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M. Robert Dawson
*Iowa State University*

Karl E. Seifert
*Iowa State University*

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M. ROBERT DAWSON and KARL E. SEIFERT

Department of Earth Sciences, Iowa State University, Ames, IA 50011/U.S.A.

Coal samples were collected from four coal mines in Iowa and analyzed by instrumental neutron activation analysis (INAA) for La, Ce, Sm, Eu, Tb, Yb, Lu, Sc, Cr, Co, As, Th, and U. A comparison of the compositions of whole coals to their high-temperature ashes indicates that essentially all of these elements reside in the ash. The abundance of most elements is consistent with a trend of decreasing elemental concentrations from east to west in United States coals. Pyrite separates were found to concentrate As, Cr and Co, while calcite separates were found to concentrate Sc. Rare earth element (REE) patterns are given for the Iowa coals.
INDEX DESCRIPTORS: coal, trace elements, rare earth elements

Coal was sampled and analyzed from 4 coal mines in Iowa. Channel-cut sections were taken from the Iowa, Mich, and Jude mines, and grab samples were taken from the Lovilia mine (Figure 1). The coals from all 4 mines occur within sediments of the Middle Pennsylvanian Cherokee Group in the northeastern part of the Forest City basin.

Iowa coals have been characterized as typically high-sulfur, high-ash coals with an apparent rank of high-volatile C bituminous (Hatch et al, 1984). Their study found a mean of 5.8% sulfur and 15.9% ash in coals analyzed. They also analyzed for many other elements, including As, Co, Cr, La, Sc, Th and U, which we have investigated in this study. Of the elements they analyzed, only As, Th, and U were determined in whole coal samples. The other elements were back calculated from analyses of coal ash. Hatch et al, (1984) used a variety of analytical techniques to determine 34 to 36 major and minor oxides and trace elements in 106 Iowa coal samples.

We have analyzed 23 whole coal samples, 11 high-temperature ashes, 8 calcite crystals, and 7 pyrite crystals by INAA for 7 REE (La, Ce, Sm, Eu, Tb, Yb, Lu), Sc, Cr, Co, As, Th, and U. Our purpose is to define the abundance of these elements in Iowa coals as well as the relative fraction of these elements residing in constituent pyrite, calcite and high-temperature coal ash. We are presenting the first INAA analyses of mineral separates and the first chondrite normalized REE patterns for Iowa coals. The role of major minerals in concentrating trace elements is important for understanding how cleaning will effect final elemental abundances in washed coal.

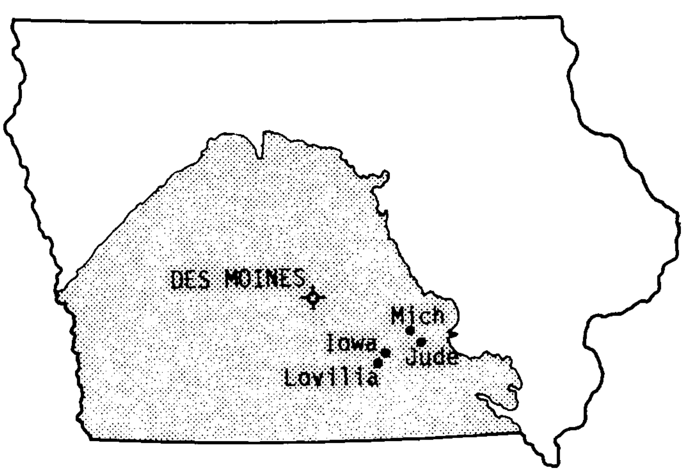


**Fig. 1. Map of Iowa showing the locations of the four coal mines sampled for this study. The shaded region defines the extent of coal strata in Iowa.**

## ANALYTICAL TECHNIQUES

A portion of each coal sample was crushed to pass a 60 mesh screen for heavy liquid and hand sorting of pyrite and calcite minerals with a binocular microscope. Another portion was cut for polished mounts to allow an estimate of the minerals present. Still another portion of each sample was ashed in a cold muffle furnace with the door partly open, allowing temperature to increase gradually to 450° over 4 hours. Then temperature was rapidly increased to 525° and held until the coals were completely ashed. The ashing technique is described in more detail by Swanson and Huffman (1976).

