Chemical influences on trace metal-sulphide interactions in anoxic sediments

G. W. Luther III
College of Marine Studies, University of Delaware, Lewes, Delaware, 19958, USA

J. W. Morse
Department of Oceanography, Texas A&M University, College Station, Texas 77843, USA

The major changes that occur in redox conditions between oxic waters and anoxic sediments can have profound influences on the speciation and bioavailability of many trace metals. Anoxic conditions in sediments are commonly sufficiently reducing to result in the microbially-mediated production of major amounts of hydrogen sulphide in marine and estuarine environments. Although most of the H_2S is usually reoxidized, a significant fraction generally reacts to form metal sulphides with pyrite (FeS_2) being by far the most abundant reaction product. However, there is also the potential for other metal sulphide minerals to form, and for minor and trace metals to coprecipitate and adsorb on iron sulphides. Although for many years observations were made on correlations between trace metals and sulphidic sediments, it was not until less than a decade ago that major direct evidence for the interactions of trace metals with sulphides in anoxic sediments began to become available. Using a modification of the pyrite-Fe extraction method of Lord (1982), Huerta-Diaz and Morse (1990) were able to determine trace metals that were co-leached with pyrite-Fe. Since the development of this technique thousands of analyses have been performed on sediments from numerous locations (e.g. Huerta Diaz and Morse, 1992; Morse, 1994, Cooper and Morse, 1996) and clear patterns of behaviour for different trace metals have emerged.

Observations of trace metal-sulphide interactions in sediments

In interpreting the behaviour of metals in sulphidic sediments it has been found useful to use a measure of the extent to which the operationally defined ìreactiveî fraction has become transformed into the fraction that extracts with pyrite-Fe. This is done in the same manner as the degree of pyritization (DOP) is calculated for Fe and is referred to as the degree of trace metal pyritization (DTMP) (Huerta-Diaz and Morse, 1990). The general pattern for extent of pyritization is $Hg > As = Mo > Cu = Fe > Co > Ni >> Mn > Zn > Cr = Pb > Cd$. If a plot of $-\log (K_{MeS}/K_{pyrite})$ versus DTMP is made an approximately linear relationship for MnS, CoS, NiS, Cu_2S, HgS is observed indicating a good relationship between metal sulphide solubility and DTMP. However, ZnS, CdS and PbS fall well below the line obtained for the other metals. Recent studies (Cooper and Morse, in press) of the extraction chemistry of pure metal sulphides provides a probable explanation for this difference in behaviour. The extent to which pure metal sulphides dissolve in cold HCl is: NiS_2 1%, HgS 1%, CuS 12%,Cu_2S18%, NiS 23%, Ni_3S_2 28%, and CdS, PbS and ZnS extract completely. For MeS compounds, this leads to $Hg < Cu < Ni < Zn = Pb = Cd$ which is close to the relationship observed for DTMP. Therefore, if Zn, Cd and Pb largely make their own sulphide minerals they would appear to have a low DTMP because they extract in the HCl fraction. Unfortunately this means that it is not possible to directly tell how extensively they are sulphidized. The other metals may *be coprecipitates with pyrite or* occur as discrete phases.

Relationship of observations to chemical properties of metals

A simple reason for the distribution of the metals found in sedimentary pyrite is not obvious based on thermodynamic considerations. The distribution appears to have kinetic processes also controlling trace metal pyritization. To a first approximation, we can use the rate of water exchange for the various metals as a guide to reactivity. Superimposed on this is the fact that certain metals form strong chloride complexes and undergo significant hydrolysis. To form sulphide minerals, water, hydroxide and chloride will need to be displaced by sulphide. In the case of Mo, As and Cu redox processes are also possible which may explain why these elements are more enriched in pyrite.

Hg, Pb, Cd and Zn have filled d orbitals and thus no ligand field stabilization is possible which would retard water loss. Cu has a d^9 electron configuration and exhibits the Jahn Teller effect of 4 short and 2 long bonds, which are weak and labile, in octahedral coordination. All the other metals have partially filled d orbitals so the rate of water loss is slower.

