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THE METAL-ADSORPTION CHEMISTRY OF BUSERITE

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ABSTRACT

Heavy-metal enrichment of Mn-rich sediments and Mn nodules relative to silica-rich sediments is a well-known geochemical phenomenon. The ubiquity of occurrence of such deposits suggests that they may act as a significant sink for metals. Surface adsorption has been hypothesized as the mechanism yielding this association. A study of the metal-adsorption characteristics of a defined Mn mineral species (buserite) was carried out. For any given pH (range 2-7), metal adsorption proceeded Ca <Zn <Cu. Positive metal adsorption was recorded at values approaching pH (ZPC). Data did not agree with a simple 1:1 (Cu:H) exchange model of adsorption; hypothesis of some degree of 1:2 surface exchange and/or specific adsorption may be used to explain this discrepancy.

RÉSUMÉ

L'enrichissement, en métaux lourds, des sédiments riches en Mn et nodules Mn par rapport aux sédiments riches en silice est un phénomène géochimique très connu. L'omniprésence de tels dépôts suggère qu'ils peuvent servir, très significativement, de récipients pour les métaux. Une hypothèse a été soulevée à savoir que l'adsorption superficielle serait le mécanisme responsable de cette association. Une étude a donc été entreprise sur les caractéristiques d'adsorption du métal d'une espèce minérale définie de Mn (busérite). Pour tout pH donné (échelle 2-7) l'adsorption du métal donnait Ca<Zn<Cu. Une adsorption métallique positive a été enregistrée et ses valeurs s'approchaient du pH (ZPC). Les données contredisaient un simple modèle d'échange d'adsorption 1:1 (Cu:H); cette divergence pourrait être expliquée par un certain degré d'échange superficiel 1:2 et/ou une adsorption spécifique.

(Traduit par le journal)

INTRODUCTION

The chemistry of manganese in natural water systems is of importance due to the close association that manganese oxides commonly exhibit with several other species, particularly heavy metals, and the strong effect which the system oxidation potential plays in determining manganese solubility. For the most part, manganese is found in sub-milligram per litre quantities in nature.

Though capable of existing in numerous oxidation states, only the II, III(?) and IV states are of any practical significance in nature. Normally only Mn^{2+} is present in anoxic waters, whereas both Mn^{2+} and Mn-oxides are found in oxygenated waters. This effect has been observed on many occasions both in fresh water (Delfino & Lee 1968) and marine environments (Spencer & Brewer 1971), and primarily reflects the strong influences of oxidation potential and slow reaction kinetics in determining manganese solubility.

The precipitation of Mn oxides in oxygenated (surface) waters, followed by their settling through the water column and eventual sedimentation, may constitute an important mechanism by which many other components are removed from the water system. The extremely small size of these precipitates effectively presents a very large surface area for adsorption, though knowledge of the relative competition for these components between Mn oxides, clay minerals and algae is still lacking. It is evident that Mn oxides will operate much better as heavy-metal scavengers than SiO_2, since they have a much higher negative surface charge in the pH range of natural waters (Murray 1974), and it is indeed a geochemical fact that most manganese-rich sediments have higher concentrations of heavy metals than do silica-rich sediments (Krauskopf 1956).

Another important natural occurrence is the manganese nodule. The existence of these unique formations has been known for many years, samples having been obtained as long ago as the Challenger expedition of 1875. Their ubiquity only became apparent a few years ago, however, with the verification of their existence in many different marine locations and dis-

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covery in the fresh-water Great Lakes of North America. A manganese nodule is actually an intimate mixture of very fine Mn and Fe oxides and may be 11-63% MnO_2 by weight (Manheim 1965). The mechanism of formation of these deposits, and indeed the ultimate source of Mn found in them, has not been satisfactorily answered at this time (for discussion with references, see Manheim 1965). One particular property common to all nodules is an enormous enrichment of heavy metals relative to sea water, volcanic rocks, and other sediments; the nodules act as an excellent sink for these environmentally important substances (*i.e.*, directly analogous to Mn-rich sediments).

