Reports

Organically Bound Metals in a Solvent-Refined Coal: Metallograms for a Wyoming Subbituminous Coal

Abstract. *Fractions of a solvent-refined coal that contain organically bound species of magnesium, calcium, titanium, iron, copper, or zinc have been isolated. The fractions represent a wide range of chemical types and molecular size. Their isolation is a step toward speciation.*

Minor metallic constituents in a coal are important for processes that convert the coal to liquid fuel products. Deposits containing metals have been implicated in the loss of catalytic activity for both primary liquefaction and product hydrotreating. Metal organics in a product can lead to the emission of fumes during combustion.

The possibility that organically bound metals are present in coals has been recognized (*1*). We have recently demonstrated that metal-organic combinations exist in a solvent-refined coal (SRC) (*2*).

We report here the chromatographic isolation of metal-organic fractions of an SRC derived from a Wyoming subbituminous coal (*3*). We achieved isolation by the direct interfacing of a liquid chromatograph (LC) with an inductively coupled plasma atomic emission spectrometer (ICP) (*4*). Compelling evidence for the presence of organically bound metals is provided by (i) a combination of a first chromatographic separation of the SRC (according to the polarity of the organic moieties) with a second separation (according to effective molecular size) and (ii) "on-line" multielement detection with the ICP during the second chromatographic separation. We have monitored 15 elements simultaneously (Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Ti, V, and Zn). Six of them (Ca, Cu, Fe, Mg, Ti, and Zn) are present in detectable quantities, and each appears to occur in more than a single chemical environment.

Few investigators have attempted quantification and speciation of trace metals in coal-derived materials. Indirect evidence for metals in organic combination has been derived from float-sink separation of either raw coal (*5*) or vitrain concentrates (*6*) into gravity fractions followed by metal analysis of the "cleanest" coal fractions. Metals so detected were inferred to possess high organic affinity. Another attack on this problem has consisted of the analysis of various coal-derived materials (SRC, H-Coal, Synthoil) for selected elements (*7*). There were experimental problems with these approaches: (i) single element analysis (*8*); (ii) relatively high detection limits for the analytical method of choice; (iii) wet ashing of the organic matrix with the inherent danger of contamination (*9*); and (iv) the possibility of contamination by process-derived nonfilterable mineral matter. The approaches gave no information about speciation. Notwithstanding, the work has suggested the organic binding of certain elements.

We have developed an ICP system for analyzing metals in an organic matrix. With our system it is possible to measure simultaneously up to 34 elements at detection limits between 10 parts per million (ppm) and 0.5 part per billion. We have used a variety of organic matrices, including heptane, chloroform, and pyridine, for placing the coaly matter in solution (*2*). The ICP (*10*) is attractive because of its inherently high temperature source, its lack of a combustion flame, the absence of a contaminating electrode as in graphite-furnace atomic absorption spectroscopy, and its applicability to flowing (that is, on-line) analysis.

