Extractability of Metal Sulfide Minerals in Acidic Solutions: Application to Environmental Studies of Trace Metal Contamination within Anoxic Sediments

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Sulfide minerals are an important sink for metals within anoxic sediments. Extraction techniques using cold HCl to measure the concentration of sulfide mineral associated trace metals have gained wide acceptance as a proxy for potential metal bioavailability within the environmental community. However, certain metal sulfide phases that can potentially release metals into a more bioavailable phase do not extract in HCl. Laboratory experiments have shown that covellite (CuS), chalcocite (Cu_2S), cinnabar (HgS), millerite (NiS), heazlewoodite (Ni_2S_3), and vaesite (NiS_2) are poorly soluble in HCl; while greenockite (CdS), mackinawite (FeS_{1-x}), pyrrohtite (FeS), galena (PbS), and sphalerite (ZnS) are highly soluble in HCl. Surface area can also affect the apparent solubility of CuS and NiS in HCl. These results indicate that use of HCl-based extraction schemes (e.g., AVS/SEM ratios) to assay sediments for metal contamination could underestimate the potential bioavailability of several metals of general interest in anoxic sediments.

Introduction

In recent years, an increasing quantity of research has examined the role of AVS minerals in sequestering toxic metals within anoxic sediments and thereby preventing them from reaching the aqueous, bioavailable phase (*1−5*). The bulk of this work (*1−3*) has examined the biouptake of Cd into a range of benthic biota and related the toxicity of the Cd to the ratio of AVS (acid volatile sulfide) to SEM (simultaneously extracted metals). The most common way to measure this ratio is to digest the sediment at room temperature for 1 h, using either 1.0 or 6.0 M HCl. The evolved sulfide is trapped in basic solution with the aid of a Soxhlet apparatus. The sediment slurry is then filtered to remove the remaining sediment, and the filtrate is analyzed for metal concentration (*1, 2*). The molar ratio of AVS-sulfide to SEM-metal is then used to predict the potential sediment toxicity (*2, 3*). This approach is based on the following solubility-driven exchange reaction:

$$\text{metal}^{2+}(aq) + FeS(s) \rightarrow \text{metal sulfide}(s) + Fe^{2+}(aq)$$
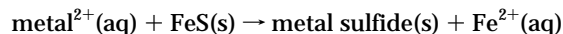
If both metal sulfide(s) and FeS(s) are extracted by an AVS/SEM digestion, then as long as there is remaining FeS, aqueous metal concentrations should not build up and the sediments should not be toxic with respect to metals. When the molar ratio is greater than 1, there is no FeS left to sequester the metal and aqueous metal concentrations can build up to dangerous levels.

Problems arise with this approach when a significant amount of metal is trapped within a sulfide phase that is not soluble in HCl but can potentially oxidize into an oxide form that is HCl soluble. Morse (*6, 7*) exposed anoxic sediments from Galveston Bay, TX, to oxic seawater and found that the HCl-soluble fraction increased 3-fold within 24 h. Many trace metals display an affinity for sulfidic sediments (*8−15*), and the metal sulfide phases are often not extracted by HCl (*16*). Thus, the use of HCl extracts alone can severely underestimate the potential bioavailability of many trace metals. This study examines the solubility of pure trace metal sulfides in acidic solution and demonstrates that the chemistry of individual metals (and their respective sulfide minerals) must be considered when performing research in this field.

Methods

CuS, Cu_2S, NiS, Ni_2S_3, NiS_2, FeS (pyrrohtite), HgS, and ZnS were purchased from Aldrich Chemical Company, washed first with 25 mL of deoxygenated 10% (by volume) acetic acid to remove any surface oxide, and then washed with 25 mL of deoxygenated water. After washing, the solid sulfide was frozen for later analysis. Covellite, greenockite, mackinawite, and galena were synthesized in the laboratory by adding 25 mL of deoxygenated 0.1 M metal stock solution to 25 mL of 0.1 M sulfide stock solution. The resultant 50-mL mixture was sealed in a glass tube and aged in the dark for 3 d. The resultant slurry was transferred to a 50-mL plastic centrifuge tube and centrifuged for 1 h at 3500 rpm to separate the solid precipitate from the supernatant. The supernatant fluid was discarded, and the solid sulfide was washed with 25 mL of deoxygenated water and frozen for later analysis. Great care was taken to isolate the solid sulfide from exposure to atmospheric O_2, and all operations that could result in sample exposure were performed in a glovebag under an inert N_2 atmosphere. Stock solutions were made from sodium sulfide ($Na_2S\cdot9H_2O$); the sulfate salts of Cu, Fe, and Ni; and the chloride salts of Cd and Pb. All samples were characterized by X-ray diffraction prior to experimentation. Water for all aqueous solutions was purified on a Milli-Q RO4 filtration system prior to use. Surface areas were measured by gas adsorption on a Quantasorb Jr. BET system.

