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Selective Separation of Metals from Deep-Sea Ferromanganese Nodules by Sulfur Dioxide Reduction

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Abstract

An investigation of the reaction of deep-sea ferromanganese nodules with SO_2 has been carried out in the temperature range 300 and 600°C. Maximum sulfation occurs with dehydrated nodules after treatment with a SO_2–O_2 gas mixture at 400°C. X-ray photoelectron spectroscopy and x-ray diffraction techniques indicate that the oxides of manganese, which are major components in the nodules, are sulfated. The oxides of Cu, Ni, and Co are also converted into their sulfates when reacted with SO_2 and O_2, and Mn, Cu, Ni, and Co can be nearly quantitatively extracted by leaching the sulfated nodules. Iron, which is also a major component and present as goethite, α-FeO(OH), is not sulfated but transformed into hematite, α-Fe_2O_3. Thus it can be separated from other metals which form water-soluble sulfates during the high-temperature sulfation process.

INTRODUCTION

In deep-sea ferromanganese nodules, the industrially important metals Cu, Ni, Co, and Mo are intimately associated with the major mineral oxides such as those of Mn and Fe (*1*). The first step in the recovery of these metals is the selective or total disruption of the nodule matrices. Low temperature sulfation appears to be efficient for the purpose of matrix disruption and has been suggested as a promising method for the extraction of metal values from marine minerals (*2*). Little work, however, has been

reported on metal extraction via high temperature sulfation reactions. In a kinetic study of the sulfation of Atlantic manganese nodules that was carried out by Van Hecke and Bartlett (*3*), complete sulfation of all metal species, including those of Fe, was reported; and the effect of oxygen on the sulfation rate was found to be quite complex. In contrast to these findings, Tamagawa and Taba (*4*) recently reported that above 400°C the effect of O_2 on the rate of sulfation of Pacific nodules was insignificant. There have been a number of studies concerned with low-temperature extraction of metals from the nodules through treatment with SO_2 (*5–8*). The low-temperature process, however, leads to extensive solubilization of Fe as the dithionate, which is undesirable, and also complicates the recovery of the metal values (*9*).

We have investigated the reaction of SO_2 with ferromanganese nodules at elevated temperatures and we have attempted to selectively separate Cu, Ni, Co, and Mn from the sulfated nodules by a simple leaching process. The results of these investigations are reported below.

EXPERIMENTAL

Sampling and Elemental Analysis

Pacific ferromanganese nodules, collected from a depth of 4300 m; longitude, 169°02′E; latitude, 45°48′N, during the *Kana Keoki* cruise in 1977, were obtained from the Hawaii Institute of Geophysics, University of Hawaii. The air-dried manganese nodules were crushed by means of a mortar and pestle, and separated according to particle size with U.S. standard mesh sieves. Extreme care was taken to avoid sample contamination during crushing and sieving operations. A nodule sample of known weight ($\sim$0.5 g) was acid-digested in a pressurized Teflon bomb (*10*). Five replicates were prepared in an identical manner. Quantitative measurements of the elements were made by atomic absorption spectrophotometry with a Varian-Techtron AA-5 equipped with appropriate single-element hollow cathode lamps. The results are summarized in Table 1.

Sulfation

Ferromanganese nodules were treated with a mixture of SO_2 and O_2 in a flow-through gas system, shown in Fig. 1, in a temperature range between 300 and 600°C. A weighed quantity of ground nodules (100/150 μm, particle diameter) packed in a Vycor glass tube was dried overnight

TABLE 1

Atomic Absorption Spectrophotometric Analysis of Major and Minor Elements in KK-77 Pacific Ferromanganese Nodules[a]

