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ENERGY DISPERSIVE X-RAY ANALYSIS OF OCEAN FERROMANGANESE CRUSTS USING CONVENTIONAL ZAF CORRECTIONS

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Abstract

Ocean ferromanganese crusts are composed of interlayered phases of manganese oxide, iron oxide and oxyhydroxide, calcium carbonate/phosphate, silica, and alumino-silicates. These interlayers are so thin and fine-grained that each phase could not be isolated under the beam of a scanning electron microscope for quantitative x-ray microanalysis. A test was conducted to determine if the grain size of the phases was small enough to allow conventional ZAF techniques to be used without serious errors in the results. A "synthetic" ferromanganese crust was prepared by pelletization of a 1:1 mix of two fine-grained (<5 micrometer) components. The mean of the energy dispersive analyses of the mix, using an area-scan method ($25 \times 30 \ \mu m$ square), shows good agreement (generally within 5 to 10 percent, relative) to the arithmetic combination of the x-ray analyses of each component. Analyses performed by x-ray fluorescence, inductively-coupled argon plasma spectroscopy, flame atomic absorption spectrometry, ion chromatography, spectrophotometry and sulfur analyzer are provided for the purposes of comparison. The results of the energy dispersive analyses were normalized using ignition-loss values and a calculation of fluorine from the P_2O_5 content to reflect the presence of light elements ($Z < 11$). The results were reasonably consistent with other methods of bulk analyses, demonstrating that this method can be used where other instrumentation is not available or where sample size is too small for other methods.

Key Words: Energy Dispersive Analysis, Scanning Electron Microscopy, Ferromanganese Oxide Crusts, Quantitative X-Ray Microanalysis, Multi-Phase Matrix, Bulk Chemical Analysis.

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Introduction

Our laboratory is actively involved with an assessment of the metal content of ferromanganese crusts from the Blake Plateau (Manheim et al., 1982) and from the mid-Pacific seamount area (Halbach and Manheim, 1984). The project received additional justification and scope on March 10, 1983 when the President of the United States proclaimed that the national domain, i.e., the exclusive economic zone (EEZ), for seafloor resources has been extended to 200 miles offshore (Rowland et al., 1983). This has stimulated considerable interest within the scientific community to evaluate the natural resource potential of those areas. In this laboratory, many of the detailed chemical analyses of the crusts are being performed on a scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectrometer (EDS).

In addition to our own research effort we have become aware that many other researchers are analyzing ferromanganese crusts by SEM-EDS or electron microprobe and are using ZAF or Bence-Albee matrix corrections. It became obvious to us early in our research that there may be fundamental problems when using the above matrix correction routines on ferromanganese crusts. This paper discusses the nature of our concerns with the purpose of informing other researchers.

The ferromanganese crusts are very porous and x-ray microanalyses of these materials result in summations which total to less than unity. Often, it is unclear whether the totals are less than unity solely because of the porosity of the samples or also because the detector cannot register x-rays from elements that have atomic numbers lower than sodium.

Ferromanganese crusts are not homogenous in composition but consist of interlayered phases of manganese oxide, iron oxide, and oxyhydroxide, calcium carbonate/phosphate, silica, and alumino-silicates (Figure 1). Because the grain size is so fine, one phase (layer) cannot be isolated from another during x-ray microanalysis. The relative peak heights of the elements present within the sample fluctuate unpredictably with each position of the beam. We analyzed the inhomogeneous areas by scanning the electron beam over an area approximately 25×35.5 micrometers in size to average each analysis over a broad area. The relative peak heights were much more consistent.