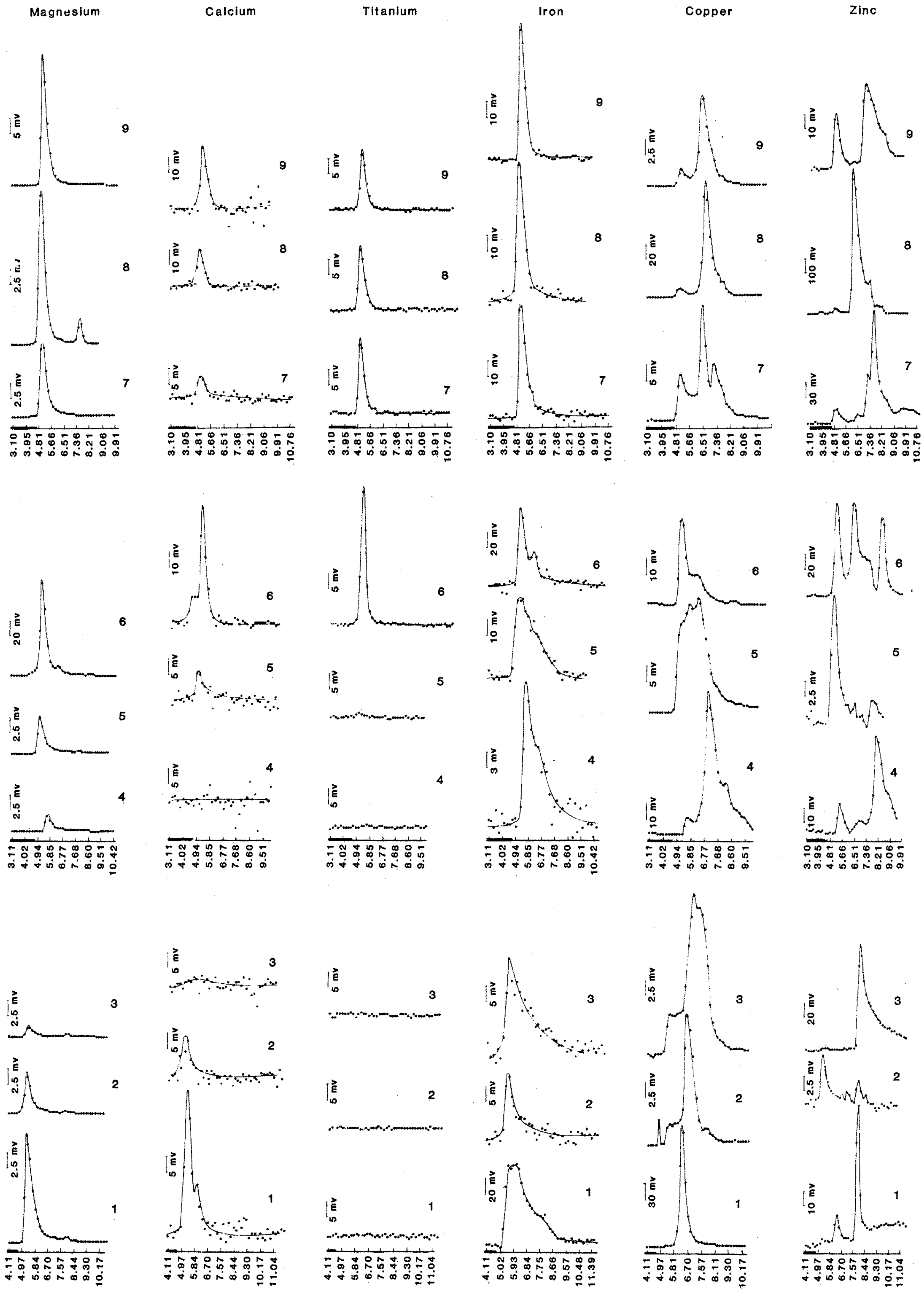
The ICP alone cannot be used to suggest speciation, but, when the ICP is coupled with a chromatograph, some knowledge of the nature of the metal species can be obtained. We have used Farcasiu's procedure (*11*) for the preparative separation of SRC by polarity on silica gel, using selective elution solvent chromatography (SESC) to yield nine fractions, designated saturates (fraction 1), aromatics (fraction 2), polar aromatics (fraction 3), simple phenols (fraction 4), nitrogen heterocyclics (fraction 5), highly functional molecules (fraction 6), polyphenols (fraction 7), and molecules that possess increasing oxygen and nitrogen content (fractions 8 and 9). We found significant quantities of a variety of metals in each SESC fraction (*2*). After removing the eluting solvent, we separated each SESC fraction further according to effective molecular size [with a size exclusion chromatographic column (*12*)] by elution with pyridine (*13*). With the ICP on-line during the size exclusion chromatography, we obtained "metallograms"—one for each metal and each SESC fraction monitored (Fig. 1). Blank runs with our solvents exclude attribution of any peak in our metallograms to an occurrence of a metal in a solvent.