The mineralogy of Mn oxides is extremely varied and often taxonomically confusing. Though the formula MnO_2 is commonly applied in reference to various mineral species, it in fact only applies to two — ramsdellite and pyrolusite (β-MnO_2). There are three other major groups, the nsutite (γ-MnO_2), birnessite, and hollandite families, all of which exhibit different atomic structures and none of which is simply MnO_2 (Giovanoli 1969). The principal Mn mineral in the nodules was first studied by Buser in 1952, at which time he named it "10Å manganite". Since then, both buserite and todorokite have been used in describing nodule manganese minerals. Considerable controversy regarding these two species has arisen due to slightly different observed *x*-ray spacings. Giovanoli *et al.* (1972) noted that buserite quickly collapses to birnessite when dried, which, in turn, readily decomposes to γ-MnOOH at room temperature; they suggested that todorokite is most probably a complex mixture of several compounds produced by dehydration and reduction of buserite. The name buserite was accepted in 1970 by the nomenclature commission of the IMA (Giovanoli *et al.* 1972). The mineral is a member of the birnessite family and has a slightly expanded structure relative to that of birnessite (also known as 7Å manganite) as a result of the presence of structural hydration water.

Structurally, buserite is composed of ordered layers of 6-fold coordinated Mn^{4+} separated by a 10Å disordered layer of Mn^{2+} coordinated with O^{2-}, H_2O and OH^-. Adsorption of ions can occur either at "exterior" crystal surfaces or at "interior" (*i.e.*, interlayer) surfaces, and the predominance of one or combination of both will result in the particular surface chemistry observed in a given environment. When it has been exposed to air, buserite is superficially (irreversibly) dehydrated, yielding the collapsed birnessite structure (Giovanoli *et al.* 1972). The mechanism of formation of this Mn oxide in the nodules is not known; synthetically, burserite may be prepared at high pH and extreme component concentrations (Stähli 1968), but attempts at preparation under conditions simulating natural conditions have thus far failed. Reports of attemps at mineral characterization of the Mn oxides collected from the water column are few, probably due to the obvious natural complexity of such samples and the difficulties inherent in analyzing them. Delfino & Lee (1968) reported that the particulate Mn oxides of Lake Mendota were amorphous, though description of their *x*-ray techniques is lacking.

Adsorption onto the Mn-oxide surface has been hypothesized as a mechanism accounting for the high heavy-metal concentrations observed for most manganese nodules, although a substantial understanding of this surface chemistry is not available. The picture is further complicated by the fact that different Mn-mineral forms may exhibit substantially different surface and structural properties; it was therefore felt desirable to work with one well-defined species (*i.e.*, buserite), which has a known occurrence in the hydrologic environment. Hence, an investigation was carried out to improve the qualitative and perhaps quantitative knowledge of the chemistry of buserite in the real environment, particiularly with respect to its obvious function as a sink for heavy metals.

EXPERIMENTAL

Buserite preparation

A sodium buserite was synthesized using a method supplied by Giovanoli involving the fast oxidation of a $Mn(NO_3)_2$—NaOH mixture (Stähli 1968). Repeated washing of the product with distilled water to remove excess base, with the resulting decrease in ionic strength of the solution, caused the formation of a progressively more stable colloid which could not be easily separated, even with centrifuging and filtration techniques. In order to circumvent this problem, a washing procedure using $10^{-2}M$ $NaNO_3$ was successfully adopted.

Characterization

Mineral composition was determined as follows:

(1) total sodium content ("structural" and "adsorbed") was determined by the difference between filtered and "total" reduced suspension samples using atomic-absorption spectroscopy (AAS), (Perkin-Elmer 306).

(2) after reduction by excess oxalate, Mn was

similarly determined by AAS.

(3) Average Mn oxidation state was determined by reduction with standard $KMnO_4$.

Metal adsorption

Metal adsorption was studied as a function of pH. Aliquots of buserite suspension ($1 \times 10^{-3}M$ total Mn; ionic strength maintained at $10^{-2}M$ with $NaNO_3$, pH = 3.5) were placed in a series of twelve Nessler tubes and spiked with appropriate quantities of Ca, Cu, Zn or no metal (*i.e.*, metal blank) and sufficient standard NaOH solution to provide pH variation throughout the range 3.5-8.5.

Metal adsorption was calculated by determining metal depletion in the supernatant liquid by AAS after thorough mixing and equilibration for 24 hours at room temperature. Similar experiments using a 72-hour equilibration time showed no significant increase in adsorption, *i.e.*, 24-hour equilibration was sufficient.