Area analysis of multiple mineral phases can present difficulties for quantitative analysis. X-ray matrix correction procedures

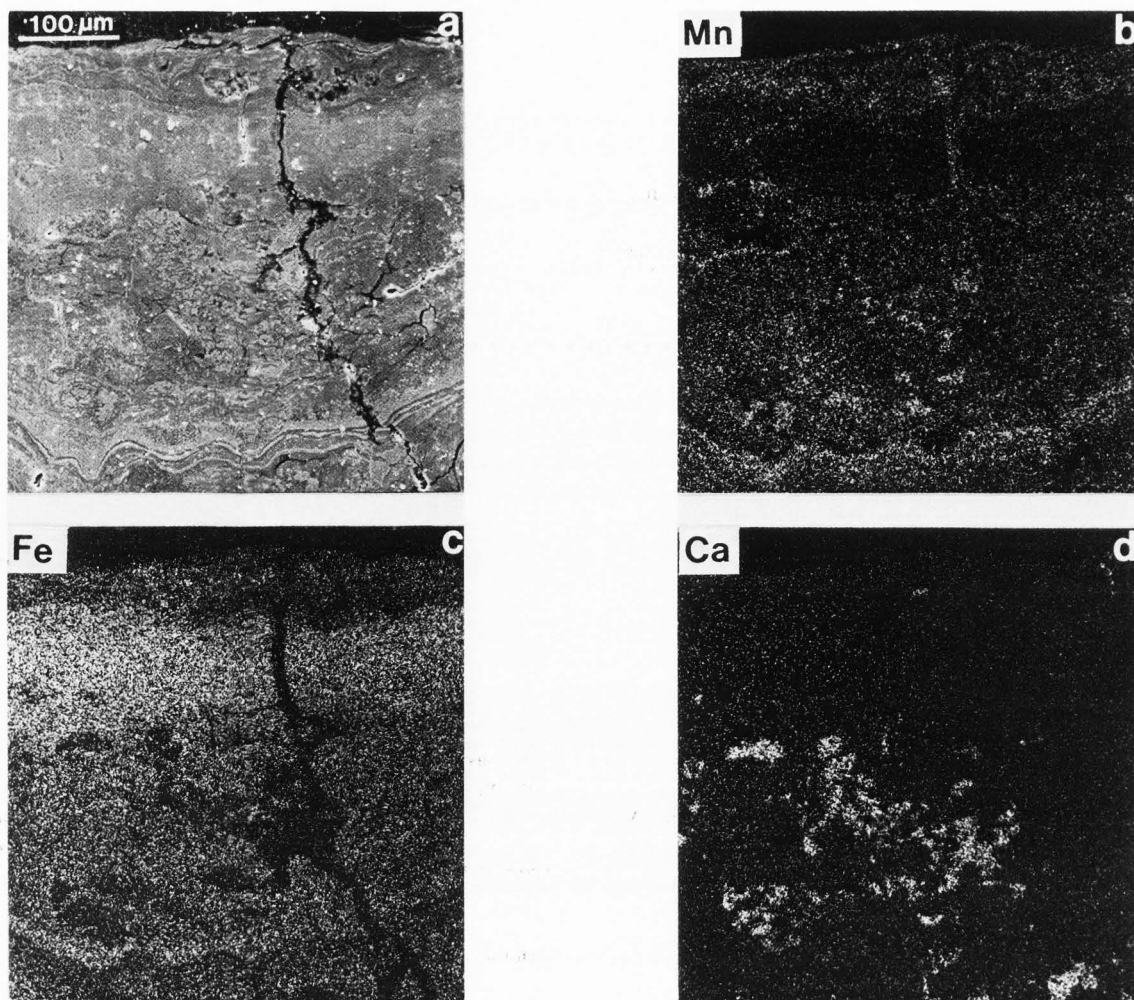R.F. Commeau, J.A. Commeau, F.W. Brown, and F.T. Manheim

Figure 1. Section of ferromanganese crust from the Blake Plateau; a, secondary electron micrograph; b, manganese x-ray intensity map; c, iron x-ray intensity map; d, calcium x-ray intensity map; x-ray maps show either banding or blotches where the micro-layering is enriched in iron, manganese, or calcium; a small amount of calcium is distributed throughout the crust.

assume that the area analyzed is homogenous, which means that each element present in the spectrum should be evenly distributed throughout the area scanned. Myklebust et al. (1981) demonstrated that gross errors in elemental composition (in excess of 100 percent, relative) may occur by an inappropriate use of matrix correction routines on particle mixtures that contain two different compounds. However, Wood et al. (1971) have reported that it is possible to use standard matrix correction routines on polished sections when the grain size of the mineral phases is less than a few micrometers.