Whole coal samples, high-temperature ashes and mineral separates were analyzed by INAA in a manner similar to that described by Jacobs et al, (1977). Irradiation occurred at the University of Missouri Research Reactor at a flux near $3 \times 10^{13}$m/cm$^2$/sec for 10 hours. Samples were allowed to cool and then were counted for La, Sm, Yb, Lu, As, and U 7 to 10 days following irradiation, and for Ce, Eu, Tb, Sc, Cr, Co, and Th about 21 to 30 days following irradiation. All samples and standards (USGS, BCR-1, NBS 1632a and NBS 1633a) were irradiated and counted in cleaned SUPRASIL tubing. Accuracy is believed to be similar to that given by Jacobs et al, (1977).

## RESULTS

Eleven coal samples were ashed; 3 each from the Iowa, Mich, and Jude mines and 2 from the Lovilia mine. The mean ash content for all samples combined is 18.4%, relatively close to the 15.9% found by Hatch et al, (1984). The means for indivdiual mines are: Iowa mine 21.1%, Mich mine 20.2%, Jude mine 15.5%, and Lovilia mine 16.9%. In a few instances the float portion of a heavy liquid separation was ashed and analyzed by INAA. The mean ash content of the float separates was 8.45%.

The mean INAA data for each mine, based on the 23 analyzed coals, are given in Table 1. Low and high values, means, and standard deviations (SD) are given for the Iowa, Mich, and Jude mines, where at least 6 samples of each were analyzed. Only mean values are given for the Lovilia mine, since only two grab samples were analyzed. The data show considerable variation between mines and within each mine. A trace element composition is listed for the average Iowa coal. Mean REE data for each mine are plotted in Figure 2. REE patterns are rather similar for the Jude, Mich, and Lovilia mine coals, with all showing light rare earth element to heavy rare earth element (LREE/HREE) enrichment. The Iowa mine coal is most enriched in the middle REE.

The mean INAA data for 8 analyzed calcite crystals and 7 analyzed pyrite crystals are given in Table 2. REE analyses were performed for 3 of the pyrite crystals. Calcite and pyrite cleat fillings were obtained from coals from all 4 mines, but the data are similar and only mean values are reported. Mean REE data for calcite and pyrite are plotted in Figure 3. It was not possible to obtain accurate Ce and Yb values for

**Table 1. Trace element data for Iowa coals (in ppm).**

| | Iowa mine | | | | Mich mine | | | | Jude mine | | | | Lovilia mine | Ave. Iowa Coal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | low | high | mean | S.D. | low | high | mean | S.D. | low | high | mean | S.D. | mean | |
| La | 2.20 | 8.37 | 3.47 | 2.20 | 1.35 | 30.1 | 9.25 | 9.76 | 4.88 | 41.4 | 14.9 | 13.7 | 6.07 | 8.42 |
| Ce | 6.56 | 17.5 | 9.78 | 3.88 | 4.45 | 51.3 | 17.6 | 15.4 | 10.3 | 68.5 | 27.1 | 22.1 | 11.3 | 16.5 |
| Sm | 1.76 | 5.06 | 2.35 | 1.14 | 1.50 | 4.52 | 2.64 | 1.00 | 1.76 | 4.60 | 2.75 | 1.12 | 1.97 | 2.43 |
| Eu | 0.42 | 1.27 | 0.68 | 0.29 | 0.41 | 0.83 | 0.63 | 0.13 | 0.47 | 0.78 | 0.60 | 0.11 | 0.50 | 0.60 |
| Tb | 0.17 | 0.87 | 0.43 | 0.25 | 0.21 | 0.57 | 0.46 | 0.11 | 0.20 | 0.45 | 0.27 | 0.09 | 0.25 | 0.35 |
| Yb | 0.43 | 1.10 | 0.81 | 0.32 | 0.60 | 1.13 | 0.83 | 0.20 | 0.50 | 1.33 | 0.86 | 0.32 | 0.51 | 0.75 |
| Lu | 0.10 | 0.21 | 0.14 | 0.04 | 0.09 | 0.16 | 0.13 | 0.02 | 0.09 | 0.27 | 0.15 | 0.07 | 0.08 | 0.13 |
| Sc | 0.86 | 6.80 | 2.93 | 2.15 | 0.87 | 7.83 | 3.22 | 2.31 | 1.51 | 11.1 | 4.31 | 3.47 | 2.50 | 3.24 |
| Cr | 1.43 | 64.9 | 12.0 | 23.4 | 1.93 | 11.9 | 7.09 | 4.17 | 6.68 | 79.5 | 23.2 | 27.8 | 10.8 | 13.3 |
| Co | 3.10 | 56.2 | 14.8 | 18.5 | 2.48 | 5.60 | 3.50 | 1.17 | 3.48 | 48.3 | 19.7 | 17.7 | 5.74 | 10.9 |
| As | 18.0 | 129 | 44.1 | 38.5 | 1.53 | 8.82 | 4.89 | 3.02 | 1.46 | 45.4 | 18.9 | 18.4 | 12.3 | 20.1 |
| Th | 0.13 | 3.14 | — | — | 0.51 | 1.56 | — | — | 0.89 | 10.3 | 3.09 | 3.59 | 1.17 | — |
| U | 0.88 | 2.22 | — | — | 0.30 | 253 | — | — | 0.63 | 5.00 | — | — | — | — |
| | | 7 samples | | | | 8 samples | | | | 6 samples | | | 2 samples | |

