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Analysis of sulfides in the presence of ferric minerals by diffusion methods

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Abstract

Ferric minerals are commonly found in soils and sediments, especially in tropical areas. Previous studies have shown that ferric minerals in sediments can cause underestimation of acid-volatile sulfides (AVS). No reliable AVS analytical procedure has been recommended for modern sediments containing significant concentration of Fe(III). We evaluated the interference of acid-soluble ferric minerals on the analysis of sulfides using cold diffusion procedures and the effectiveness of two amendments, i.e., $SnCl_2$ and ascorbic acid (AA), respectively, to prevent the interference. The presence of acid-soluble ferric minerals caused various degrees of AVS underestimation depending on the level of acid-soluble Fe(III) and the nature of a sample. Addition of 2 ml 1 M AA to the sample effectively protects AVS from oxidation in the presence of 0.39 mmol acid-soluble Fe(III). Addition of 1 g $SnCl_2$ powder to the sample did not prevent the ferric interference on AVS. The presence of 0.39 mmol acid-soluble Fe(III) caused 10% and 35% loss of disulfides in a specimen pyrite, respectively, during an 18-h and a 48-h AVS diffusion procedure. The AA amendment also protected pyrite from oxidation in the presence of acid-soluble Fe(III) during a sequential diffusion procedure to separate AVS and disulfides. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Separation and quantification of inorganic sulfides in sediments, crucial steps to the study of sulfur cycle, can be accomplished by hot distillation or cold diffusion procedures. In a sequential hot distillation procedure, a cold solvent (e.g., acetone) is used first to extract elemental sulfur (ES) followed by hot 6 M HCl to separate acid-volatile sulfides (AVS), and finally, acidic Cr(II) solution to separate Cr(II)-reducible sulfide (CRS) (Wieder et al., 1985; Canfield et al., 1986). In a sequential cold diffusion procedure, cold 6 M HCl is used to separate AVS, followed by a cold acidic Cr(II) solution to separate disulfides (CRS), and finally, *N*,*N*-dimethylformamide (DMF) and Cr(II) to separate ES. Both hot distillation and cold diffusion procedures are specific and effective in the separation of organic and inorganic sulfides (Wieder et al., 1985; Canfield et al., 1986; Hsieh and Yang, 1989).

Previous studies have shown that in the presence of acid-soluble ferric minerals, AVS can be underestimated using the hot distillation procedure (Pruden

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and Bloomfield, 1968; Berner, 1974; Cornwell and Morse, 1987). The underestimation is caused by the dissolution of ferric minerals in strong acid, presumably allowing soluble Fe(III) to oxidize sulfide. To minimize oxidation of AVS by Fe(III) during the hot distillation procedure, addition of $SnCl_2$ to the mixture has been recommended (Pruden and Bloomfield, 1968; Berner, 1974; Cornwell and Morse, 1987). Close examination of the $SnCl_2$ amendment, however, revealed that $SnCl_2$ in a hot acid might also cause dissolution of some disulfides (Chanton and Martens, 1985; Cornwell and Morse, 1987; Rice et al., 1993). Other investigators also found that $SnCl_2$ in hot, phosphoric acid can recover, in various degrees, some organic-S, ES, disulfides and sulfate as sulfide (Reacke-Madsen, 1949; Kiba et al., 1955; Pirela and Tabatabai, 1988). The $SnCl_2$ amendment, therefore, is not recommended for the analysis of modern sediments (Rice et al., 1993). Currently, no reliable AVS method is available for modern sediments that contain significant amount of acid-soluble ferric minerals.

Ferric minerals are common weathering products of the earth crust (Schwertmann and Taylor, 1989). Ferric minerals are abundant in soils and sediments of many tropical areas (Horng et al., 1992). They are also found, almost ubiquitously, in soils and sediments of other areas (Schwertmann and Taylor, 1989). Most ferric minerals are quite insoluble in seawater or neutral freshwater and could be preserved in anoxic sediments along with sulfides for extended period of time (Roberts and Turner, 1993). Ferric mineral interference on AVS analysis of soils and sediments, therefore, may be quite common in tropical environments and may be more common than generally realized in other parts of the world.

The hot distillation procedure takes approximately 2–4 h to complete the separation of ES, AVS and CRS; up to four samples can be processed simultaneously. The cold diffusion procedure takes 84–96 h to complete the separation of AVS, CRS and ES, yet up to 60 samples can be processed simultaneously. The cold diffusion procedure is particularly suitable for handling a large number of modern sediment samples that need to be processed immediately and simultaneously. The labor and time savings of the diffusion procedure over the distillation procedure becomes more apparent as the number of samples

becomes larger. That is, although the whole diffusion process takes 84–96 h to complete, only a few minutes of attention is required for each sample (Hsieh and Shieh, 1997).