Based on observations of morphological features and energy dispersive x-ray analysis, we believe that the average grain size of the multilayered ferromanganese crusts is well below 2 micrometers and, therefore, it should be possible to use standard matrix correction routines with a reasonable degree of accuracy (5–10 percent, relative). We designed an experiment to determine the degree of accuracy which could be expected. The study involved the analysis of materials that are similar in composition, mineralogy, and texture to that of the ferromanganese crusts.

Materials and Methods

Analytical Procedures

Two chemically distinct powder samples, a southern California phosphorite (called Phase A) and prime[1] Pacific deep-water nodule material (Phase B), were wet sieved through a stainless steel screen to assure a grain size of 5 micrometers and below. Each phase was split into a number of subsamples, which were used in the following manner. 1. A split of each phase was analyzed for chemical composition by wavelength dispersive x-ray fluorescence (XRF) using the fusion method of Rose et al. (1963). 2. Another split from each phase was submitted for "rapid rock" (RR) analysis (Shapiro, 1975). This type of analysis determines chemical composition using a variety of methods, including inductively-coupled plasma (ICP) emission spectroscopy, flame atomic absorption spectrometry (FAAS), ion chromatography, spectrophotometry, and the LECO sulfur analyzer. 3. Splits from each phase were prepared for x-ray microanalysis

[1]"Prime" is used to refer to abyssal nodules considered for economic recovery.

Table 1. Analyses of a California Phosphorite (Phase A) and the prime Pacific deep-water nodule material (Phase B).

Element Oxide	Phase A[a]			Phase B[a]		
	EDS[b] n = 6	XRF	RR[c]	EDS[b] n = 5	XRF	RR[c]
F	2.08[1]	1.90[1]	1.9[5]	.03[1]	.04[1]	.03[5]
Na_2O	.96± .18	n.d.	1.0[3]	2.23± .27	n.d.	2.5[3]
MgO	1.01± .20	1.00	1.2[3]	2.19± .18	2.12	2.6[3]
Al_2O_3	2.70± .39	2.42	2.4[4]	3.78± .44	3.33	3.7[4]
SiO_2	11.26± .99	12.66	13.3[4]	11.15± .68	11.76	12.4[4]
P_2O_5	18.89± .75	17.29	17.7[4]	.24± .13	.33	.26[4]
SO_3	1.23± .36	n.d.	1.22[6]	.52± .12	n.d.	.17[6]
Cl	.32± .04	n.d.	.04[5]	1.01± .09	n.d.	.56[5]
K_2O	1.52± .14	1.12	1.0[3]	1.10± .10	1.06	1.0[3]
CaO	41.86±1.15	39.74	39.5[3]	2.08± .11	1.93	2.1[3]
TiO_2	<.1[8]	.12	.11[4]	.60± .07	.56	.52[4]
Mn_3O_4	<.1[8]	.01	.01[3]	36.68±1.05	37.04	37.5[3]
Fe_2O_3	3.77± .41	3.59	3.4[3]	8.04± .47	7.78	7.4[3]
CoO	<.1[8]	<.1[8]	14ppm[2,7]	.36± .23	.40	.48[2]
NiO	<.1[8]	<.1[8]	9ppm[2,7]	1.74± .16	1.65	1.3[2]
CuO	<.1[8]	<.1[8]	2ppm[2,7]	1.23± .10	1.24	1.5[2]
Modified[d] Ignition-loss	14.40	-	-	27.02	-	-
TOTAL[e]	100.00	-	-	100.00	-	-

a   Data reported as oxide weight percent.
b   Mean values for n analyses, plus or minus one standard deviation for n-1 analyses.
c   A composite of various types of analyses. See superscript next to data and check below.
d   The ignition-loss has been modified to show the loss of H_2O^+, H_2O^-, and CO_2 only (see text). The unmodified ignition-loss value for Phase A is 18.60 weight percent and for Phase B is 28.92 weight percent.
e   Normalized.