	Major elements[b]			Minor elements[b]	
	% (w/w)	Standard deviation		mg/kg	Standard deviation
Mn	11.23	0.05	Pb	1303	78
Si	11.14	1.44	Sr	670	45
Fe	10.77	1.76	Zn	580	45
Na	3.28	0.54	Mo	277	21
Ti	1.72	0.19	Ge	170	15
Mg	1.54	0.09	Cr	160	16
Ca	1.25	0.18	As	78	13
Al	1.11	0.15	Tl	28	2
K	0.97	0.07	Rb	14.3	1.6
Y	0.55	0.04	Be	7.1	1.3
Ba	0.34	0.01	Cd	6.2	0.4
Ni	0.03	0.04	Se	<1	
Co	0.16	0.01			
Cu	0.15	0.02			

[a]Surface area of the ground nodules (100/150 μm in particle diameter) measured by the B.E.T. method: 389 m^2/g; particle density: 1.55 g/cm^3.

[b]Concentrations based on air-dry sample weights. Data obtained from five replicate measurements.

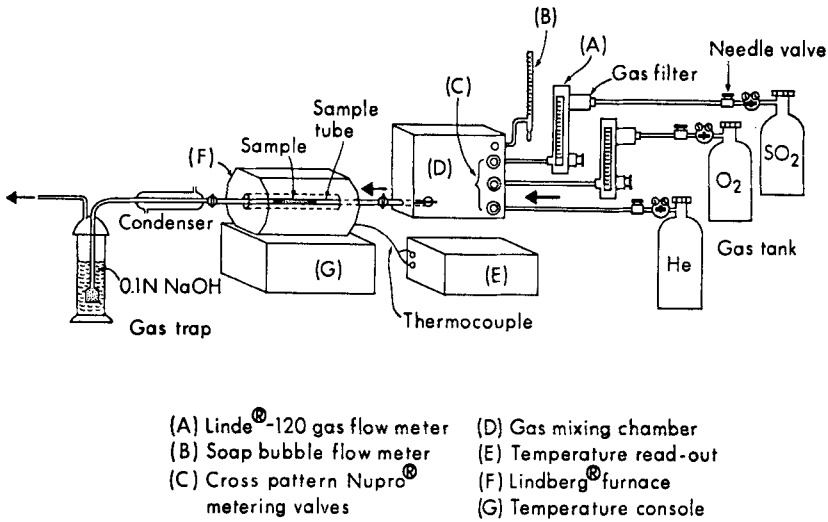

FIG. 1. A schematic illustrating the flow-through gas system for sulfation of ferromanganese nodules at elevated temperatures.

at 450°C in a helium gas stream. The dehydrated sample was then maintained at a desired temperature, and SO_2 gas passed through the sample tube at a flow rate of 15 mL/min with helium as the carrier gas until the gas–solid reaction was complete. The flow rate of the total gas mixture was adjusted to 50 mL/min during the course of all sulfation tests. For the sulfation carried out in the presence of O_2, SO_2 was premixed with controlled quantities of O_2 (0 to 50% by volume) in a gas mixing chamber, and the SO_2–O_2 mixture was allowed to react with the solid nodules. The amount of SO_2 not absorbed by the nodules was passed into a gas impinging bottle containing 0.1 *M* NaOH, and determined titrimetrically with a standard iodine solution. A Lindberg single-zone tube furnace was used for the tests, which was mounted on a temperature control console with a controlling range between 200 and 1200°C. The control unit equipped with a platinel-II/chromel thermocouple was calibrated against a chromel/alumel couple which was connected to a digital read-out meter (M-175K, Omega Engineering). Flow rates of SO_2 and O_2 were measured with Linde-120 flow meters that had been precalibrated with these gases. The sulfated nodules were leached with boiling water (0.5 g/L) for $2\frac{1}{2}$ h with continuous stirring. The filtered aqueous extracts were analyzed for Mn, Fe, Cu, Ni, and Co by atomic absorption spectrophotometry. All chemicals, reagents, and gases were of analytical reagent quality. Water was distilled and deionized prior to use.