pyrite. In the case of Ce, the very large Fe gamma-ray peak completely buries the much smaller Ce gamma-ray peak.

## DISCUSSION

Our arithmetic means for mutually analyzed elements As, Co, Cr, La, Sc, Th, and U are in good agreement with the means of Hatch et al, (1984). Our As, Co, and La means are slightly higher and our Cr and Sc means are slightly lower than their means. We did not obtain Th and U for several of our samples, but the data obtained are in general agreement with their data.

The REE pattern for whole coal from the Iowa mine is similar to that of our average calcite, but lower in magnitude. It is possible that calcite in the Iowa mine coal has controlled the REE pattern, although microscopic observation indicates the Iowa mine coal appears to have a lower average calcite content than the other coals. Coal from other mines has a greater LREE/HREE enrichment than even average pyrite, as well as a greater total REE content. Arsenic, Cr, and Co concentrate in pyrite and Sc concentrates in calcite (Table 2). It is difficult to find any correlation between trace element content and observed abundances of minerals such as pyrite and calcite, although very small mineral grains could easily be overlooked. The high ash content of our float separates indicates considerable fine-grained mineral matter is mixed with the organic fraction of the Iowa coals. Perhaps trace minerals or the clay minerals present are controlling elemental concentrations (Finkelman, 1980).

The vast majority of the trace elements determined in this study appear to reside in the high-temperature ash fraction derived from the Iowa coals. When trace element concentrations in high-temperature ashes are multiplied by the fraction of ash in each coal, they agree to a first approximation with the trace element concentration in whole coal samples. There are no consistent exceptions, except perhaps U, which is not well determined in many of our samples. This indicates that the elements reported have inorganic associations in Iowa coals.

Arithmetic means for As, Cr, and Sc values fit geographically into the east-west decreasing elemental trends observed in United States coals (Zubovic, 1976; Gluskoter et al, 1977; Kuhn et al, 1980). Our REE means are similar to eastern coals (Zubovic et al, 1979), slightly higher than Illinois coals (Schofield and Haskin, 1964; Gluskoter et al, 1977), and considerably higher than western coals (Gluskoter et al, 1977). Our Th values are lower than most other United States coals (Swanson et al, 1976), and our Co values are higher than most other

**Table 2. Trace element date for pyrite and calcite mineral separates from Iowa coals (in ppm).**

| | Pyrite | | | | Calcite | | | |
|---|---|---|---|---|---|---|---|---|
| | low | high | mean | S.D. | low | high | mean | S.D. |
| La | 1.35 | 4.04 | 3.03 | 1.47 | 1.46 | 11.1 | 4.89 | 3.01 |
| Ce | — | — | — | — | 4.16 | 45.9 | 20.9 | 13.5 |
| Sm | 0.68 | 1.78 | 1.12 | 0.58 | 1.92 | 11.3 | 6.35 | 2.71 |
| Eu | 0.16 | 0.51 | 0.30 | 0.19 | 0.58 | 2.28 | 1.61 | 0.55 |
| Tb | 0.16 | 0.25 | 0.205 | 0.064 | 0.40 | 1.76 | 1.08 | 0.43 |
| Yb | — | — | — | — | 1.07 | 4.57 | 3.46 | 1.26 |
| Lu | 0.12 | 0.17 | 0.145 | 0.035 | 0.23 | 0.53 | 0.39 | 0.12 |
| Sc | 0.09 | 1.62 | 0.69 | 0.56 | 0.03 | 36.4 | 14.6 | 13.0 |
| Cr | 3.99 | 31.6 | 15.9 | 11.9 | — | — | — | — |
| Co | 3.81 | 55.7 | 21.2 | 16.7 | 0.64 | 1.62 | 1.03 | 0.33 |
| As | 5.38 | 105 | 31.2 | 34.9 | 0.55 | 4.33 | 1.56 | 1.85 |
| | | 3 to 7 samples | | | | 8 samples | | |