1, Fluorine content calculated from F/P_2O_5 ratio of .11 (see text); 2, inductively-coupled argon plasma spectroscopy; 3, flame atomic absorption spectrometry; 4, spectrophotometry; 5, ion chromatography; 6, sulfur analyzer; 7, reported as element in parts per million; 8, elements present in amounts below detection limits; n.d., not determined.

on the SEM. Each split was pressed under 20,000 P.S.I. (1406 kg/cm²) to form a one-half inch (12 mm) diameter pellet. In addition, another split from each phase was blended together in a 1:1 ratio by weight using a mixer mill for 20 minutes. This mixture was also pressed into a pellet. The pellets were carbon-coated and analyzed by the area-scan method. 4. An ignition-loss was determined on a split of each phase by weighing them before and after they had been heated for one hour at 1000°C.

SEM/EDS Analysis

The x-ray microanalysis was performed using an ETEC Model U-1, SEM equipped with a Kevex 7700 energy dispersive x-ray analyzer. The analyses were carried out at a 20-kV accelerating potential using approximately 200 pico-amps of beam current and a 45° beam incidence with respect to the surface of the sample. The x-ray detector was positioned at a 53° take-off angle, the highest angle possible. The counting time for each analysis was 100 sec (live time). The elemental concentrations for the

Table 2. Comparison of EDS (area scan) analysis of a one to one mix (by weight) of a California Phosphorite (Phase A) and the prime Pacific deep-water nodule material (Phase B) to an arithmetic combination of the analysis of each phase as analyzed by EDS, XRF, and RR.

Element Oxide	Calculated Analysis of Phase AB Mix (from analysis of Phase A plus analysis of Phase B)[a]			EDS Analysis of Phase AB (1:1) mix[a,d]
	XRF	RR[b]	EDS[c]	n = 15
F	.97[1]	.97[5]	1.05[1]	.97[1]
Na_2O	n.d.	1.7[3]	1.59± .32	1.61± .27
MgO	1.56	1.9[3]	1.60± .27	1.83± .16
Al_2O_3	2.88	3.0[4]	3.24± .59	3.27± .24
SiO_2	12.21	12.8[4]	11.21±1.20	11.78± .41
P_2O_5	8.81	9.0[4]	9.57± .79	8.87± .71
SO_3	n.d.	.69[6]	.87± .38	.70± .08
Cl	n.d.	.30[5]	.66± .10	1.42± .11
K_2O	1.09	1.0[3]	1.31± .17	1.25± .07
C_aO	20.84	20.8[3]	21.98±1.15	19.81± .84
TiO_2	.34	.31[4]	.30± .03	.49± .03
Mn_3O_4	18.53	18.8[3]	18.35± .52	19.21± .75
Fe_2O_3	5.69	5.4[3]	5.90± .62	6.15± .47
CoO	.20	.24[2]	.18± .12	.19± .11
NiO	.83	.65[2]	.87± .08	1.00± .13
CuO	.62	.75[2]	.61± .05	.74± .13
Modified[e] ignition-loss	-	-	20.71	20.71
TOTAL[f]	-	-	100.00	100.00

a Data reported as oxide weight percent.
b A composite of various types of analyses. See superscript next to data.
c Addition of mean values, plus or minus one standard deviation.
d Mean values for n analyses plus or minus one standard deviation for n-1 analyses.
e The ignition-loss has been modified to show the loss of H_2O^+, H_2O^-, and CO_2 only (see text). Unmodified ignition-loss value is 23.76 weight percent.
f Normalized.

