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PROTON MICROPROBE ANALYSIS OF TRACE-ELEMENT VARIATIONS IN VITRINITES IN THE SAME AND DIFFERENT COAL BEDS

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Abstract

The PIXE (proton-induced X-ray emission) microprobe can be used for nondestructive, in-situ analyses of areas as small as those analyzed by the electron microprobe, and has a sensitivity of detection as much as two orders of magnitude better than the electron microprobe. Preliminary studies demonstrated that PIXE provides a capability for quantitative determination of elemental concentrations in individual coal maceral grains with a detection limit of 1-10 ppm for most elements analyzed. Encouraged by the earlier results, we carried out the analyses reported below to examine trace element variations laterally (over a km range) as well as vertically (cm to m) in the I and J coal beds in the Upper Cretaceous Ferron Sandstone Member of the Mancos Shale in central Utah, and to compare the data with the data from two samples of eastern coals of Pennsylvanian age. The data obtained illustrate the sensitivity of detection obtainable with the PIXE microprobe in analysis of coal macerals. Such data are of value in tracing the geochemical conditions during deposition and diagenesis of a coal bed, and in assessing potential applications and problems of combustion, gasification, or liquefaction of particular coals.

Key Words: Proton microprobe, proton-induced X-ray emission, microprobe analysis, bituminous coal, vitrinite, trace element concentrations, trace element modes of occurrence, detectability limits, quantitative analysis, X-ray maps.

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Introduction

The use of microprobe methods for the direct determination of minor-and trace-element contents in coal macerals and minerals has great potential value in coal quality and coal geochemical research. Knowledge of the modes of occurrence, distribution and concentrations of various elements in a given coal bed is vital for intelligent planning of coal utilization and pollution control. Moreover, knowledge of the vertical and lateral variations of elemental characteristics can be applied in reconstruction of the paleogeochemical environment of deposition of the coal bed.

For the past 15 years or more the scanning electron microscope equipped with an energy-dispersive X-ray analyzer (SEM-EDX) has found widespread use in coal research. Dutcher et al. (1973) suggested use of the SEM-EDX to study the partitioning of elements between the organic and inorganic phases in coal. Huggins and co-workers (1980) developed automatic image analysis procedures for the SEM-EDX to determine mineral compositional and size distributions in coal samples. Finkelman (1982) utilized the SEM-EDX to conduct a comprehensive study of the modes of occurrence of trace elements in minerals in coal. In routine use, the SEM-EDX is capable of semiquantitative analysis of all elements of atomic number 11 (sodium) and greater, it does not destroy the area analyzed, and it has a minimum detection limit of about 0.5 weight percent for most elements.

Another instrument which has proven valuable in coal research is the electron probe microanalyzer (EPMA). A number of investigators, e.g. Harris et al. (1977) and Raymond (1982), have utilized the EPMA for direct determination of organic sulfur in macerals. EPMA determination of the distribution of various elements in different macerals at different depths in a given coal bed was reported by Minkin et al. (1979). Minkin et al.(1984) also reported on use of the EPMA in a study of arsenic and selenium occurrences in pyrite in coal. Similar to the SEM-EDX, analysis with the EPMA is non-destructive, and it can be used for routine analysis of elements of atomic number 11 and greater. However, EPMA analysis is quantitative and the minimum level of detectability is 0.01-0.05 weight percent in routine measurements.

More recently, laser microprobe mass analysis (LAMMA) has been used by Lyons et al. (1987) to demonstrate that the mass spectra for different macerals in coal are distinctive. LAMMA can be used for the detection of all elements from hydrogen through uranium, and it has sensitivity at the ppm level, but quantitative analysis requires assured equivalence between standard and sample (Echlin, 1981). In addition, LAMMA is a destructive technique, in that the laser beam excavates a crater about 10 to 15 micrometers in diameter and a few micrometers deep.

Yet another microprobe technique was used by McIntyre et al.(1985) and Martin et al. (1986) to obtain qualitative characterization of the distribution of trace and minor elements in coal macerals. The method used in this case was secondary ion mass spectrometry (SIMS). Like LAMMA, SIMS can detect all elements in the range hydrogen through uranium. Moreover, it can detect elements present in concentrations as low as 20 ppb. However, it is also a destructive technique, in which the bombardment of the surface of the target material by energetic ions causes atoms to be ejected by sputtering. Quantitative analysis by SIMS is made difficult because the rate of sputtering varies with the mass density of the area bombarded.

Consideration of the combined attributes of all of the above techniques (Table 1) points to the remaining need for another complementary microprobe technique that is capable of in situ, non-destructive, multielement quantitative analysis and capable of detection at the ppm level. The feasibility of using the PIXE (proton) microprobe to fill this need was explored by Chen et al.(1981a) and Minkin et al. (1982). These preliminary studies established the suitability of PIXE microprobe analysis for the study of distributions of trace elements of atomic number 11 and greater in coal macerals, and encouraged us to pursue the more detailed experiments described below.

TABLE 1. COMPARISON OF MICROPROBE ANALYTICAL CAPABILITIES

(Routine operating conditions)

Technique	Minimum Detection Limit	Elements Analyzed	Nondestructive	Quantitative
SEM-EDX	0.5 wt. %	Na and greater	Yes	Semi
EPMA	0.01-0.05 wt. %	Na and greater	Yes	Yes
PIXE	1-10 ppm	Na and greater	Yes	Yes
LAMMA	1 ppm	H - U	No	No
SIMS	20 ppb	H - U	No	Semi

Materials and Methods

Sample strategy

The suite of samples selected for analysis consisted entirely of small blocks of vitrain. (The lithotype vitrain is a macroscopically visible coal unit, usually in bright bands at least 3-10 mm thick, that consists dominantly of the microlithotype vitrite (Fig.1). The microlithotype name vitrite is applied to a coal unit that consists essentially only of the maceral group vitrinite and extends in a band at least 50 micrometers wide. See Stach et al., 1975.) The decision to limit the analyses to vitrinite areas was based on the consideration that because vitrinites are the dominant components (generally 80 volume percent or more) of high quality bituminous coals, vitrinites may be regarded as the probable major source of trace elements attributable to macerals in bituminous coals of economic importance.