Oxidation-potential study

In order to confirm thermodynamic stability of buserite, an oxidation-potential study was initiated. Eh of the buserite/Mn^{2+}/H_2O system was measured while continuously de-oxygenated with high-purity N_2, using a Pt electrode versus a saturated calomel electrode (separated from the suspension by a $NaNO_3$ salt bridge) over a known series of H^+ and Mn^{2+} concentrations (both measured). A 1-2 day equilibration time was allowed between each new reading with continuous potential monitoring (recorder).

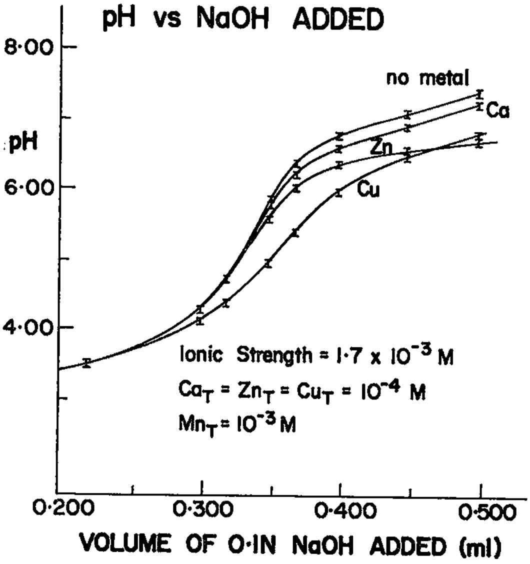

FIG. 1. Study 1: pH versus volume of NaOH added.

Surface-area determination

When buserite is dried, dehydration results in structural collapse to birnessite; because of this phenomenon, it was felt desirable to attempt a surface-area determination in suspension rather than by the more commonly used N_2 adsorption method which requires drying of the solid. The method of negative adsorption of an ion of the same charge as the buserite surface (*i.e.*, negative NO_3^- in this case) was selected (Huang & Stumm 1972; Lyklema & Van der Hul 1969). "Apparent" nitrate concentration ($0\text{-}2.0 \times 10^{-4}M/1$) was determined by *uv*-absorbance measurement (224 mμ - Beckman DB-G grating spectrophotometer) after suspension sedimentation by centrifuging. Only approximate surface-area determination was possible due to variable *uv*-absorbance readings resulting from incomplete sedimentation of colloidal material.

RESULTS

Results of buserite characterization (five different preparations) are summarized as follows:

average Mn oxidation state = 3.2 — 3.8
[Na]/[Mn] molar ratio = 0.26 — 0.34
approximate surface area = 200 m^2/g

The idealized buserite formula expected from preparation under the conditions used is $Na_4Mn_{14}O_{27} \cdot 9H_2O$ (Giovanoli, personal communication) which has an average Mn oxidation state of 3.6 and a [Na]/[Mn] molar ratio of 0.29. Since composition is dependent on preparation conditions, subsequent washing, chemistry of supernatant, *etc.*, these results are reasonable. This point is very important. Washing of the buserite with distilled water rather than $10^{-2}M$ $NaNO_3$ resulted in the formation of an extremely stable colloid, as mentioned previously, with [Na]/[Mn] only about ⅕ that implied by the above idealized formula. Hence the Na included in the above formula is primarily adsorbed. This is as expected, given the observed colloid destabilization when the supernatant is $10^{-2}M$ in $NaNO_3$.

Several titration studies (*i.e.*, adsorption as a function of pH) were attempted. Titration curves plotted from the results of Study 1 and Study 2 are given in Figures 1 and 2 respectively. Small decreases in pH resulting from the addition of the metals were expected and observed and Figures 1 and 2 have been corrected for this deviation; similarly, calculations performed to obtain Figure 3 took this factor into consideration. Qualitatively it is immediately apparent that a greater quantity of base was required to reach a given pH in the order no-metal <Ca<Zn<Cu added (Fig. 1). Similarly, the larger the amount of Cu present (Fig. 2), the greater the divergence between the Cu and no-Cu curves. The magnitude of divergence was also directly related to the absolute quantity of metal adsorbed. This behavior was entirely as expected and reported by others (Morgan & Stumm 1964; Murray *et al.* 1968; Murray 1973). An attempt to quantify this relationship is given in Figure 3. This is a plot of moles of Cu adsorbed (absolute quantity) vs. Δ base, that is, the number of moles of base represented by the distance between the metal/no-metal curves of Figure 2 at a given pH in the range 4.5 to 6.0. A straight-line plot of slope 1.22 was obtained. This pH range was chosen so that the major soluble Cu species is Cu^{2+} (aq). At pH values greater than this, hydroxyl-species form a significant proportion of soluble Cu and serve to complicate the adsorption model discussed later. It is also important to note that by taking the difference between the no-metal and metal curves, the possible errors resulting from adsorption of Mn^{2+} (in competition with Cu^{2+}) are minimized since the Mn^{2+} concentration was essentially the same at pH = 3.5 for each of the four titration series.