1, Fluorine content calculated from F/P_2O_5 ratio of .11 (see text); 2, inductively-coupled argon plasma spectroscopy; 3, flame atomic absorption spectrometry; 4, spectrophotometry; 5, ion chromatography; 6, sulfur analyzer; n.d., not determined.

various areas scanned were determined by a conventional matrix-correction technique, MAGIC (Colby, 1968), using polished standards. Six areas were analyzed on Phase A, five areas on Phase B, and 15 areas on the Phase AB mix (Tables 1 and 2).

XRF and "Rapid Rock" Analysis

XRF and RR analysis were performed on the individual phases and compared against the EDS data. This was done to determine whether or not any systematic matrix effects were evident in the EDS analyses of the individual phases that might be carried over into the EDS analyses of the Phase AB mix. XRF and RR analyses are performed on samples which have been fused and/or dissolved into solution and are not affected by the matrix of the sample.

There was not enough sample remaining on which to conduct XRF and RR analysis on the phase AB mix. Theoretically, however, the analysis of the mix should equal the average of the compositions of the two separate phases.

Results and Discussion

Table 1 shows the analyses of the individual phases (i.e., the southern California phosphorite (Phase A) and the prime Pacific deep-water material (Phase B)). Table 2 shows analyses of the mix AB. The data are presented as oxide weight percent, ± 1 standard deviation. The degree of uncertainty, or the values of standard deviation in the EDS results of Phases A and B, indicate the level of homogeneity within each phase, as well as the analytical error. Mean values were calculated from the EDS analyses for each phase and for the mix and were compared to data derived from XRF and RR analyses.

The data obtained by EDS totaled to less than 100 percent. Again, this is because we cannot analyze any element lighter than sodium with our EDS detector, and the phases are naturally porous. The EDS values listed in Tables 1 and 2 are normalized to 100 percent by calculating a probable fluorine content and making an ignition-loss determination for each phase.

Fluorine, which is known to be present in the phosphorite phase was calculated from a F/P_2O_5 ratio of .11. This ratio is assumed to be representative of marine phosphorites and is based on the average of typical marine carbonate fluorapatites, as documented in data collected from samples from Florida, Morocco and the western U.S. (Manheim and Gulbrandsen, 1979); from the Blake Plateau (Manheim et al., 1980); and from southern California (Inderbitzen et al., 1970).

When determining the ignition-loss values for each phase, we considered the possibility that components such as F, Na_2O, Cl, SO_3, and K_2O could be volatilized during ignition. The EDS, XRF, and RR analyses of each phase (Table 1) and the mix (Table 2) were performed on material which was not ignited and, therefore, contained the above components. It would be erroneous to use ignition-loss determinations to normalize the above data without taking into account the loss of such volatile components.

The ignition-loss values should be reduced by an amount which is equal to the fraction of the volatile components (elements and oxides) listed in the data. Using EDS, we analyzed the phases that had been ignited and compared the results to the EDS analyses of each phase which had not been ignited. Analyses of Phase A after ignition revealed the loss of all of the Cl and K_2O components and part (approximately two-thirds) of the Na_2O fraction and analyses of Phase B showed the loss of all of the Cl and part (approximately one-half) of the Na_2O fractions. Chlorine is present in both phases in the form of NaCl. Part of the sodium fraction for each phase, which is listed as Na_2O in the tables, is also tied up as NaCl. Upon ignition, this part of the sodium fraction is released from the sample along with the chlorine. Fluorine is known to volatilize at 950°C and, therefore, we have assumed that the fluorine fraction of each phase is released upon ignition. The modified, or reduced, ignition-loss values for each phase are listed in Table 1. The modified values reflect the presence of H_2O^+ [essential (bound) water], H_2O^- (hygroscopic water) and carbonate (lost as CO_2) only. The modified ignition-loss value listed in Table 2 is the result of averaging together the ignition-loss values from each phase. The actual ignition-loss values are listed in the footnote section of each table.