X-Ray Photoelectron Spectroscopy (XPS)

Oxidation states of the major metal components present in ferromanganese nodules were investigated by x-ray photoelectron spectroscopy with a McPherson ESCA-36 spectrometer. The sample chamber in the instrument was maintained at $\sim 10^{-7}$ torr with a turbomolecular pumping system (Sargent-Welch). The spectrometer was calibrated with the aid of a pure gold foil, and the instrumental constant was adjusted to give a value of 84.0 eV for the binding energy of the Au $4f_{7/2}$ line. The binding energies for Mn, Fe, and Si were measured relative to this value. The nodule samples were finely powdered and loaded on Kapton-taped aluminum planchets that were placed in a rotary sample holder and each sample was irradiated with Al K_α (1486.6 eV) x-rays. Each energy spectrum that was obtained was compared with the corresponding energy spectrum of each transition element in the SO_2-treated manganese nodules.

X-Ray Powder Diffraction Analysis

X-ray diffraction patterns for the mineral phases in the nodules were

obtained with an XRG-2600 X-Ray Diffractometer (Phillips Electronic Instruments) equipped with a molybdenum x-ray tube as the radiation source. The solid samples were finely powdered and treated under varying conditions prior to the analysis: (a) dried at ambient temperatures, (b) dehydrated at 600°C, and (c) sulfated with SO_2 alone and with a SO_2–O_2 mixture at 400 and 600°C, respectively. Approximately 0.3 mg of the sample was sandwiched between thin layers of Duco cement on a glass slide. After the cement layers were dried, a portion containing the solid sample was cut out and attached to the open end of a special collimator (*11*) which was then mounted horizontally in a Debye-Scherrer camera. Each sample was irradiated with Mo K_α (λ_α = 0.71069 Å) x-rays for about 100 h to obtain a well-defined diffraction pattern.

RESULTS AND DISCUSSION

Ferromagnanese nodules (KK-77) dehydrated at 450°C were treated with SO_2 under varying conditions. At this temperature the oxides of Mn exist as a mixture of MnO_2 and Mn_2O_3, the iron oxides are converted to hematite, α-Fe_2O_3, and silicate and calcite remain unaltered. Cu, Ni, and Co are probably present as CuO, NiO, CoO, and Co_3O_4, and it is this complex mixture of transition metal oxides that interacts with SO_2. Figure 2 shows the extent to which SO_2 is absorbed by the nodules both in the presence and absence of O_2 in the temperature range of 300–600°C.

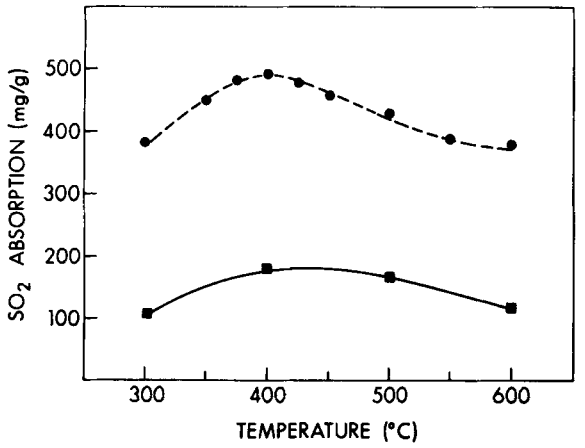

FIG. 2. Absorption of SO_2 by KK-77 Pacific ferromanganese nodules as a function of reaction temperature. Flow rates of gases: SO_2 15 mL/min; O_2 15 mL/min; total flow rate 50 mL/min adjusted with He carrier. Gas-solid contact time was 200 min for all cases.