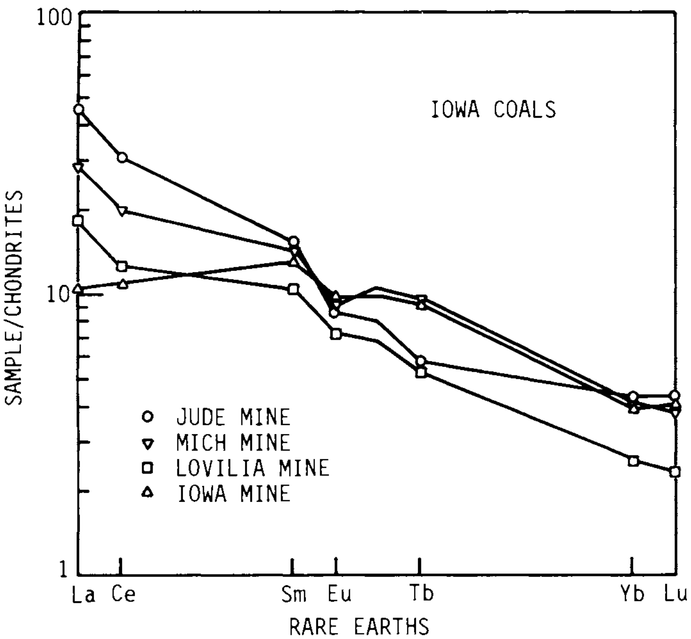


Fig. 2. Chondrite normalized REE plot of average values for coal samples from the Iowa mines.

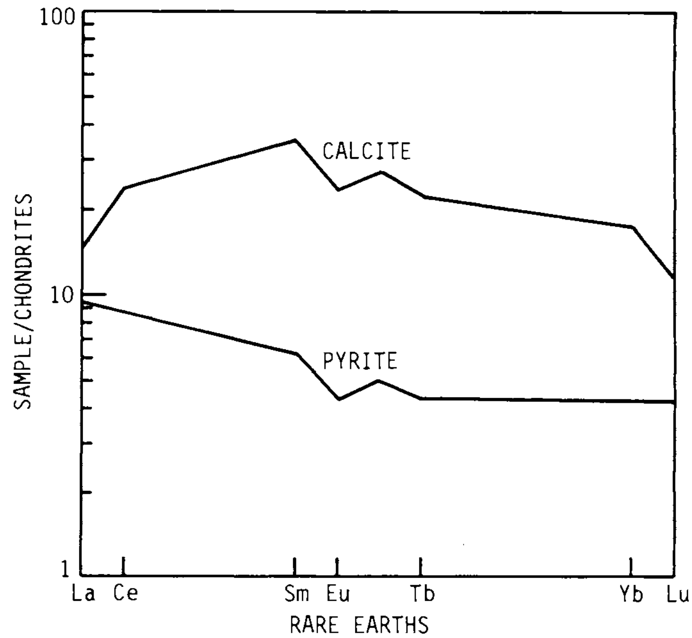


Fig. 3. Chondrite normalized REE plot of average calcite and pyrite mineral separates from the Iowa coals.

United States coals (Zubovic, 1976; Gluskoter et al, 1977; Kuhn et al, 1980; Wedge and Hatch, 1980).

Since the trace elements determined in this study are concentrated in the inorganic coal fraction, they should be expected to increase as coal rank increases. A positive correlation between coal rank and elemental abundances could largely explain the increasing elemental concentrations in United States coals from west to east as coal rank increases. Arsenic was observed to concentrate slightly in pyrite and Sc concentrates somewhat in calcite (Tables 1 and 2). For a further discussion of elemental associations, see Dawson (1982).

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