The divalent ions of Hg, Pb, Cu, Cd, Zn, and Mn have faster rates of water exchange than Fe whereas Co and Ni have slower rates of water exchange than Fe. These data indicate that Hg, Pb, Cu, Cd, Zn, and Mn should form a sulphide mineral faster than Fe and thus not be incorporated into FeS and eventually FeS_2. Co and Ni should be incorporated into FeS_2 since these metals have slower kinetics for water exchange than Fe; thus, they should tend to adsorb on or coprecipitate with iron sulphide phases.

Based on trace metal incorporation data above, Pb, Cd and Zn fall below the $-\log (K_{MeS}/K_{pyrite})$ versus DTMP line. This behaviour appears to be related to the faster water exchange rates for these metals relative to Fe. Mn, Co, Ni, Cu and Hg fall on the line, which suggests that there is similar or slower reactivity for these metals with sulphide relative to Fe. Co and Ni have slower water exchange rates than Fe so they should adsorb to FeS phases and be pyritized. The distribution of the five metals (Pb, Cd, Zn, Co and Ni) into pyrite appears to follow a simple kinetic pattern related to water exchange.

However, Mn, Cu and Hg do not follow this kinetic pattern. Mn has a faster water exchange rate than Fe but Mn does not form a sulphide mineral readily, but Mn can adsorb onto FeS phases and be pyritized. Hg and Cu have higher water exchange rates so would be expected to form their own discrete minerals before FeS forms; thus, they would not be expected to fall on the the $-\log (K_{MeS}/K_{pyrite})$ versus DTMP line. However, Hg has the strongest chloride complexation and highest hydrolysis constant. Thus, Cl^- and OH^- must be displaced from Hg for sulphide mineral formation to occur. This should retard Hg reactivity with sulphide and allow incorporation of Hg in FeS_2 rather than discrete HgS phases to form. Cu undergoes redox chemistry with sulphide and forms S_2^{2-} ions in covellite suggesting a common reactivity with Fe.

The general pattern of trace metal pyritization for the divalent cations of Cd, Pb, Zn, Mn, Ni and Co shows a decrease of the metal in pyrite with an increase in the kinetics of water exchange in the order shown. Pb and Cd have comparable chloride complex strengths but Pb hydrolyzes at a lower pH than Cd indicating that Cd may be expected to be the least enriched metal in pyrite. Hg and Cu have different chemical reactivities, which can enhance their incorporation into pyrite. For Hg, chloride complexation and hydrolysis become important whereas Cu undergoes reduction with sulphide.

The dissolution of FeS, ZnS, CdS and PbS by HCl and the complete recovery of these metals and sulphide indicate that there is no kinetic inhibition to H_2S formation. The Fe^{2+} (d^6 electron configuration) in FeS is high spin and labile; Zn, Cd and Pb have filled d orbitals and have no ligand field stabilization which would retard water loss or sulphide loss on acidification. In FeS_2, there is significant kinetic inhibition due to the S_2^{2-} ion causing the Fe^{2+} ion to be low spin. Kinetic inhibition can occur with other MS_2 minerals that have the S_2^{2-} ion such as Ni. Other NiS minerals will be slow to dissolve because of the slow kinetics of Ni substitution. This is due to the d^8 electron configuration for Ni^{2+}. Cu minerals such as covellite have both S^{2-} and S_2^{2-} ions present so complete recovery of Cu and sulphide is not possible. HgS in cinnabar has S−S interactions in the crystal, which stabilize HgS to dissolution by HCl.

Acknowledgements

This research was in part support by NSF grant OCE-9714302 (Luther).

References

Burgess, J. (1988) *Ions in solution*, John Wiley & Sons, New York, pp. 191.

Cooper, D.C. and Morse, J.W. (1996) *Estuaries* **19**, 595–611.

Cooper, D.C. and Morse, J.W. (in press) *Environ. Sci. and Technol.* (in press).

Huerta-Diaz, M.A. and Morse, J.W. (1990) *Marine Chem.* **29**, 119–144.

Huerta-Diaz, M.A. and Morse, J.W. (1990) *Geochim. Cosmochim. Acta*, **56**, 2681–702.

Lord, C. J. III (1982) *J. Sed. Petrol.*, **52**, 664–6.

Morse, J.W. (1994) *Marine Chemistry* **46**, 1–6.