For the wet chemical extractions, samples were split into ~0.1-g aliquots and subjected to two series of wet chemical extraction. Series 1 was digested at room temperature in 250 mL of 1.0 M HCl for 24 h (*16*) and then filtered with a 0.45-μm polypropylene filter. The filtrate was stored for later analysis, and the remaining solid was digested for 1 h in 20 mL of concentrated HNO_3. Series 2 was digested at room temperature in 250 mL of 6.0 M HCl for 1 h (*1*) and then treated in the same manner as series 1. The four solutions for each sample (series 1 HCl, series 2 HCl, series 1 HNO_3, series 2 HNO_3) were analyzed for metal concentration on a Perkin-Elmer 2380 flame AAS. Hg was analyzed spectrophotometrically with a Laboratory Data Control UV monitor equipped with a 30-cm path length cell using the cold vapor technique (*17*). All standard solutions were commercially available standards diluted in the respective extraction

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TABLE 1. Extraction Efficiency[a]

metal sulfide	series 1 HCl (%)	series 1 HNO₃ (%)	series 2 HCl (%)	series 2 HNO₃ (%)
CuS*	8	92	24	76
Cu₂S*	25	75	12	88
NiS*	22	78	25	75
Ni₃S₂*	25	75	31	69
NiS₂	1	99	1	99
HgS*	1	99	1	99
FeS (pyrrhotite)	99	1	97	3
Fe(s)₁₋ₓ (mackinawite)	100	0	99	1
CdS	99	1	100	0
PbS	99	1	100	0
ZnS	100	0	100	0

[a] An asterisk (*) indicates metal sulfides that were not fully recovered by the combined HCl + HNO₃ extractions.

TABLE 2. Effect of Surface Area[a]

metal sulfide	series 1 HCl (%)	series 1 HNO₃ (%)	series 2 HCl (%)	series 2 HNO₃ (%)	surface area (m²/g)
CuS*, purchased	8	92	14	86	0.71
CuS, synthetic	32	68	12	88	46.31
NiS*, purchased	23	78	25	75	2.27
NiS, synthetic	55	45	42	58	8.49

[a] See footnote in Table 1.

medium. Calculations were based on standard calibrations, and detection limits were determined with replicate standards. All analyses were within detection limits. Acidic working standards were always freshly prepared, and glassware and plasticware were cleaned using established acid leaching procedures.

Results

Values in Table 1 are the percentage of metal extracted by each step in a sequential extraction scheme based upon HCl and HNO₃ digestions. Cases where even the concentrated HNO₃ failed to extract all the metal sulfide are marked by an asterisk (the washing steps and problems with rapid oxidation of sulfide minerals steps prevented us from measuring the dry weight of solid sulfide and calculating how much of the original metal sulfide was recovered through these extractions). The sulfide minerals of Cu, Ni, and Hg were predominantly extracted by HNO₃ and not HCl. Considering that even 250 mL of concentrated HNO₃ could not extract all of the solid CuS, Cu₂S, NiS, Ni₂S₃, and HgS, the percentage extracted by HNO₃ has to be considered a minimum. FeS, FeS₍₁₋ₓ₎, CdS, PbS, and ZnS were all predominantly extracted by HCl. No significant difference could be discerned between the 6.0 M HCl digestion and the 1.0 M HCl digestion for any of the metals.

Table 2 compares the extraction efficiency of these digestion schemes on coarser grained purchased CuS and NiS and finer grained synthetic CuS and NiS and demonstrates the potential role of grain size on the efficiency of these extractions. For NiS, HCl extraction efficiency increases with increasing surface area. CuS demonstrates the same trend for the 1.0 M HCl digestion but not for the 6.0 M HCl digestion. This discrepancy may result from the dissolution kinetics of CuS and NiS, as CuS is much less soluble in aqueous solution than is NiS, and the 1.0 M HCl extraction lasts for 24 h whereas the 6.0 M HCl extraction lasts for just 1 h.

Discussion

These experiments demonstrate that metal sulfide extractions are not as straightforward as many researchers believe them to be. HCl digestions cannot by themselves be used to predict the potential bioavailability of metals whose sulfides are not readily soluble in HCl. Although it is useful to use HCl-based approaches (e.g., AVS/SEM ratios) to attempt to predict the potential bioavailability of metals such as Cd, Pb, and Zn (whose metastable oxides and sulfides are fully soluble in HCl), current knowledge limits our ability to extend these predictions to metals such as Ni, Cu, and Hg. Speciation studies examining the role of sulfide minerals in trace metal diagenesis (18, 19) have shown that the fraction of Cu, Hg, and Ni extracted by HNO₃ (HNO₃-metal/HCl-metal + HNO₃-metal) generally exceeds the fraction of Fe in the same extract, often by a large margin. The opposite is generally true for Cd, Pb, and Zn. Based on careful studies of Fe (20), this has been interpreted to mean that Cu, Hg, and Ni are preferentially incorporated into pyrite while Cd, Pb, and Zn are excluded. Results from this study demonstrate that previous results are open to alternative interpretation and indicate that this extraction technique (16) may only assess a more general degree of sulfide mineral association.

Our results indicate that the nature of trace metal interactions with sulfide minerals cannot be generalized without first considering the chemistry of the individual metals. Most of the research into the role that sulfide minerals play during trace metal diagenesis have utilized extraction techniques that are not well documented with respect to trace metals. Consequently, no one has yet identified and measured the important mechanisms controlling the interactions between trace metals and sulfide minerals. Interpretation of field data will be limited until future research can solve this problem. The observed relation between extraction efficiency and surface area for NiS and CuS indicates that dissolution kinetics may be important in designing better extraction schemes. Additionally, the incomplete dissolution of Cu, Ni, and Hg sulfide minerals suggest that total mass of metal plays an important role as well. The extremely small concentrations of metals within natural systems imply that the metal sulfides exists in a much less crystalline state. It is quite possible that they do not exists as discrete mineral phases but rather as coprecipitates with iron. Thus, these findings should be considered as a "worst case scenario" with respect to our ability to predict metal "reactivity" within anoxic sediments. Future research needs to examine these problems and describe extraction methods that are more meaningful with respect to trace metals incorporated within sulfide minerals.

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