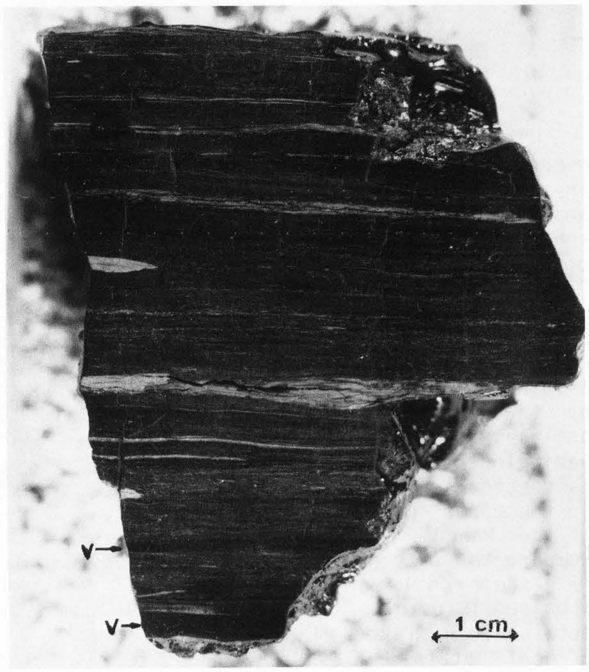

Fig. 1. Hand sample of Pennsylvanian age Kentucky No. 6 coal, Webster County, Kentucky. Darkest bands (V) are composed of vitrain.

An earlier PIXE experiment (Minkin et al., 1982) included analyses of vitrinites selected from along the length of a single drill core sample (M1) of the J and I coal beds of the Upper Cretaceous Ferron Sandstone Member of the Mancos Shale, Emery County, Utah (Fig. 2). For the present study we therefore selected two companion drill cores, M3 and M5 (Fig. 2), for similar analysis, to explore the usefulness of PIXE microprobe data in delineating trace element variations laterally as well as vertically within a coal bed. Locality 3 is approximately 3,700 ft (1,125 m) northeast of site 1, and site 5 is 4,350 ft (1,300 m) northeast of site 3 (Fig. 2).

In addition to the Utah samples, columnar sections of two eastern coal beds of Pennsylvanian age were chosen for analysis. One columnar section was from the Upper Freeport coal bed from the top of the Allegheny Formation in Indiana County, western Pennsylvania, and the second was from the Kentucky No. 6 coal bed from the base of the Carbondale Formation, Webster County,

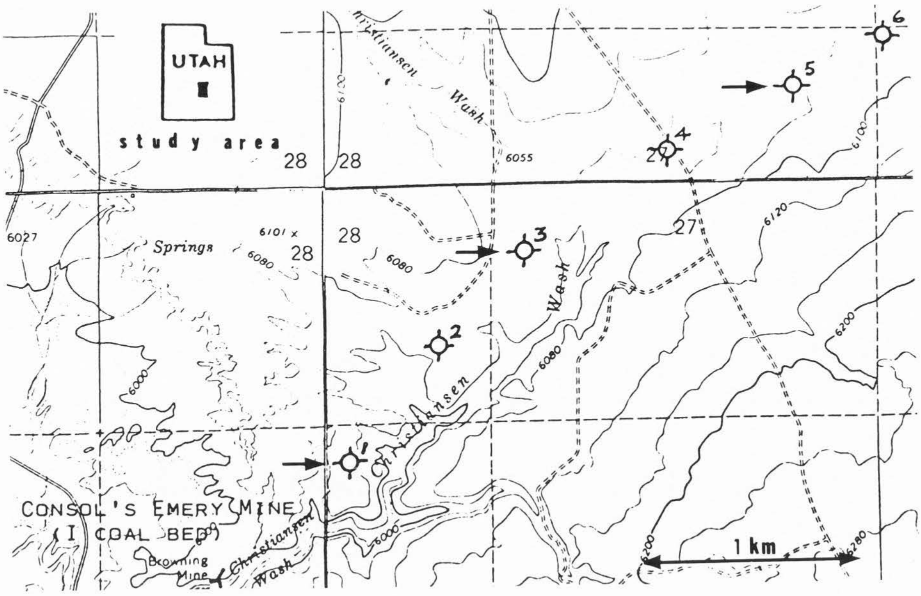

Fig. 2. Map (modified from Ryer, 1981a) showing locations 1, 3, and 5 (note arrows) from which the drill core samples M1, M3, and M5 were obtained for the study of the Upper Cretaceous I coal bed, Emery County, Utah.

western Kentucky. For this latter suite of samples the objectives of the PIXE analyses were to develop profiles of trace element variations with depth in vitrinites in each sample, and to compare the data from these eastern, Pennsylvanian age coal samples with those of the Utah, late Cretaceous, coal.

Sample preparation

The procedure used for sample preparation was the same as described and illustrated in Minkin et al. (1982). Small blocks, about 1 cm across and 2 mm or more thick, were mounted in epoxy and polished, using diamond abrasives, after removal from selected vitrain bands (> 2 mm thick) along the length of each drill core or columnar sample. In all, for the Utah coal, 17 blocks had been prepared from vitrain samples from drill core M1 for our earlier study (total thickness of the coal 8.2 m), and, in the present work, 12 were prepared for core M3 (coal thickness 7.7 m), and 16 for core M5 (coal thickness 7.4 m). A total of 4 blocks were prepared from the Kentucky No. 6 columnar sample (coal thickness 1.1 m) and 7 blocks were prepared from the Upper Freeport coal (1.2 m thick). Areas for microprobe analysis were chosen on the basis of homogeneity when viewed in the optical microscope at a magnification of 500X. The chosen areas were outlined by circles, 500 micrometers in diameter, inscribed with a diamond object marker accessory for the petrographic microscope. Marking the areas designated for analysis in this manner greatly facilitated finding them after the samples were mounted in the target chamber of the PIXE microprobe.