Under the experimental conditions of high dispersion and frequent agitation, the complete removal of Cu to non-detectable levels in the supernatant was achieved at pH values approaching 8, that is, within the pH range of most natural waters. The adsorbed Cu to Mn molar ratio was then observed to reach a value of 1:2.4. The same ratio observed for Pacific Ocean manganese nodules is 1:45. Clearly, buserite has a large Cu-adsorption capacity and as found in marine manganese nodules, is greatly undersaturated with respect to its total, although probably unachievable capability.

Finally, another feature of the titration curves is the obvious inflection present in some in the pH = 6-7 range (more pronounced in Study 1 and only immedately apparent in the no-Cu curve of Study 9). This is caused by the adsorption of previously-desorbed Mn^{2+} (when the suspension pH lowered to 3) and must not be confused with the large inflection in the 3 $\times 10^{-4}$ Cu curve which is simply the result of the Cu hydrolysis reaction.

The suspension used for the oxidation-potential study had an average Mn oxidation state of 3.76 corresponding to the formula $MnO_{1.79}$. The reaction under investigation was then

$$MnO_{1.79} + 3.58\ H^+ + 1.58\ e^- \rightleftarrows Mn^{2+} + 1.79\ H_2O$$

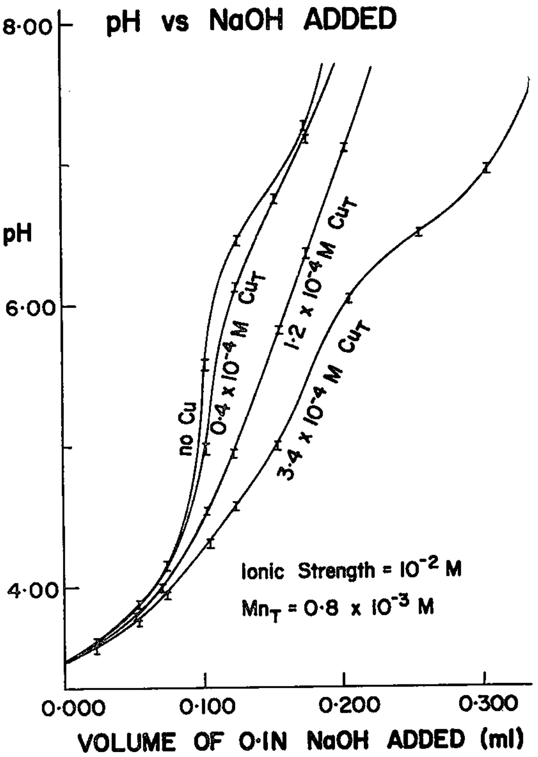

FIG. 2. Study 2: pH versus volume of NaOH added.

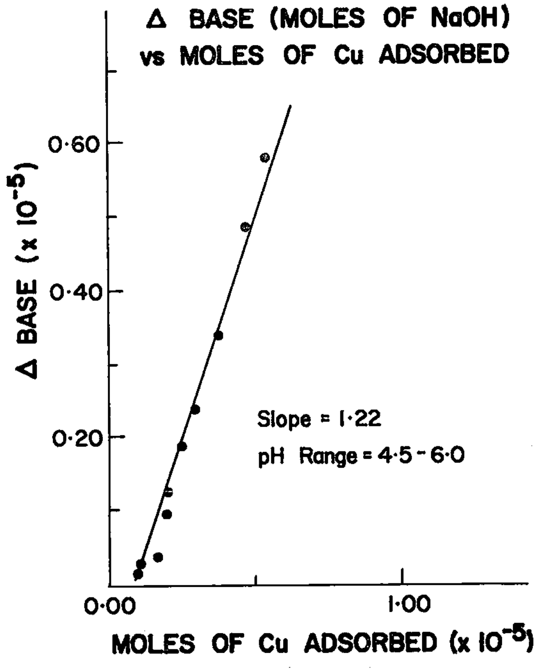

FIG. 3. Study 2: Δ base (moles NaOH) versus moles of copper adsorbed.