The manganese, cobalt, and nickel oxide values in both tables are listed as Mn_3O_4, CoO, and NiO, respectively. These are the oxides that would be stable after heating to 1000°C, but these oxide states do not necessarily occur within Phase A or Phase

B. These oxide states are compatible with the ignition-loss values used to normalize the EDS data.

Comparisons of the data obtained for Phase A and for Phase B by EDS, XRF, and RR techniques (Table 1) generally show agreement to within 5–10 percent, relative. The agreement for the SiO_2 values is in the range of 15–20 percent, relative. The agreement between the techniques for the Cl and K_2O values for Phase A and the SO_3 and Cl values for Phase B is significantly poorer than this.

After careful study of the system we have concluded that a major source of the Cl discrepancy is the conversion of bound water to mobile water during pressing of the pellet. This carries with it soluble Cl to the surface of the pellet where it is reprecipitated, and thereby preferentially enhanced in the EDS analysis.

Discrepancies in the SO_3, Cl and K_2O values and, to a lesser extent, in the SiO_2 values may also occur because the subsamples (splits) are subject to variability in elemental composition if the samples are not homogenously mixed. EDS area-scan analyses of ferromanganese crusts seem to indicate a wider variability in the SiO_2, SO_3, Cl, and K_2O contents than that found in the other components. For example, a share of the SiO_2 content is related to the presence of quartz. The proportion of quartz could vary from subsample to subsample or locally within each subsample, if not homogenously mixed. The standard deviations associated with the EDS values for the SiO_2, SO_3, Cl, and K_2O contents indicate that the inhomogeneity, if present, occurs between the subsamples and not within the subsample used for EDS analysis.

Comparisons of the EDS area-scan analyses of a 1:1 mix (by weight) of Phase A and Phase B to the arithmetic combination of the area scan analyses of the individual phases (Table 2) also show general agreement to within 5–10 percent, relative. Discrepancies occur in the Cl values, and are interpreted in the light of the above factors. An arithmetic combination of the analysis of each phase as analyzed by XRF and RR is listed in Table 2 for the purposes of comparison.

Conclusions

The results of the analyses presented here (Table 2) indicate that energy dispersive analysis of multiple-phase (multilayered) ferromanganese crusts can be conducted by using the area-scan method and conventional matrix correction routines. In general, the analyses are accurate to within 5 to 10 percent, relative, and may be more accurate if part of the observed differences are due to inhomogeneities in our comparison samples. For our purposes this is within acceptable limits. We find the data to be particularly useful to determine phase relationships, detect inter-element correlations, and isolate localized elemental enrichments within the crusts.

Ferromanganese crusts are composed of multiple phases or layers whose proportions vary from one location to the next. This is demonstrated by the banding and blotches in the x-ray maps of Figure 1. Just as one would not perform an analysis on the boundary between two minerals, one should not analyze an area straddling dissimilar bands. On occasion, this may require adjustment of the size of the area scanned at the expense of determining an average of the composition of any particular band.

The results of the EDS, XRF, and RR analyses of each separate phase (Table 1) indicate that EDS can also be used to determine

bulk compositions for systems similar to those analyzed (i.e., manganese crusts and nodules from other locations), even when some of the elements present cannot be "seen" by the detector because of their low atomic number. The use of the modified ignition-loss value to reflect the presence of H_2O^+, H_2O^-, and CO_2 and a calculation of the sample's fluorine content from the F/P_2O_5 ratio appear to be reasonable. The matrix corrections performed did not consider the presence of fluorine and CO_2 in the sample, but their omission seems to have had a minimal effect on the data.

The determination of the bulk compositions of ferromanganese crusts by SEM/EDS analysis can be useful when there is not enough sample to be analyzed by other methods (i.e., one gram of sample is needed for XRF and 30 grams is needed for RR, whereas less than 0.5 grams are needed for EDS) or there are a large number of elements to be analyzed.

We wish to state here that we do not endorse the use of area-scan or so-called "diffuse beam" analysis as a universal method to determine the average composition of multiphase matrices. However, we have determined that the grain size of the individual phases in ferromanganese crusts is small enough to permit analyses by this method.