We placed a more conventional, differential refractive index detector in series with the ICP to obtain additional information on the size distribution of organic constituents in each SESC fraction. Fraction 1 is weighted toward smaller molecular size than the other fractions. There is a trend toward larger species with increasing SESC fraction number. A large part of fractions 7 through 9 elutes at the totally excluded volume. Some highly colored material, however, continuously elutes from the size exclusion chromatographic column throughout the selectively permeated region in all cases.

The metallograms for each SESC fraction in Fig. 1 disclose a variety of metal-organic species. The presence of Mg and Ca in fraction 1 is a surprise. It seems unlikely that "alkyl-like" species of these metals would be present in SRC, since no model systems of this type are known. Perhaps a molecule of high aliphatic content with one bound Mg or Ca elutes as an organic saturate. The elution behavior of Ca salts of aliphatic carboxylic acids or phenols, for example, is unknown on both silica gel (used in SESC) and polystyrene–divinyl benzene copolymer (our packing in size exclusion chromatography).

The Mg metallogram for fraction 8 exhibits a sharp peak near the totally permeated region, indicating molecules of small "size." Titanium is not detectable (less than 4 ppb) in fractions 1 through 5. Only more polar fractions (fractions 6 through 9) show measurable

Fig. 1 (facing page). Metallograms for magnesium, calcium, titanium, iron, copper, and zinc: on-line ICP detection for these metals during size exclusion chromatographic separation of nine SESC fractions of Amax SRC on a 30-cm, 100-Å μ-Styragel column with pyridine elution. The exclusion volume was 4.75 ml.



Magnesium
Calcium
Titanium
Iron
Copper
Zinc
9
8
7
6
5
4
3
2
1
5 mv
2.5 mv
10 mv
20 mv
20 mv
30 mv
100 mv
3 mv
3.10 3.95 4.81 5.66 6.51 7.36 8.21 9.06 9.91 10.76
3.11 4.02 4.94 5.85 6.77 7.68 8.60 9.51 10.42
4.11 4.97 5.84 6.70 7.57 8.44 9.30 10.17 11.04
4.11 5.02 5.93 6.84 7.75 8.66 9.57 10.48 11.39
4.11 4.97 5.81 6.70 7.57 8.11 9.30 10.17
Retention volume (ml)

Ti, in each case at the totally excluded volume. Fraction 6 shows the highest Ti concentration (~ 0.2 ppm).

The elution of Fe species commences at the totally excluded volume for each SESC fraction. This is not the case with Cu and Zn, for which molecules of "size" smaller than an n-C_{35} alkane are predicted to elute.

Major Cu and Zn peaks eluting from fraction 1 correspond to ~ 1.3 ppm (Cu) and 0.4 ppm (Zn). The Cu metallogram from fraction 7 has relatively sharp peaks from which concentration can be estimated: progressing to smaller "sized" species (increasing elution volume), the concentrations are ~ 0.8, 2.3, and 1.1 ppm, respectively. Since fraction 7 is reputed to be polyphenols, these Cu signals may be due to the elution of Cu phenolates.

The Zn metallogram from fraction 7 exhibits the largest number of discrete peaks, four. The largest "sized" Zn compound elutes at the totally excluded volume and is ~ 6 ppm. Elution of the species at 10.5 ml indicates a molecule at the "size" of n-decane.

Fraction 8 has a Zn concentration of ~ 45 ppm, all of which elutes in a narrow band at the "size" of n-C_{24} alkane.

Fraction 9 displays a bimodal separation of totally excluded and selectively permeated (~ 0.25 ppm) Zn-containing matter.

As far as we know, we are the first to report distributions of organically bound metals in coal-derived products. The isolation of metal-organic fractions is a first step toward their speciation, which could yield information significant for both producing and utilizing coal liquids. Evidence for the survival of organometallic combinations of biological origin may be useful to geochemists concerned with the chemistry of coalification.