The curves show that O_2 plays a significant role in the reaction of SO_2 with the solid manganese nodules. The quantity of SO_2 absorbed in the presence of O_2 is significantly higher than that absorbed in the absence of O_2. For instance, the weight gain in the presence of O_2 was 379 mg/g at 300°C and 447 mg/g at 350°C on a dry weight basis, and a maximum weight gain of 493 mg/g at 400°C. This corresponds to 98% of the theoretical quantity of 502 mg/g, that would be absorbed assuming a stoichiometric uptake of SO_2. The absorption decreased slightly to 455 mg/g at 450°C, and finally to 379 mg/g at 600°C. In the absence of O_2, however, the SO_2 absorption was considerably lower in the same range of temperatures: the highest among the absorption values obtained was 182 mg/g at 400°C, corresponding to only about 35% sulfation. The absorption of SO_2 by the nodules expressed as a weight gain is based on the reaction of the SO_2 with participating metal oxides, and the percentage values given are calculated from the elemental analysis data presented in Table 1. It was assumed that the oxides of Fe and Si did not participate in the solid–gas reaction under these experimental conditions.

The percentages of Mn, Fe, Cu, Ni, and Co extracted by water from the nodules which were treated with SO_2 under varying conditions are presented in Table 2. The data show that recovery of metals is in good agreement with the quality of SO_2 absorbed in the solid–gas reaction (Fig. 2). In addition, these results show that the extent to which the metal salts are extracted from the SO_2-treated nodules depends upon the reaction conditions. When the nodules are treated with a SO_2–O_2 mixture in the range 375–425°C, and leached Mn, Ni, and Co are extracted quantitatively and about 75% of the Cu is recovered. At higher or lower temperatures under the same sulfation and extraction conditions, there is

TABLE 2

Hydrometallurgical Separation of Selected Metals from Ferromanganese Nodules (KK-77) Sulfated at Elevated Temperatures

Temperature (°C)	Percent extraction from the nodules sulfated in the presence of O_2					Percent extraction from the nodules sulfated in the absence of O_2				
	Mn	Fe	Cu	Ni	Co	Mn	Fe	Cu	Ni	Co
300	74.5	1.0	2.7	56.0	14.1	60.0	ND[a]	1.9	2.7	12.0
350	87.8	1.0	3.3	76.0	41.4	64.7	ND	1.7	3.1	15.2
375	92.0	4.1	64.3	85.8	94.2	73.0	0.3	2.0	5.3	11.6
400	97.4	2.0	70.6	82.7	91.0	82.2	0.4	3.0	4.7	10.1
500	88.0	1.4	56.1	57.3	72.8	76.3	0.3	0.8	6.7	8.1
600	81.2	1.4	16.0	61.0	46.8	72.4	0.3	0.6	6.5	9.7

[a]Not detected.

a decrease in the concentration of metals recovered. If O_2 is excluded, the results are different. The percentage of the metals recovered is only slightly dependent upon the reaction temperatures. The extraction of only Mn is significant but it is not quantitative. Small amounts of the other metals were extracted, probably because their oxides are slightly soluble in dilute acid solutions. Under the conditions employed, the pH of the aqueous phase is invariably less than 7.

As suggested by Zeitlin et al. (*12*), the reaction of SO_2 with deep-sea ferromanganese nodules can be utilized as an approach to the understanding of the chemical environment of the complex nodule matrices. If SO_2 absorption by the solid nodules occurs via a redox reaction between SO_2 and the metal oxides, then a change in the oxidation states of the metals must take place. In this event the sulfation technique can be employed in conjunction with x-ray photoelectron spectroscopy (XPS) to demonstrate the chemical changes that occur at the mineral surface. Figure 3 presents the Mn $2p$ x-ray photoelectron spectra of manganese nodules treated with SO_2 under different conditions. Spectra of pure MnO_2 are also included for comparison. The Mn binding energies of the untreated and the SO_2-treated manganese nodules are significantly different. The Mn $2p_{3/2}$ core line spectrum of the untreated nodules appears at 641.8 eV, close to the energy of the Mn $2p_{3/2}$ line of an authentic MnO_2 sample