Acknowledgements

The authors wish to express their appreciation to John C. Hathaway, Michael H. Bothner, and Richard R. Larson, U.S. Geological Survey, for their constructive reviews of the manuscript. We also wish to thank Zoe Ann Brown and Herbert Kirschenbaum, U.S. Geological Survey, for their capable assistance with the samples submitted for "rapid rock" analysis.

Any use of tradenames in this paper is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

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Discussion with Reviewers

J.C. Russ: Why do you use "the highest angle possible" as your take-off angle? This would further aggravate your problem with inhomogeneity.

Authors: A high take-off angle was selected for this experiment because we use this configuration to analyze ferromanganese crusts. Many of the crust samples require a significant amount of time to polish properly for microanalysis. In order to handle a larger number of samples per unit time we polish very little, if at all. We try to accommodate for surface roughness by using a high take-off angle. We agree that high take-off angles would aggravate problems which are due to inhomogeneity. Therefore, the results of our experiment would reflect a "worst case" scenario.

J.C. Russ: Would not the normalization of the calculated results using estimated concentrations of the other elements (such as fluorine which is not included in the ZAF correction) easily hide errors in the analysis?

Authors: There is always that risk when one uses a normalization procedure. However, because of the porous nature of the ferromanganese it is known that the results will total to less than unity, even if all the elements could be measured. We believe the method we used to normalize the data by including fluorine values which have been calculated from known relationships in phosphorites and by including the H_2O^+, H_2O^-, and CO_2 fraction as measured by ignition loss is more accurate than not normalizing at all. Comparisons of the EDS data (normalized) with the XRF and Rapid Rock data (unnormalized) tend to support this technique (Tables 1 and 2).

G. Remond: Why did you not show the unnormalized EDS data in the tables?

Authors: The original x-ray intensities were not recorded with a reference (i.e., beam current or x-ray counts). This means that inter-element concentration ratios were obtained without concern for absolute concentrations. The inter-element concentration relationships are preserved in the normalized EDS data in the tables. A separate column for unnormalized data is not necessary.

G. Remond: Why do you use bulk polished reference specimens rather than pellets made of natural or artificial particles prepared in the same way you used for each specimen A and B and the mixture (A,B)?

Authors: The use of standards which are similar in composition (phases) and texture (porosity) to that of the unknowns would be a preferred method of analysis. This would not require the use of a matrix correction routine, but we did not use this approach for two reasons: (1) Ferromanganese crusts from different areas have different phase relationships. Because there are many different phase relationships with many different resultant compositions a large number of standards would be necessary. This would be time consuming to prepare. (2) Researchers are presently using polished standards with ZAF or Bence-Albee matrix correction routines to analyze ferromanganese crusts. We wanted to test the validity of these techniques.

G. Remond: Could you discuss, based on the study of your porous and hydrated materials, what is the best procedure to be used for expressing the x-ray intensities in terms of concentrations. As an example, in the case of small particles one approach consists in comparing peak/background ratios being characteristic of the particle and the same bulk material respectively (see for example, J.A. Small et al. "Procedure for the quantitative analysis of single particles with the electron probe" in NBS No. 533, Characterization of particles, KFJ Heinrich ed., 1980, 29–38). Could this procedure lead to more accurate experimental concentrations than that based on the usual approach in quantitative analysis of homogeneous bulk compound?

Authors: The peak to background method of Small et al., could indeed be useful to minimize unpredictable absorption effects which occur in porous materials. Further experimentation using this routine on ferromanganese materials should be pursued. However, we believe that the over-riding factor limiting the accuracy of the existing matrix correction routines is the size of the individual phases (degree of inhomogeneity) with the ferromanganese crusts. These phases range in size from well below 0.5 micrometers up to a few micrometers. This range is in a "gray area" where the present matrix correction routines perform with varying degrees of accuracy. Except for the possible incorporation of the peak to background method into the matrix correction routine, we are unable to suggest a better method of analyzing ferromanganese crusts at this time.