Instrumental parameters

As in our earlier work, the instrument used in the present study was the PIXE microprobe of the Max-Planck-Institute for Nuclear Physics (MPI), Heidelberg, F.R. Germany (Bosch et al., 1978; Chen et al., 1981b; Cabri et al., 1984). The basic components of a proton microprobe are illustrated in Fig. 3. The energy of the incident proton beam was 3 MeV, and the size of the incident beam was approximately 3 micrometers by 5 micrometers. In the Heidelberg instrument X-rays from the target are detected with a Si(Li) detector fitted with a 150-micrometer beryllium proton shield. In addition, for the collection of accurate data for elements of atomic number 20 (calcium) and above, a 50-micrometer aluminum absorber was placed in front of the detector to

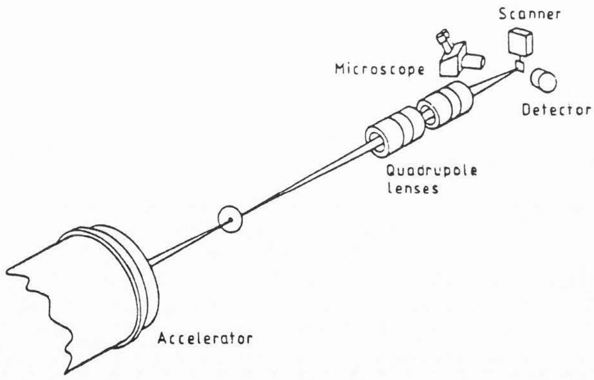

Fig. 3. Basic components of a proton microprobe (from Carlsson, 1983).

suppress the dominant low energy part of the spectrum that is characteristic of coal maceral grains. A separate run without the use of the Al absorber was necessary if data for the lighter elements (atomic numbers 11 to 19) were required. Each measurement was run until a charge of 0.5 micro Coulomb was accumulated, as monitored by Rutherford scattering at an auxiliary target. A single analysis generally required 40 to 50 minutes.

Data reduction

A curve-fitting computer routine was applied to each X-ray spectrum to determine net peaks above background and to identify each element detected (Bosch et al., 1978). Quantitative calculations were based on four vitrain standards from bituminous coals (Minkin et al., 1987), for which elemental concentrations had been determined by instrumental neutron activation, quantitative spectrographic analysis by powder D.C. arc, and energy-dispersive X-ray fluorescence (Johnson et al., 1980). Use of standards for which the matrix is the same or similar to the unknowns greatly simplifies determination of concentrations of elements in the unknowns (Blank and Traxel, 1984).

Analytical results

Concentrations were determined for 20 elements: Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Sr, Y, Co, Sc, Rb, and Zr, for the Utah drill core samples M3 and M5 and the two columnar samples from western Pennsylvania and western Kentucky. For each area designated for analysis, measurements were made at at least two points within a given 500-micrometer circle. Concentration values for most elements have an uncertainty of about 20 percent of the amount present. The uncertainty attributed to instrumental factors alone is less than 10 percent (Minkin et al., 1982). For elements that are extremely heterogeneously distributed in a given maceral or microlithotype area, the uncertainty figure may rise to 50% or more (Minkin et al., 1982). The detailed analyses are compiled in Minkin et al., 1987. Only notable trends and correlations are highlighted in the present paper.

Utah coal

The drill core samples of the I and J coal beds were selected from a series of 10 cores that constitute a landward-to-seaward sampling across the seaward edge of the paleoswamp in which the precursor materials of the I and J coal beds accumulated (Ryer, 1981a). Drill core M1 was the most landward of the 10 samples. As had already been observed for core M1 (Minkin et al., 1982), it was found that in cores M3 and M5 the concentration of Fe tends to increase with depth in the I coal bed (Fig. 4 and Table 2) while that of S (determined by EPMA: Minkin et al., 1987) generally decreases with depth (Fig. 5 and Table 2). Because the J coal at the three sites is very much thinner than the I coal (1 to 1.4 m versus 6 to 6.5 m) and the J coal has very few vitrain bands sufficiently thick (greater than 2 mm) for sampling, there are not enough data to determine the pattern of Fe variation with depth in the J coal. Sulfur levels, as determined by EPMA, are consistently greater than 2 weight percent for all subsamples of the J coal. For the I coal bed the average concentrations of V, Cr, Fe, Ge, Sr, Y, and Zr tend to be highest in the vitrinites of core sample M3. No consistent trends are apparent in concentrations of any elements corresponding to change from landward to seaward locations.

TABLE 2. INDICATED TRENDS AND CORRELATIONS

- Fe-S
  - a. Fe tends to increase with depth while S decreases with depth in the vitrinites of all three cores of the Upper I coal (Upper **Cretaceous** age).
  - b. Fe and S both increase with depth in the Kentucky no. 6 sample (Pennsylvanian age).
  - c. No trend is apparent in Fe or S variations in the Upper Freeport sample (Pennsylvanian age).
- Zn concentrations are highest in the Kentucky no. 6 vitrinite, somewhat lower in the Upper Freeport sample, both of Pennsylvanian age,and lowest in the Late Cretaceous I coal sample.
- Average Ti levels are highest for the Pennsylvanian age Upper Freeport coal sample,and comparably lower in the Late Cretaceous I coal and Pennsylvanian age Kentucky No. 6 coal samples.
- Sr, Cu, Zr, and Mn are generally present at higher levels in the vitrinite of the Late Cretaceous I coal sample than in the two Pennsylvanian age eastern coal samples; the reverse is true for Br.
- V, Ni, and Zr vary in a similar manner in the Upper Freeport and Kentucky no. 6 coal samples of Pennsylvanian age, but no corresponding trend is observed in the vitrinites of the Upper Cretaceous I coal.
- For the Upper Cretaceous I coal bed, the data suggest that average concentrations of V, Cr, Fe, Ge, Sr, Y, and Zr tend to be highest in the vitrinites of core sample M3. No clear trends of variation are apparent, however, from the center toward the seaward edge of the paleoswamp for the three sample locations studied.