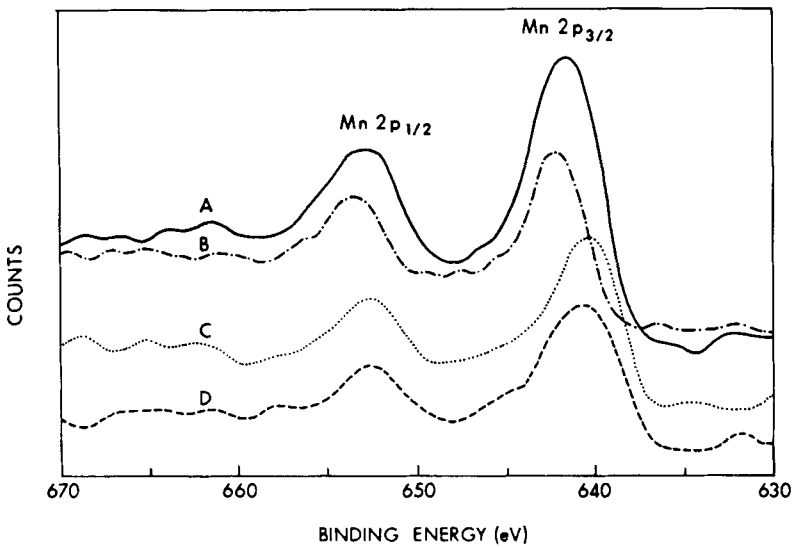

FIG. 3. Mn $2p$; x-ray photoelectron spectra of (A) ferromanganese nodules dried at 25°C; (B) MnO_2; (C) $MnSO_4$; (D) ferromanganese nodules treated with a SO_2–O_2 gas mixture at 400°C.

(642.2 eV). The Mn 2*p* peak (640.6 eV) of the nodules after the SO_2 treatment is shifted approximately 1.2 eV to a lower binding energy, a position almost identical to the Mn 2*p* peak in pure $MnSO_4$. This indicates strongly that the oxides of the Mn present in the manganese nodules consist largely of MnO_2, and the Mn is reduced to $MnSO_4$ during the gas–solid reaction. The presence of sulfate in the SO_2-treated manganese nodules was verified by the presence of characteristic sulfate S–O stretching vibrations in the infrared spectrum between 800 and 1500 cm^{-1}.

In order to determine whether the oxides of iron in the nodules also participate in the reaction with SO_2, the iron XPS spectra of both air-dried and SO_2-treated nodules were determined (Fig. 4). For comparison, the Fe 2*p* binding energies of hematite (α-Fe_2O_3) and goethite (α-FeOOH) were also determined and found to be 711.0 and 711.4 eV, respectively. These values are in good agreement with the results reported by McIntyre and Zetaruk (*13*). The Fe binding energy obtained from the spectrum of the SO_2-treated manganese nodules (711.2 eV) is only slightly shifted (0.2 eV) to the lower energy side from the Fe 2*p* line of the manganese nodules taken prior to the absorption of SO_2. It is about 1.7 eV higher than the Fe core line of pure $FeSO_4$. The chemical shifts found for the Fe 2*p* spectra from these two nodule samples are minimal whereas the chemical