and

$$\text{Eh} = \text{Eh}^\circ - \frac{1}{1.58}\, 2.303 \left(\frac{RT}{F}\right) \log_{10} [\text{Mn}^{2+}]/[\text{H}^+]^{3.58}$$

where Eh and Eh° = system oxidation potential and standard oxidation potential (volts) respectively, R = gas constant, T = absolute temperature (°K), F = Faraday constant, $[\text{Mn}^{2+}]$ and $[\text{H}^+]$ = molar concentrations of Mn^{2+} and H^+, respectively.

A plot of $\text{Eh}/2.303(RT/F)$ vs. $\log_{10}[\text{Mn}^{2+}] + 3.58$ pH is given in Figure 4. The slope of the resultant straight line is –0.63 which compares favourably with the expected theoretical slope $(-1/1.58 = 0.63)$. From the intercept, calculation of E° gave 1.32 volt ($T = 25\,^\circ\text{C}$) when corrected for ionic strength (*i.e.*, to $I = 0$). This E° compares favourably with the Latimer value of 1.23 volt for pyrolusite and Briker's (1965) value of 1.29 volt for a δ-MnO_2, neither of which is buserite, of course.

The Mn^{2+} concentration in this experiment was measured by AAS after filtration of the suspension through 0.2 μm Millipore membrane, and varied between $1.5\text{-}1.8 \times 10^{-4} M/l$ in the pH range 2.6-6.2 with a mean of $1.7 \times 10^{-4} M/l$. Using this average Mn^{2+} concentration, the relationship corresponding to the reaction $\text{O}_2\text{(g)} + 4\text{H}^+ + 4e^- \rightleftharpoons \text{H}_2\text{O}$ is also included in Figure 4 over the above pH interval. The intersection of the lines corresponds to pH $\approx$ 3.4; above this pH, buserite is the stable phase, whereas below, it is thermodynamically unstable with respect to water. Hence it is theoretically unsuitable to work with buserite below this pH, although this pH restriction has often been disregarded, both in this study and others.

DISCUSSION

It has become apparent that any study of buserite will be immediately complicated by the fact that its stoichiometry is not fixed, but is a function of method of preparation, refining and sub-sample handling. It is for this reason that the characterization results span a considerable range. Further, it has been experimentally proven that washing of the suspension at low pH results in the release of substantial quantities of Mn^{2+} and Na^+ (approximately 10% of Mn_T for a

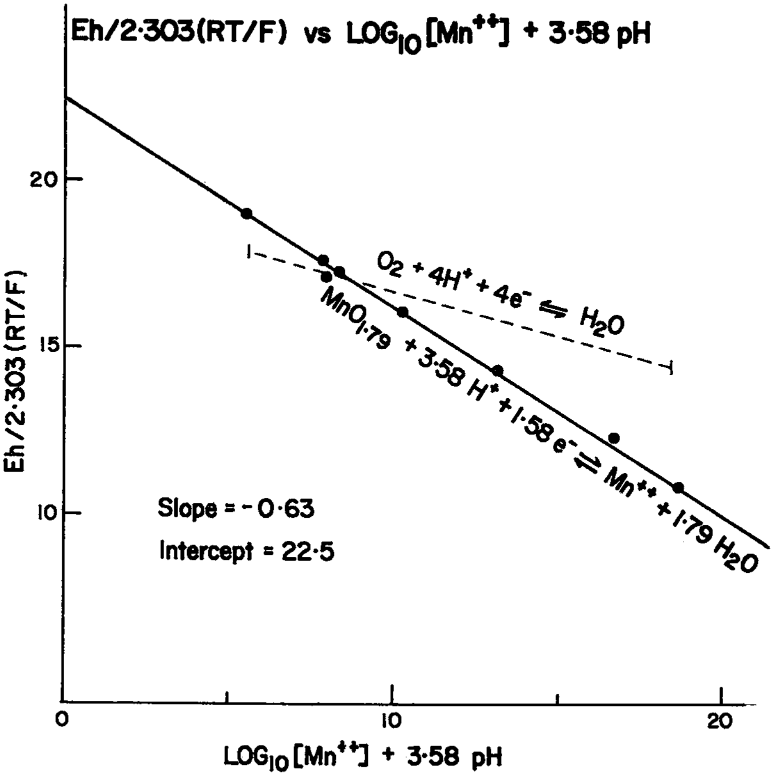

FIG. 4. Oxidation-potential study: $\text{Eh}/2.303(RT/F)$ versus $\log_{10}[\text{Mn}^{2+}] + 3.58$ pH.