Comparison of Eastern and Utah coal samples

Iron and sulfur both increase with depth in vitrinites in the western Kentucky No. 6 sample of Pennsylvanian age, but there is no apparent trend with depth in iron and sulfur variations in the Upper Freeport vitrinites of Pennsylvanian age sampled in western Pennsylvania. Zinc concentrations are consistently highest in the Kentucky No. 6 vitrinite, somewhat lower in the Upper Freeport sample, and lowest in the Upper Cretaceous, central Utah coal. Average titanium levels are highest for the Upper Freeport coal sample, and comparably lower in the Kentucky and Utah samples. Strontium, copper, zirconium and manganese are generally present at higher levels in the vitrinite of the Utah coal samples than in the two eastern samples; the reverse is true for bromine. Vanadium, nickel, chromium and zirconium vary in the same general manner in the vitrinites of the Upper Freeport and Kentucky No. 6 coal samples (Fig. 6), but no similar trend

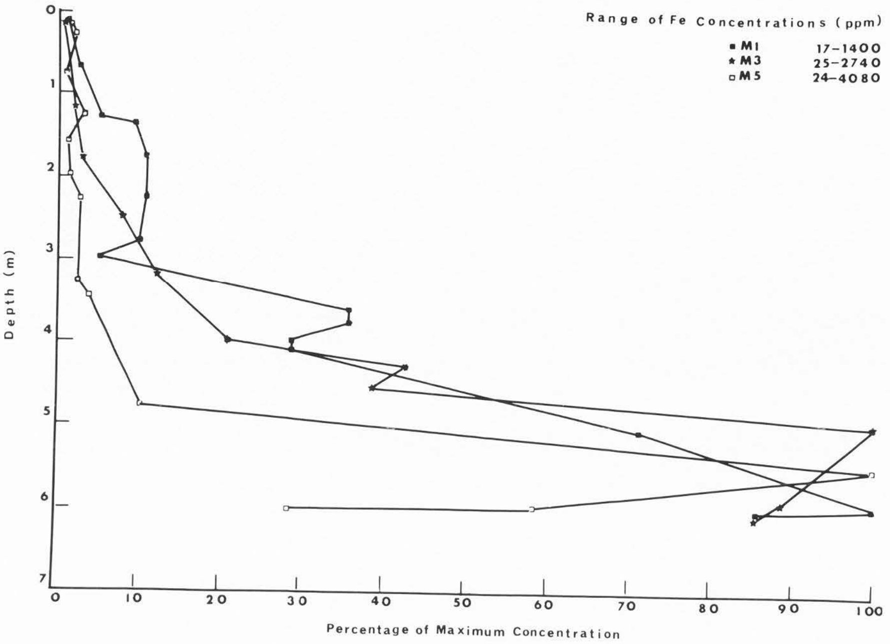

Fig. 4. PIXE data showing the trend of general increase with depth of iron concentrations in vitrinites for the three drill core samples of the Upper Cretaceous I coal, Emery County, Utah. "Depth" values at the left of Figs. 4, 5, 6 and 7 represent the distances along the drill core or columnar sample from the top of the coal bed.

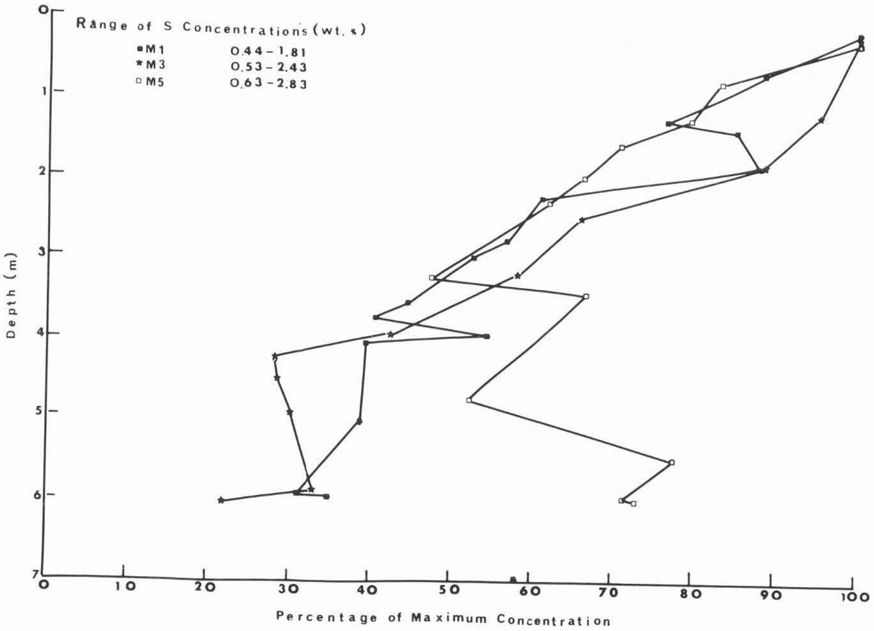

Fig. 5. Diagram depicting the general trend of decrease of sulfur concentration (electron microprobe data) with depth in vitrinites of the three drill core samples of the Upper Cretaceous I coal.

is apparent in the Utah coal (Fig. 7). The indicated trends and correlations are summarized in Table 2, and a comparison of selected elemental characteristics is presented in Table 3.