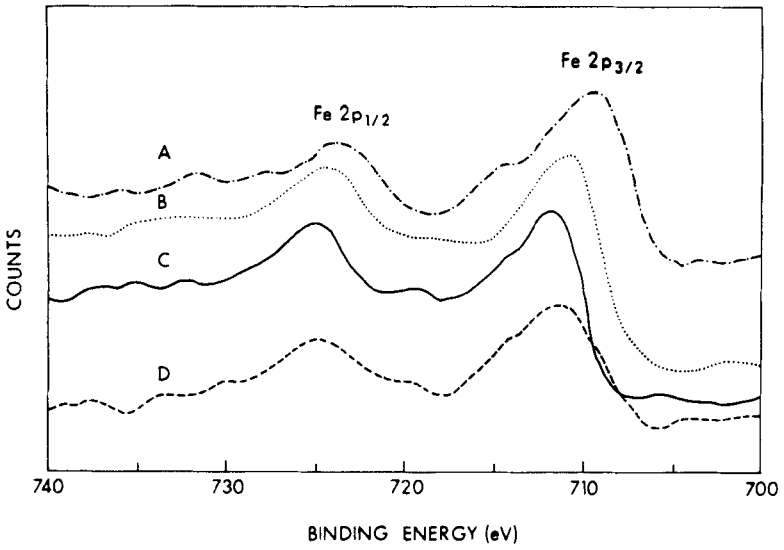

FIG. 4. Fe 2*p* x-ray photoelectron spectra of (A) $FeSO_4$; (B) hematite, α-Fe_2O_3; (C) ferromanganese nodules treated with a SO_2–O_2 gas mixture at 400°C.

shifts of the Fe 2*p* spectra in pure $FeSO_4$ and in the SO_2-treated nodules are significant. This indicates that there is little or no change in the chemical state of Fe in the nodules when reacted with SO_2, and that the Fe does not form sulfates. The binding energy of the Fe 2*p* peak of the manganese nodules is very close to the corresponding peak in hematite, thereby indicating that there is a similarity in the chemical environment of the iron in both materials. It is commonly accepted that the dominant iron-bearing mineral present in the nodules is goethite, and at elevated temperatures the mineral phase is readily transformed into hematite (*14*). XFS, however, is not capable of determining whether a reaction such as

$$Fe_2O_3(s) + 3SO_2(g) + \tfrac{3}{2}O_2(g) \rightarrow Fe_2(SO_4)_3(s)$$

that was previously proposed by Van Hecke and Bartlett (*3*), has occurred, since there would be only a small difference in the binding energies of Fe in ferric sulfate and hematite.

The mineral phases present in ferromanganese nodules have been identified qualitatively by x-ray powder diffraction. In the nodules treated with a SO_2–O_2 gas mixture at 600°C, the major phases identified are α-SiO_2, $MnSO_4$, and α-Fe_2O_3; the latter is the most abundant. The diffraction pattern obtained from the nodules treated with the gas mixture at 400°C shows the same major phases, but $MnSO_4$ is more abundant. $Fe_2(SO_4)_3$, however, was not detected in these SO_2-treated nodules. The major mineral phases identified in manganese nodules heated at 600°C for 24 h without SO_2 treatment include α-Fe_2O_3, Mn_2O_3, and α-SiO_2, which indicates that the goethite has been transformed into hematite at high temperatures. The Mn_2O_3 most likely originates from the thermal reduction of MnO_2, a major phase in the nodules matrices. Previously, MnO_2 has been found to revert to Mn_2O_3 at about 535°C (*15*).

None of the metal oxides thought to be present in the dehydrated nodules are significantly soluble in water at near neutral pH and only the oxides of manganese react rapidly or appreciably with pure SO_2 at 400°C. If minute traces of water are present, MnO_2 is known to rapidly form the sulfate (*16*):

$$MnO_2(s) + SO_2(g) \rightarrow MnSO_4(s)$$

In the completely anhydrous state it reacts in a complex fashion to form Mn_2O_3 and Mn_3O_4 in addition to $MnSO_4$ (*17*). The trioxide (*18*) can also form manganese sulfate:

$$2Mn_2O_3(s) + SO_2(g) \rightarrow Mn_3O_4(s) + MnSO_4(s)$$

Although this reaction is usually not considered important below about 700°C, it may contribute to the formation of $MnSO_4$, especially at the

higher temperatures employed in this study. Only manganese, therefore, will be converted to a soluble sulfate upon reaction with SO_2 in the absence of O_2, and it is not surprising that it alone is extracted to a significant extent after sulfation under oxygen-free conditions (Table 2). The fact that it cannot be extracted quantitatively may result from incomplete sulfation due to the diminished rate of the reaction under anaerobic conditions, the formation of an impermeable sulfate coating, or the presence of the unreactive higher manganese oxides.

