaluation perspective, the most significant variations occur within and between coal basins. The rest of the paper will discuss factors that cause these variations.

DISCUSSION

Ash Related Variations

The amount of ash in a coal is a major factor influencing trace element content. In general, trace element concentrations increase as ash content increases. This relationship reflects the fact that most inorganic elements in coal are associated with minerals (5). Figures 1 and 2 illustrate this relationship for K in eastern Kentucky coals and for Ti in coals from the Uinta Region.

The above relationship also holds when comparing trace element concentrations among coal basins. Table I compares trace element data for coals from the Black Mesa Field, the Powder River Region, and the San Juan Region. As shown in Table I, the concentrations of the following elements increase as the ash contents of the coals increase: Si, Al, Na, K, Cu, Th, V, Li, Pb, and Se. The reason for the variation of these elements with ash content is that most are, or were, associated with the silicate (detrital) minerals brought into the depositional basins during the formation of the coals. Chemical alteration of minerals within the coal basin can remobilize some elements, which then precipitate as authigenic nonsilicate minerals, e.g., Cu and Pb, as sulfides or selenides (14). The good correlation between element concentration and ash content indicates that most elements have remained within the coal basin despite remobilization (15).

Table I. Concentrations of Selected Elements in Coal Samples from Black Mesa, Powder River, and San Juan Regions[1]

	Black Mesa	Powder River	San Juan
Ash, %	8.0	9.9	21.1
Si, %	1.1	1.5	5.4
Al, %	0.69	0.78	2.7
Ca, %	0.78	1.1	0.67
Mg, %	0.1	0.2	0.1
Na, %	0.09	0.1	0.2
K, %	0.04	0.05	0.16
Fe, %	0.31	0.54	0.54
Ti, %	0.05	0.04	0.11
Cu, ppm	5.5	11.2	13.3
Th, ppm	2.2	4.3	5.9
Zn, ppm	5.6	20	15.1
Cr, ppm	3	7	5
Ni, ppm	2	5	3
V, ppm	7	15	20
Mn, ppm	9.7	51	29
Li, ppm	3.9	5.9	19.7
Pb, ppm	2.7	5.6	13.1
Se, ppm	1.6	1.7	2
Ba, ppm	300	300	300
Sr, ppm	150	200	100
Nb, ppm	1.5	1.5	3
Zr, ppm	15	15	50

[1]Data from Reference 4; results are calculated on a moisture-free coal basis (mf coal).

Elements not increasing in concentration with ash content are generally those with (a) organic affinities (Ca, Mg, Sr, Ba); (b) sulfide affinities (Fe, Zn); (c) carbonate affinities (Ca, Mn, Mg); or (d) sulfate affinities (Ba, Sr, Ca). Sulfides, carbonates, and sulfates are generally epigenic phases. Presence of these phases affects element concentration more than ash content. The concentrations of Zr and Nb would be expected to increase with ash content. The reason that this

behavior is not apparent in Table I may be the poor resolution of the technique (semiquantitative spectrographic analysis) used to obtain the data.

Rank-Related Variations

Several elements exhibit a distinct variation in concentration with coal rank. Table II illustrates the general decrease in concentration of alkaline-earth elements (Mg, Ca, Sr, Ba), Na, and B with increasing coal rank. It is generally accepted that these elements are associated with organic functional groups (e.g., carboxylic acids) in low-rank coals. With increasing coal rank, these groups are destroyed, thus displacing organically associated inorganic trace elements.

Table II. Rank-Related Variations[1]

	Anthracite	Bituminous	Subbituminous	Lignite
Ca, %	0.07	0.33	0.78	1.2
Mg, %	0.06	0.08	0.18	0.31
Na, %	0.05	0.04	0.10	0.21
B, ppm	10	50	70	100
Ba, ppm	100	100	300	300
Sr, ppm	100	100	100	300

[1]Data from Reference 1; mf coal.

Organic association has been proposed for other trace elements, such as Be, Sb, Ge, U, and some halogens (3,16). Finkelman (15) suggests that organic association of these elements is significant mainly for low-rank, low-ash coals.

Concentrations of organically bound elements in coal can decrease with increasing amount of detritus (Figure 3). Also, note that the concentrations of boron decrease with increasing ash contents (Table I).