X-ray maps

In addition to information on the concentration of trace elements present in coal macerals, the PIXE microprobe can also furnish valuable indications of the modes of occurrence and distribution of these elements. This is accomplished by generating X-ray scans (Kneis et al., 1981). Instrumentation and software for the present configuration for generation of such scans with the MPI instrument were developed by K. Traxel and C. Ender of MPI. Scans were run in 2-micrometer steps over a target area 150 X 150 micrometers square. Five cycles were generally necessary to collect enough counts for useful X-ray maps. The time required for data collection for one target area was about three hours, and maps for a maximum of 15 elements could be produced by one such run. Because of the penetration

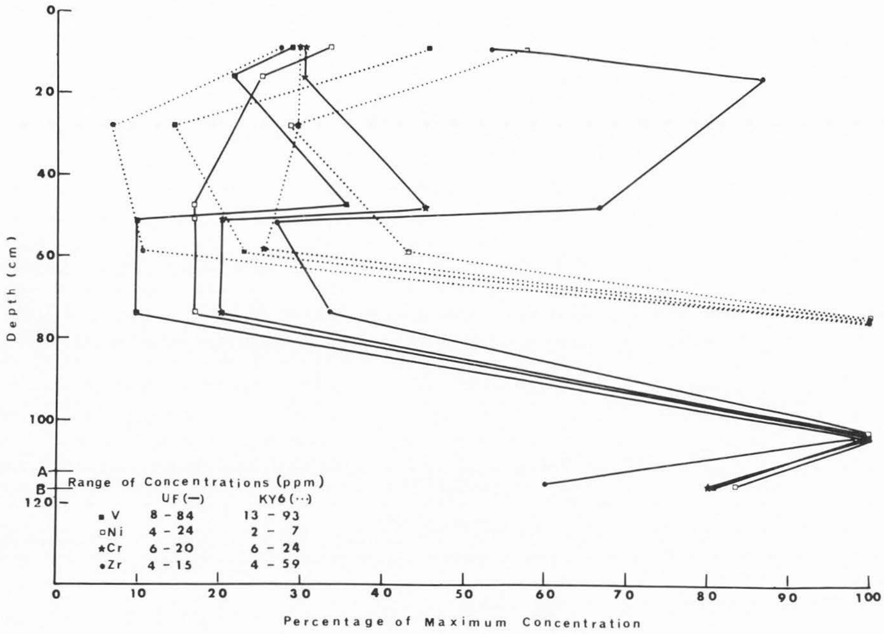

Fig. 6. Similarities in the variations with depth of vanadium, nickel, chromium and zirconium concentrations in vitrinites of the two Pennsylvanian age eastern coal samples analyzed. "A" marks the bottom of the Kentucky No. 6 coal bed; "B" marks the bottom of the Upper Freeport coal bed.

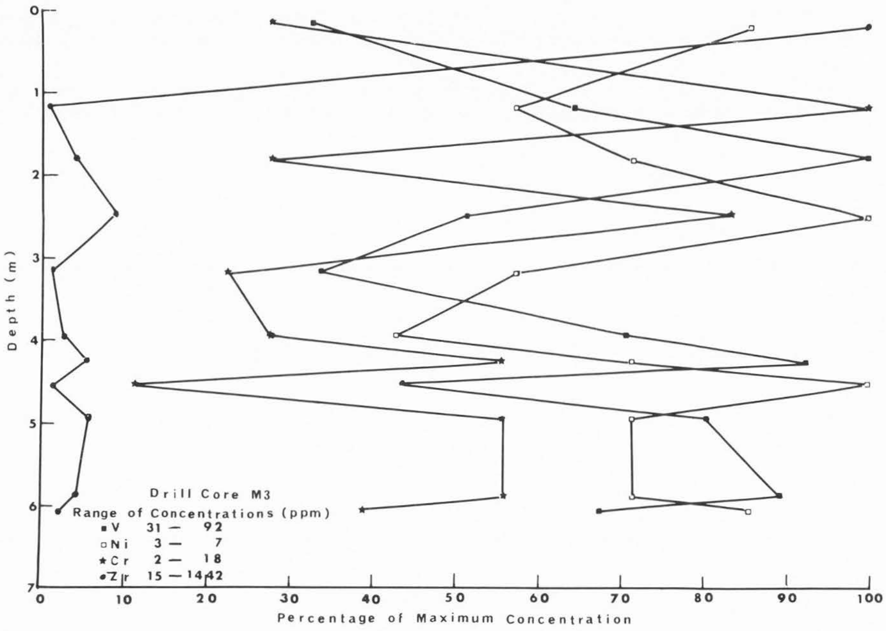

Fig. 7. Plot for sample M3 of concentration variations of the same four elements as in Fig. 6, emphasizing the absence of any similarities in variation of these elements in the Utah Upper Cretaceous coal samples.

of the proton beam into the target (Fig. 8 and Minkin et al.,1982), each X-ray map generated represents the distribution of a given element in a block of vitrite 150 X 150 square micrometers in area and approximately 50 micrometers thick.

Illustrations of the type of information gained from PIXE-generated X-ray maps are shown in Figs. 9a and b and 10a through e. These are projections of the distribution of various elements within the same target area in vitrite from the depth interval 75 - 76 cm from the top of the coal in the Kentucky No. 6 sample. Figures 9a and b are projections showing the distribution of sulfur and silicon respectively, in which intensity (net counts) is shown as the "third dimension." The distribution of sulfur is seen to be very uniform, implying that it is dominantly organically associated in the vitrinite. The few elevations seen are attributed to mineral inclusions within the 150 X 150 X 50 cubic micrometer target block, and clues as to what minerals these may be are gained by examining the projections for other elements

TABLE 3. COMPARISON OF SELECTED ELEMENTAL CHARACTERISTICS (PPM) OF VITRINITES IN THE THREE COALS STUDIED

	I coal (Utah) Core M1	I coal (Utah) Core M3	I coal (Utah) Core M5	Upper Freeport (Pennsylvania)	No. 6 Coal (Kentucky)
Br					
Range	<1-14	<1-3	<1-13	90-120	74-100
Average	6	1	3	108	89
Cu					
Range	3-11	<1-44	-- -53	<1-3	1-2
Average	6	10	10	1	2
Mn					
Range	2-26	3-12	3-9	1-3	2-5
Average	5	6	6	2	3
Sr					
Range	24-300	45-523	5-187	25-52	13-18
Average	119	161	103	36	17
Ti					
Range	1-2600	12-648	26-603	132-1335	25-350
Average	251	165	148	450	143
Zn					
Range	4-12	1-9	1-10	8-20	42-55
Average	7	3	6	12	50
Zr					
Range	n.d.	15-1442	<1-66	4-13	4-59
Average		180	25	9	21

n.d. not determined -- below level of detection

such as iron or calcium. In the right center portion of Fig. 9a a depression is noted, indicating a lack of sulfur in that region and therefore suggesting that a mineral that does not contain S is present there. Examination of Fig. 9b , the corresponding projection for silicon, shows a well-defined elevation in the same area where the depression is noted for sulfur. Whether this inclusion consists of quartz or another silicate mineral can be investigated by examination of the projections for other elements.