The source of organically bound metals in coal-derived materials is still uncertain. They may be present in the raw coal. They may be produced as a result of chemical reaction during the coal conversion process. They may originate with the processing equipment; we have observed large Cr concentrations in the process solvent used for the production of the SRC studied.

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References and Notes

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3. The SRC was produced in a pilot plant at Wilsonville, Ala., operated by the U.S. Department of Energy and the Electric Power Research Institute. The coal was from the Amax mine in the Wyodak seam, near Gillette, Wyo. Conversion of organic matter in the coal to SRC was 85 to 90 percent. For a flow sheet of the SRC process, see D. D. Whitehurst, T. A. Mitchell, and M. Farcasiu [*Coal Liquefaction* (Academic Press, New York, 1980), p. 348].
4. We have also measured quantitatively a variety of trace elements in both pyridine and toluene extracts of the chloroform solubles in the Amax SRC, in distillables from this SRC, in an SRC process solvent, and in tars from coal gasification.
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12. We used a μ-Styragel column (Waters Associates, Milford, Mass.). Molecules of large effective molecular size are not retained by a size exclusion column and therefore elute first at the totally excluded volume.
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14. Supported by the Commonwealth of Virginia and the Department of Energy under grant EF-77-01-2696. We thank E. Denyszyn for technical assistance in preparing the metallograms for publication.

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Polycrystalline Echinoderm Calcite and Its Fracture Mechanics

Abstract. *Polycrystalline calcite was revealed by scanning electron microscopy of fractured skeletal ossicles of the sea star* Echinaster spinulosus *(Echinodermata, Asteroidea). Whisker-like calcite crystals were observed in specimens that were loaded in stress relaxation before being fractured; rapidly broken surfaces were smooth and glassy. The crystallites were 1300 angstroms wide and at least 3600 angstroms long and were packed together in lamellae. The lamellae were wound into spirals that formed the trabecular bars. All the crystallites in an ossicle appear to be aligned in the same direction. Geometric considerations indicate that the requirement for packing the crystallites smoothly may explain the high magnesium ion concentration of echinoderm calcite.*

Virtually all echinoderms have an endoskeleton composed of calcite ossicles or spicules. As a skeletal material, echinoderm calcite has several unusual features: (i) macroscopically, the calcite forms a fenestrated structure of trabeculae pierced by roundish holes (stereom); (ii) the calcite is "impure," containing 4 to 16 percent Mg^{2+} substituted for Ca^{2+} (*1*); (iii) evidence for an organic matrix within the calcite is equivocal (*2*); and (iv) each skeletal element, excepting echinoid teeth, behaves optically as a single crystal (*3, 4*). It is not clear whether each skeletal element (spine, plate, or ossicle) is monocrystalline or an aggregation of crystallites with perfectly aligned optical axes. X-ray crystallographic analyses indicate that each skeletal element could be referred to a single crystal lattice (*4*). Although the data did not rule out a polycrystalline substructure (*5, 6*), the perfect alignment of crystallites required to explain the x-ray data had seemed unlikely. Furthermore, since extensive scanning electron microscopy of fractured skeletal surfaces had failed to reveal a polycrystalline substructure (*3–5*), most workers preferred the monocrystalline hypothesis (*3–5, 7, 8*).

I now present evidence that the skeletal elements of echinoderm calcite are polycrystalline. Carinal and dorsolateral ossicles of the sea star *Echinaster spinulosus* (Asteroidea: Spinulosida) were

Fig. 1. Scanning electron micrograph of a fractured trabecular bar within a skeletal ossicle of the sea star *E. spinulosus*. Whisker-like calcite crystallites aligned in spiral lamellae demonstrate the polycrystalline substructure of the calcite ossicle. Scale bar, 10 μm; magnification, ×5000.