Variations Due to Geochemical Factors

Geochemical factors, such as Eh and pH during and subsequent to coal formation, can have dramatic effects on trace element contents. The effect of these geochemical factors can be seen in Table III, in which selected data for Appalachian and Interior Province coals are compared. Coals from both areas are similar in rank and ash content, but the Interior Province coals have significantly higher contents of all six trace elements. The higher content of Ca is perhaps due to carbonate mineralization (high pH), whereas that of Fe, Cd, Pb, and Zn is attributable to sulfide mineralization (low Eh). The higher content of B is perhaps attributable to greater marine influence (high salinity).

Table III. Concentrations of Selected Elements in Coal Samples from Appalachian and Interior Coal Basins

	Appalachian[1]	Interior[2]
Ash, %	13.3	15.7
Ca, %	0.12	1.2
Fe, %	1.9	3.3
Cd, ppm	0.7	7.1
Pb, ppm	15.3	55
Zn, ppm	20	373
B, ppm	30	100

[1]Data from Reference 2; mf coal.
[2]Data from Reference 4; mf coal.

The occurrence of cleat-filling sphalerite and galena in the Interior Province coals is a classic example of how epigenetic mineralization can affect trace element content (17). Dramatic intra- and interseam variations are common. Cobb (18) reports that zinc content from benches of the Herrin (No. 6) coal varied from 20 to 14,900 ppm.

Variations Due to Geologic Factors

Ash chemistry is another important factor affecting trace element variations. Its influence is, however, generally more subtle than the other factors. In Table IV the trace element contents are compared for Appalachian Province coals and Wasatch Plateau coals. Both are bituminous coals with similar ash contents and rank. However, with a few exceptions, the trace element contents of the Wasatch coals are lower than those of Appalachian coals. The lower content of chalcophile elements in Wasatch coals may be due to a lower pyrite content. The lower concentration of lithophile elements (e.g., Li, Zr, Nb, Th, Sc, Y) but higher Si content may reflect a higher quartz content in the detrital component of Wasatch coals; this, in turn, may be a reflection of differences in the mineralogy of the source rocks.

Table IV. Concentrations of Selected Elements in Coal Samples
from Appalachian Province and Wasatch Coal Field

	Appalachian[1]	Wasatch[2]
Ash, %	13.3	11.3
Ca, %	0.2	0.41
Fe, %	1.9	0.26
Cd, ppm	0.7	0.06
Li, ppm	27.6	16
Pb, ppm	15.3	5.8
U, ppm	1.4	1.2
Zn, ppm	20	11
B, ppm	30	100
Nb, ppm	5	0.3
Ni, ppm	15	5
Zr, ppm	50	30
As, ppm	27	0.8
Cu, ppm	24	9.3
F, ppm	80	67
Th, ppm	4.9	1.8
Ba, ppm	100	70
Co, ppm	7	1.5
Cr, ppm	20	10
Mo, ppm	3	0.7
Sc, ppm	5	3
V, ppm	20	15
Y, ppm	10	7

[1]Data from Reference 6; mf coal.
[2]Data from Reference 19; mf coal.

Other Factors Affecting Trace Element Content

Other factors that could modify the ash chemistry or the availability of trace elements include the salinity of waters in contact with the coal or peat, the type of chemical weathering process (arid vs. humid), and hydrologic conditions (Br and Cl may be especially sensitive to this factor). In general, these factors are still poorly understood.

31

CONCLUDING COMMENTS

In this paper, we made several broad generalizations regarding factors that influence trace element variations. We urge that in interpretative work these generalizations be applied carefully.

A critical evaluation of existing trace element data would probably result in identification of anomalous values and elimination of suspect data. Several questions might be answered by such an evaluation; for example, do the two K values in the high-ash region of Figure 1 deviate significantly from the trend of the other data because of analytical errors or recording errors? Are they legitimate geochemical anomalies? We encourage analytical chemists and geologists to interact closely because this is one of the best ways to improve the quality of analytical methodology and data, and geological interpretation.

The nature of trace element variations, for whatever cause, highlights the need to more judiciously select representative samples for reliable quantitative analyses.

Statistical techniques, such as principal component analysis, should help in resolving the influence of the factors affecting trace element variations in coal.