Another method of presentation of such projections is illustrated in figs. 10a - e, in which the net counts are represented by the density (blackening) of each picture element (pixel). Projections of this type included for illustration are for the elements sulfur (Fig. 10a), iron (Fig. 10b), silicon (Fig. 10c), aluminum (Fig. 10d), and potassium (Fig. 10e). Examination of these figures shows, for example, that the denser areas in Fig. 10a, the sulfur projection, at approximate coordinates x=45,y=20; x=4, y=25; and x=66,y=46 all have corresponding dense areas in Fig. 10b, the projection for iron, implying the presence of pyrite grains at these locations. Examination of Figs. 10b through e indicates the probable presence of clay, or possibly potassium feldspar, particles at coordinates x=50,y=35; and x=45,y=15. Thus, although the surface of this target area, when examined in reflected light at magnifications as high as 500 X, appeared completely homogeneous, the X-ray maps of this area can be correlated with the compositional data obtained to indicate whether the elements detected are organically associated (i. e., homogeneously distributed) or inorganically associated (i.e., heterogeneously distributed) or both. These maps also serve to indicate the abundance, size and composition of any mineral inclusions present within the 50-micrometer layer immediately under the polished surface.

Discussion and Conclusions

The fact that no clear trend in lateral variation of any element was shown by the data for the Upper Cretaceous I and J coal beds of the Emery coalfield, central Utah, may indicate that the three drill cores chosen for study, although approximately 1 km apart, are all relatively central in the paleoswamp. An increase in ash or mineral, and hence trace element, content would be expected toward the seaward edge of the swamp according to the depositional model (Ryer, 1981b).

The Kentucky No. 6 coal bed of Pennsylvanian age lies in the southern part of the Illinois basin. The finding that for the suite of samples in this study zinc concentrations are highest in the Kentucky No. 6 vitrinite is in accord with Gluskoter et al.(1977), who concluded on the basis of analysis of 172 bulk samples of U.S. coals that coals from the Illinois basin have the highest concentration of zinc. Unfortunately, no PIXE X-ray maps for Zn were generated for the Kentucky No. 6 sample in the present experiment, so that it was not possible to determine whether the zinc in the vitrinite occurs in a zinc-bearing mineral such as sphalerite, or is perhaps at least partially organically associated. On the basis of indirect methods, previous authors (see, for example Zubovic et al.,1960) have concluded a very low organic affinity for zinc.

Also in agreement with the findings of Gluskoter et al.(1977) that titanium levels are highest in coals from the Appalachian basin, our PIXE data show that titanium levels are highest in the one sample we analyzed from the Appalachian

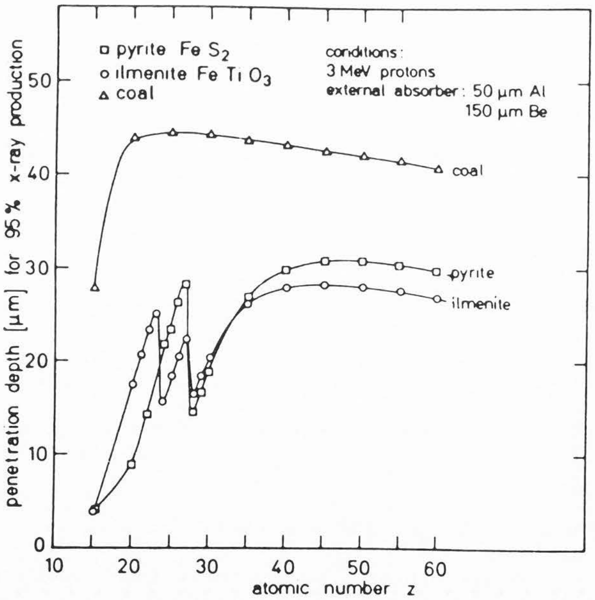

Fig. 8. Comparison of penetration depths, as a function of atomic number, for 3 MeV protons into various target materials (Blank and Traxel, 1984).