If O_2 is introduced during sulfation, SO_2 will be partially converted to SO_3:

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftarrows SO_3(g), \qquad \Delta H = -22.00 \text{ kcal}$$

This reaction is slow unless catalyzed. Fe_2O_3 is known to be a catalyst for the reaction and, in fact, has been employed in the initial oxidation stage of the Mannheim Contact Process for the manufacture of sulfuric acid. Additional transition metal oxides in the nodules may perform a similar function. The well-established (*19*) optimum temperature for the conversion of SO_2 to SO_3 is about the temperature (400°C) that has been observed in this study to yield sulfated manganese nodules containing maximum amounts of water-extractable metal salts. The $SO_2 \rightleftarrows SO_3$ equilibrium favors SO_2 at a high temperatures and consequently the conversion of SO_2 to SO_3 is not complete at temperatures above 500°C, with the result that the extent of sulfation decreases. Below 400°C the SO_3 formation is slow despite the presence of a catalyst. Although the reaction is exothermic and liberates 44 kcal/m of O_2 consumed, there is a 97 to 98% conversion of SO_2 to SO_3 if the reaction is carried out between 380 and 450°C. In sharp contrast to SO_2 the Lewis acidity of SO_3 is very high, and it will interact with all the metal oxides except for Fe_2O_3 to form water-soluble sulfates or polysulfates (*20*). The most favorable temperature for these reactions would be that at which the SO_3 concentration is maximized. In fact, the highest percentage of extractable metal salts was formed at about 400°C during the sulfation. Most likely, then, the principal reactions involved in the sulfation of ferromanganese nodules at elevated temperatures are:

$$MnO_2(s) + SO_3(g) \rightarrow MnSO_4(s) + \tfrac{1}{2}O_2(g)$$
$$Mn_2O_3(s) + 2SO_3(g) \rightarrow 2MnSO_4(s) + \tfrac{1}{2}O_2(g)$$
$$Co_3O_4(s) + 3SO_3(g) \rightarrow 3CoSO_4(s) + \tfrac{1}{2}O_2(g)$$
$$CaCO_3(s) + SO_3(g) \rightarrow CaSO_4(s) + CO_2(g)$$
$$MO(s) + SO_3(g) \rightarrow MSO_4(s)$$

where M = Cu, Ni, and Co.

The sulfation with respect to Fe is of considerable interest. It was reported previously (*3*) that 43% of the total weight gain in the sulfation of Atlantic Ocean nodules above 400°C was due to the sulfation of Fe_2O_3 yielding $Fe_2(SO_4)_3$. The report concluded that the sulfation of Fe had been complete, even though little Fe was found in the aqueous extracts following leaching. If the iron oxide had been completely sulfated in the gas-phase reaction, there would have been considerable amounts of Fe detected in the water extracts, since ferric sulfate is water soluble. Our work shows that the iron concentrations following sulfation in the presence of O_2 and extraction with water were extremely low over the entire temperature range. As mentioned above, XPS and XRD also indicate that the iron oxides are transformed into hematite in this temperature range, and are not involved in the sulfation under the conditions employed. Therefore, it is our conclusion that Fe_2O_3, the iron-bearing mineral present in the nodules at elevated temperatures, is not significantly sulfated with either SO_2 or SO_3. Moreover, the reaction between Fe_2O_3 and $SO_2 + O_2$ or between Fe_2O_3 and SO_2 is known to be unfavorable for the formation of $Fe_2(SO_4)_3$ (*21*). In fact, at above 400°C $Fe_2(SO_4)_3$ is unstable and dissociates:

$$Fe_2(SO_4)_3(s) \rightarrow Fe_2O_3(s) + 3SO_3(g)$$

The Fe present in ferromanganese nodules can thus be conveniently separated as its insoluble oxide from other metals, including Mn, Cu, Ni, and Co, which form water-soluble sulfates during the high-temperature sulfation process.

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