$pH = 3$ wash). It has also been observed that the buserite structure breaks down at low pH (Giovanoli, personal communication) which may be of particular importance when considering the results of the oxidation-potential experiment where the sample was originally acidified to $pH = 3$, and then equilibrated at successfully higher pH's.

The inflections in titration curves relate to the presence of Mn^{2+}, that is, they reflect the adsorption of this species with increasing pH. In support of this is the fact that the inflection is much more pronounced for Study 1 than Study 2. Partial removal of desorbed Mn^{2+} by repeated washing and decantation of the $10^{-2}M$ $NaNO_3$ supernatant at $pH = 3$ (prior to metal spiking) was accomplished prior to Study 2. The magnitude of the inflection is thus directly related to the quantity of Mn^{2+} present, prior to beginning the titration. The possibility that buserite is, in practice, behaving as an acid with two acidity constants must also be investigated. The presence of Mn^{2+} also constitutes a further problem when trying to intercept the metal-adsorption results, and as noted previously, correction for Mn^{2+} adsorption was made when Figure 3 was prepared.

The slope of Figure 3 may be interpreted in terms of surface exchange equilibria as follows:

$$Mn - OH + Cu^{2+} \rightleftarrows Mn - OCu^{+} + H^{+} \,.\,. \quad (1)$$

$$2Mn - OH + Cu^{2+} \rightleftarrows (MnO)_2Cu + 2H^{+} \quad (2)$$

In effect, the manganese oxide is acting as a mono-dentate ligand in (1) and as a bidentate ligand in (2). Theoretically, the slope of Figure 3 should be 1 if Equation (1) is operative, and 2 if (2) describes the system. The fact that an intermediate value was obtained may indicate that a mixture of the two is occurring although it should be noted that the errors involved in Figure 3 are substantial (exact magnitude of possible error not determined). Another possibility is that buserite is acting as an acid with two or more metal association constants corresponding to adsorption at "interior", "exterior", or plate-edge surfaces. Further investigation in this regard has not been carried out.

Murray *et al.* (1968) reported structural incorporation of Ni^{2+}, Cu^{2+}, Co^{2+} and perhaps Ca^{2+} (for 10Å manganite) when present at "high concentration" and cite finite adsorption of these species at pH(ZPC) in evidence. This study also confirmed Cu^{2+} adsorption at system acidity approaching pH(ZPC), *i.e.*, $pH \approx 2$, and is the reason for the failure of Figure 3 to pass through the origin.

It is interesting to note that the order of "strength" of adsorption observed in these experiments ($Ca < Zn < Cu$) is the same as that calculated by Riley & Sinhaseni (1958), Table 1, when they determined the relative order of enrichment of heavy metals in manganese nodules relative to sea water. Similar titration studies by Murray (1973) using a 7Å manganite for these metals, plus Co and Ni, also follow Riley's order.

TABLE 1. RELATIVE ENRICHMENT OF ELEMENTS IN MANGANESE NODULES

$Mn > Fe > Ti > Co > Al = Cu = Ni > Zn = La$
$> W > Ga > Pb > Sc > V > Ag > Ge > Ba = Cd$
$= Sn = Y > Mo > Cr > K > B > Ca > Na > Mg$

Fundamental questions on the environmental occurrence and role of manganese oxides still remain. The "degree of success" that buserite will have in competing for heavy metals with other organic and inorganic ligands present may be understood better when values for the association constants measured previously are determined. In order to do this, experiments of greater precision and control are required. Also, determination of just what manganese oxide actually precipitates in the water column must be carried out, although the technical problems involved are enormous.

CONCLUSIONS

1) At the pH of most natural waters ($pH = 6$-8), buserite has a tremendous heavy-metal adsorption capacity and in the natural marine environment is grossly undersaturated.
2) The adsorption chemistry of buserite is more complicated than a simple 1:1 surface exchange of metal for hydrogen ion; the existence of specific adsorption effects is indicated.
3) Adsorption studies show the same sequence as that observed for metal enrichment in natural manganese nodules (Riley's sequence).

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