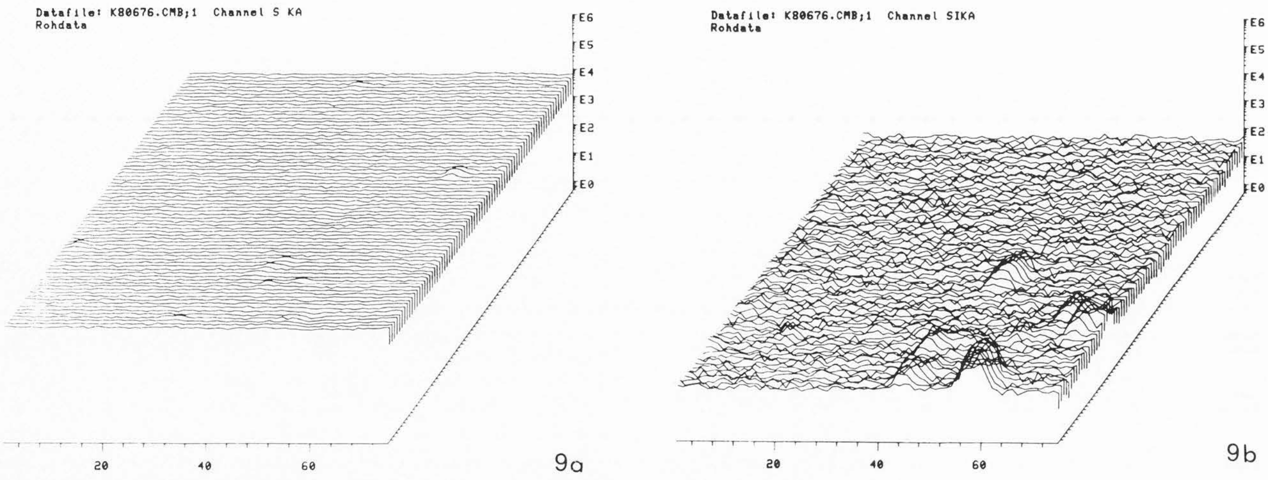

Fig. 9. PIXE-generated two-dimensional projections of the distribution of sulfur (a) and silicon (b) in an area of vitrite in Kentucky No. 6 coal of Pennsylvanian age. These projections represent the elemental distribution in a block 150 X 150 square micrometers in area and approximately 50 micrometers thick. Each unit distance along the X and Y axes represents a two-micrometer step. X-ray intensity (net counts) is plotted logarithmically as the "third dimension" in these diagrams.

basin, i.e. the Upper Freeport sample. The PIXE X-ray map generated for titanium in this sample appears mostly homogeneous, strongly suggesting a partial, perhaps dominant, organic association, in support of the conclusion reached for some other coals by investigators using other techniques (e.g. Zubovic et al., 1960; Kuhn et al., 1978). From the evidence in the literature (Finkelman, 1980) it seems clear that the modes of occurrence of Ti in coals are probably multiple. Use of PIXE X-ray scans on vitrain samples from a wide suite of coals could help to determine and document these variations more specifically and clearly.

The parallelism of variation of V, Ni, Cr and Zr in the two eastern coals and the lack of such covariation in the Utah coal may imply association of these elements with illite and mixed-layer clays, which are abundant in the two eastern coals of Pennsylvanian age, but very rare in the late Cretaceous I and J coals.

It is our conclusion that proton microprobe analysis, on the basis of its sensitivity of detection and capability for in-situ, nondestructive, quantitative analysis of specific maceral grains, promises to be an important tool in tracing the geochemical conditions of deposition and diagenesis of a coal bed, and has particular value in assessing potential applications and problems in utilization of particular coals in particular processes.

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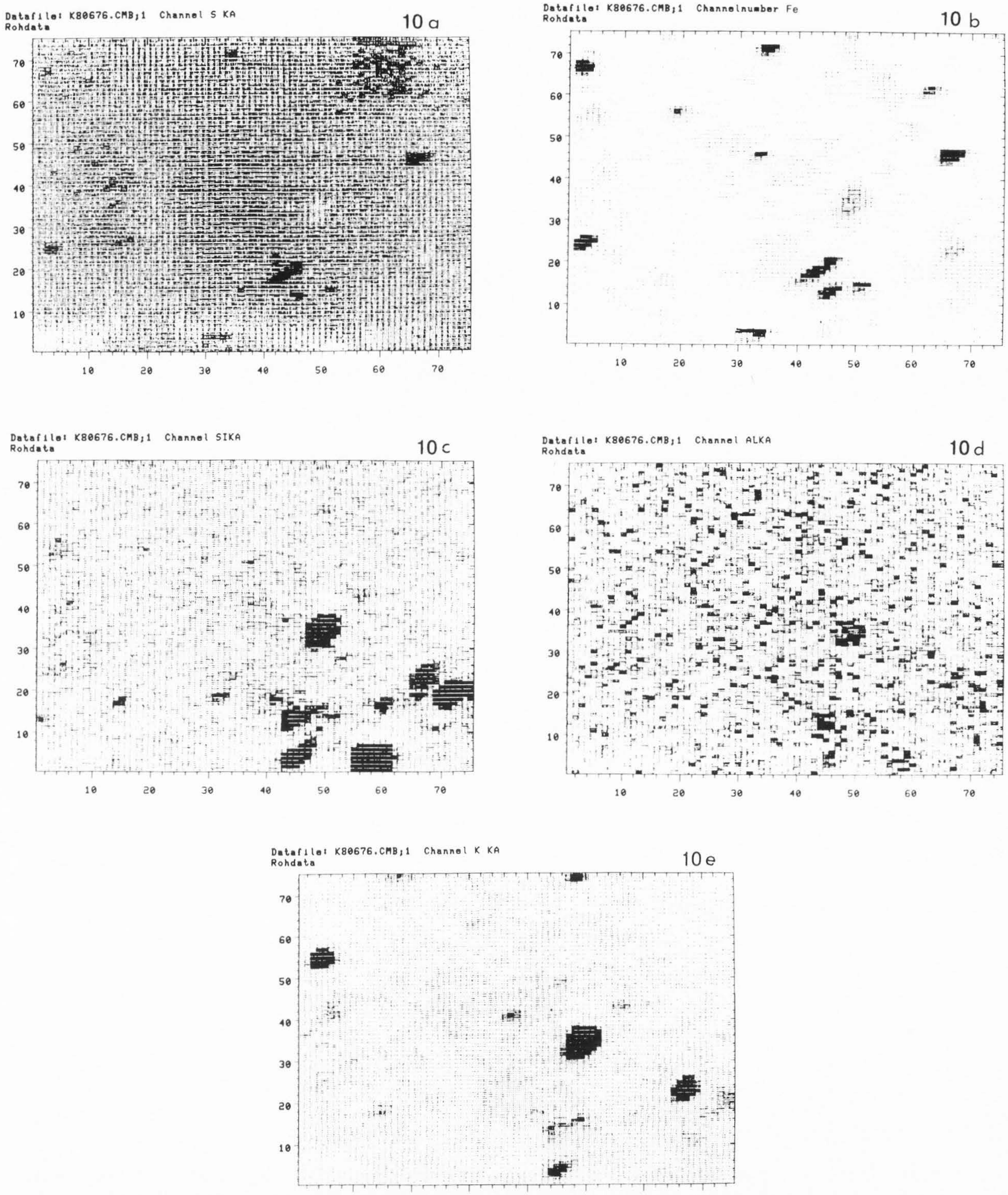

Fig. 10. PIXE X-ray maps for the same sample area as in Fig. 9, showing projections for (a) sulfur, (b) iron, (c) silicon, (d) aluminum, and (e) potassium. For each map the degree of blackening in each block of the grid is proportional to the net counts for that element for that step in the scan. Each unit distance along the X and Y axes represents two micrometers.