It is hoped that this paper will encourage more detailed study of factors influencing trace element variations in coals.

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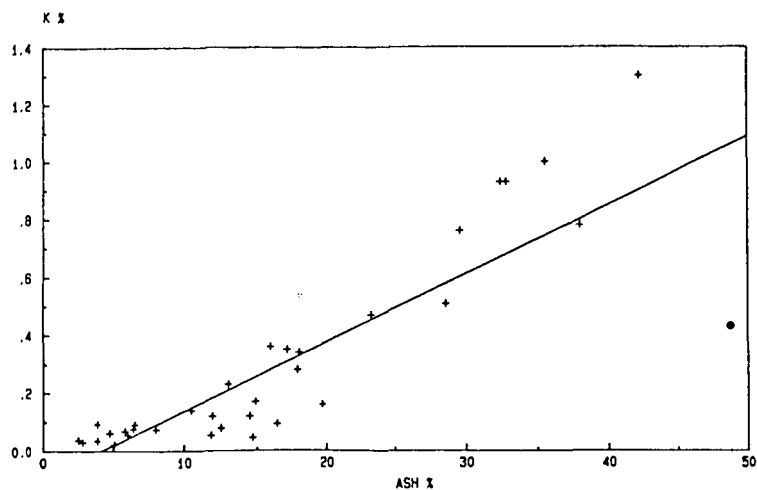
Figure 1. Relationship between K concentration in the coal and ash content for 34 coals from eastern Kentucky. R = 0.86. Data from Reference 1.
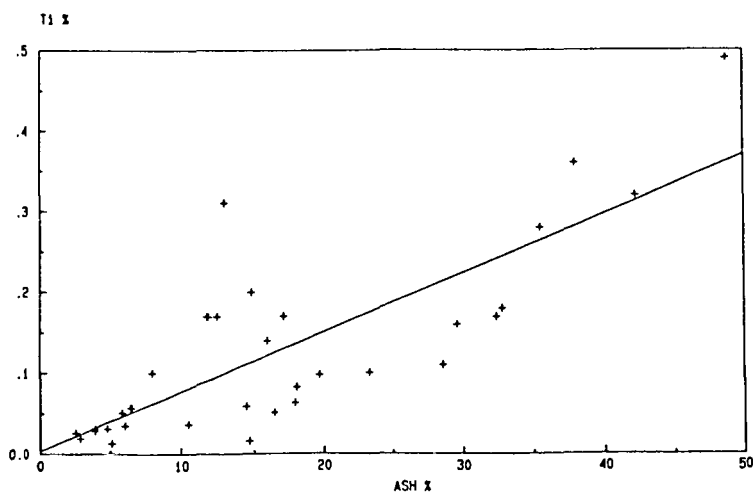

Figure 2. Relationship between Ti concentration in the coal and ash content for 26 coals from the Uinta Region. R = 0.86. Data from Reference 1.
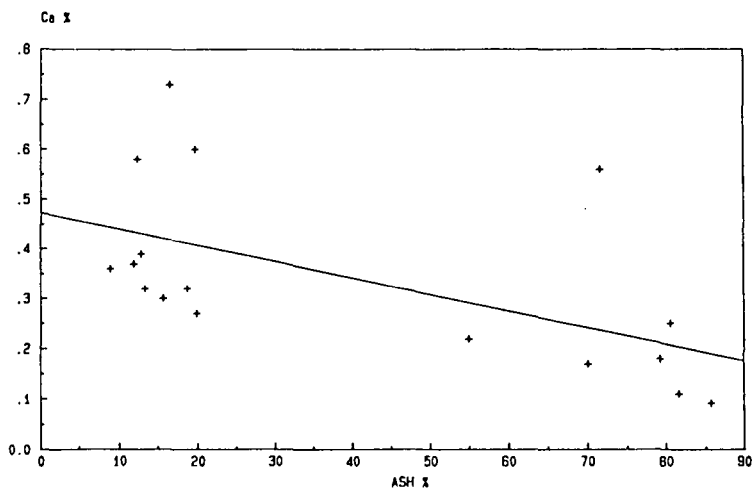
Figure 3. Relationship between Ca concentration in the coal and ash content for 17 coals and shales from the Emery Coal Field. R = -0.57. Data from Reference 18.