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Discussion with Reviewers

R. Raymond, Jr.: Concerning the vitrain standards, how reproducible are analyses for the full continuum of elements for which you collect data? Do some elements vary a great deal more than others?

Authors: This subject was treated in Minkin et al. (1982), in a test of hemogenity and reproducibility of PIXE data for one of our vitrain standards. The results showed that elements such as S and Cl, which we generally interpreted to be organically associated, show excellent uniformity and reproducibility. Other elements, such as Si, Ca, Fe were found to be much more heterogeneously distributed. Please see Minkin et al. (1982) for the detailed findings and discussion.

R. Raymond, Jr.: You state that vitrinite tends to dominate most bituminous coals of high quality and therefore trace elements associated with vitrinite will be the dominant source of the inorganic chemistry attributable to macerals in these coals. How does this account for the more massive mineralization occurring in the much larger pores and open cells of inertinites (fusinites)?

Authors: For development of such models the trace element data for specific examples from specific depths must be coordinated with the petrographic analysis of companion samples. This consideration points up the importance of working with columnar or drill core samples in order to preserve the stratigraphic record of the coal bed.

G. Remond: Although the total acquisition time (40-50 minutes) suggests that the intensity of the primary proton beam at 3 MeV is low, is there any risk of composition changes or of strong absorption effects due to surface contamination over such an extended acquisition time?

Authors: The current density at 3 MeV on the Heidelberg proton microprobe is about 1 p A/ µm^2 (Blank and Traxel, 1984). We have not observed any composition changes or surface effects as a result of the irradiation.

G. Remond: The y modulation profile in Fig. 9a shows low intensity variations, whereas higher contrast seems apparent in the digital X-ray map of Fig. 10a. Is there any contrast enhancement procedure applied to the raw data in Fig. 10a-e? Is there a difference in the imaging techniques or total acquisition times for Figs. 9 and 10?

Authors: Figs. 9 and 10 are based on the same X-ray data. The only difference between the two sets of figures is in the graphics methods used to present the data.

J.R. Chen: Some emphasis is placed on the result that the average Ti concentration in the Upper Freeport coal is larger than those of the three Utah core samples. The maximum value for core M1 is 2600 ppm, (range 1-2600 ppm), twice as large as the maximum for the Upper Freeport coal (1335 ppm, range 132-1335 ppm). How many data points were obtained for each sample, and how reproducible were the results?

Authors: In our earlier PIXE study (Minkin et al., 1982) we found that for four coal samples for which we analyzed vitrinites, exinites, and inertinites, highest concentrations of given elements occurred most frequently in vitrinites. Although widely variable concentrations of trace elements do occur in fusinites, we believe the amount of vitrinite present is enough to overwhelm the trace element contribution attributable to fusinite. We are in accord with the conclusion by Bouska (1981) that the dominant process of trace element concentration in coal is sorption by humic acid and humic substances (vitrinite precursors) in the early stage of coalification.

R. Raymond, Jr.: By comparing analysis of vitrains from the lower part of a coal bed to the upper part you may be comparing vitrains that result from possibly different environments. Each plant may have its own nutrient requirements, which in turn will result in a variety of different element concentrations in the resulting vitrain. How would you take this into account when developing geochemical models for coal deposition?

Authors: A total of about 40 measurements were made on the 17 vitrain samples representing the total 8 m thickness of the I coal bed, and about 20 measurements were made on the 7 blocks prepared for the 1.2-m thick Upper Freeport coal. The significance of the uniquely high 2600 ppm value for one determination in core M1 (the range except for this point is 1-400 ppm) is that the volume analyzed here most probably involved a Ti-bearing mineral inclusion below the surface of the sample.

J. R. Chen: Are the confidence levels the same for Sr, Cu, Zr, Mn, and Br in Table 2?

Authors: For Sr, Cu, and Br, even if the uncertainty in their concentrations is 50% of the amount present, it can be seen from Table 3 that the differences in average values are significant over and above the uncertainties. The uncertainty in the concentration of Mn, which is relatively homogeneous, is probably 20%; thus the differences seen in Table 3 are also significant above the level of uncertainty. The confidence level for Zr, which appears rather heterogeneous, is probably lower than for the other elements.

Reviewer V: Much has been reported about the advantages of the PIXE technique. What are the disadvantages of this technique in comparison with other microbeam techniques? Which do you prefer, PIXE or EPMA, if you are analyzing a concentration of approximately 30 wt.%?

Authors: For us as users the three principal disadvantages of micro-PIXE analysis compared to other microbeam techniques are (1) the penetration depth of the proton beam (Fig. 8), which always presents the possibility of including in an analysis material that is different from what is observable at the surface, (2) the relatively long time required for a single analysis, and (3) the small number of proton microprobes (about 20) that exist worldwide, severely limiting access to beam time for guest users. PIXE analysis should be employed strictly as a complement or extension of EPMA. EPMA is without question the method of choice for major elements: PIXE provides the capability to detect, at a similar level of spatial resolution, elements present at concentrations as much as two orders of magnitude below the MDL with EPMA.

Reviewer V: Could you compare the X-ray maps by EPMA or SEM-EDX with those of PIXE (e.g., Fig. 10)? What are the advantages and disadvantages?

Authors: The advantage of PIXE-generated X-ray maps over those generated by EPMA or SEM-EDX rests in the superior MDL's of PIXE. The disadvantage is the possible complications of interpretation of PIXE X-ray maps, because they result from the contribution of a 50-µm thickness of samples rather than 2-3 µm below the surface as is the case for EPMA and SEM-EDX analysis of coal samples.