We initiated this study to investigate the interference of acid-soluble ferric minerals on AVS analysis of specimen sulfides and tropical sediments using the cold diffusion procedure. We also identified an effective amendment that can prevent the ferric interference on AVS analysis of modern sediments.

2. Materials

2.1. Ferric oxides and zinc sulfide

Ferric oxides/oxyhydroxides (will be referred to as ferric oxides hereafter, for brevity) were prepared by titrating 0.5 M $FeCl_3$ with 0.5 M NaOH to pH 7. The precipitate was separated from the solution and washed twice with distilled water through centrifugation. The precipitate was oven-dried, ground and stored in an airtight bottle. Chemical analysis (i.e., 0.5 g powder was extracted with 50 ml 6 M HCl overnight, filtered and determined by an atomic absorption spectrometer) indicated that the powder consists of 10.4 ± 0.8 mmol Fe/g, presumably all ferric. Zinc sulfide was prepared by diffusing H_2S into an alkaline Zn solution under a pure N_2 atmosphere using a diffusion apparatus described by Hsieh and Shieh (1997). The zinc sulfide precipitate was washed once with 2 M NaCl solution and twice with distilled water through centrifugation. The zinc sulfide was oven-dried, ground and stored in an airtight bottle. The zinc sulfide contains 10.1 ± 0.2 mmol S/g as determined by acid dissolution and iodometric titration of the soluble sulfide (American Public Health Association (APHA), 1976).

2.2. Pyrite and sediment samples

The pyrite sample was ground powder of a well-developed crystals of rock pyrite (courtesy of Y.N. Shieh, Purdue University, IN, USA) that contained 18.4 ± 0.3 mmol S/g (Hsieh and Yang, 1989; Hsieh and Shieh, 1997). The sediment samples were collected from the Dan-Shui River Estuary of Northern

Taipei, Taiwan and from a campus wastewater drainage ditch of the National Taiwan University (NTU), Taipei, Taiwan. The Dan-Shui River sediment contained 0.18–0.26 mmol Fe(III)/g and 0.04–0.07 mmol Fe(II)/g (dry weight basis) as determined by the 6 M HCl overnight extraction under a pure N_2 atmosphere followed by determinations of ferrous and ferric iron using ferrozine buffer (pH 7) and hydroxylamine (Lovely and Phillips, 1987). The NTU sediment contained 0.01 mmol Fe(III)/g and 0.02 mmol Fe(II)/g.

3. Experimental methods

The separation and determination of AVS, disulfide (CRS) and ES were conducted following the diffusion procedure described by Hsieh and Shieh (1997). Briefly, AVS, disulfide and ES were separated sequentially by 6 M HCl (18 h), acidic Cr(II) (48 h) and Cr(II) plus DMF (24 h), respectively, under a pure N_2 atmosphere, at ambient temperature $(25 \pm 3°C)$. The liberated H_2S was passively trapped in an alkaline Zn solution. The trapped ZnS was quantified by iodometric titration (APHA, 1976).

3.1. Influence of ferric oxides on ZnS analysis and the $SnCl_2$ and ascorbic acid (AA) amendments

About 3 mg of ZnS powder was placed into each of the eight 250-ml flasks. Four treatments with duplication were (1) 30 mg ferric oxides powder + 1 g $SnCl_2$ powder, (2) 30 mg ferric oxides powder + 2 ml 1 M AA, (3) 30 mg ferric oxides powder + 2 ml O_2-free water and (4) 2 ml O_2-free water (control). The ferric oxides and $SnCl_2$ powders were added to the flasks prior to purging with a pure N_2 gas. The AA and O_2-free water were injected after the flasks were purged with a pure N_2 gas. Fifteen milliliters 6 M HCl was then injected into each flask to liberate AVS. The flasks were allowed to sit at room temperature for 18 h. After 18 h, the alkaline–Zn traps were retrieved from the flasks and the sulfide collected was determined by iodometric titration (APHA, 1976). The CRS and ES diffusion procedure were immediately followed after the AVS procedure to determine disulfide and ES (Hsieh and Shieh, 1997).

3.2. Effect of ferric oxides on pyrite analysis

About 3 mg freshly ground pyrite powder were weighed into each of the eight 250-ml flasks. Four treatments with duplication were (1) 30 mg ferric oxides and 18-h AVS procedure, (2) 30 mg ferric oxides and 48-h AVS procedure, (3) 30 mg ferric oxides and 2 ml AA solution and 48-h AVS procedure, (4) control (pyrite powder only). Sequential separation of AVS, CRS and ES were carried out by the diffusion procedure at ambient temperature.

3.3. AA amendment on sulfide analysis from two sediments

Three grams of fresh sediment sample collected from the Dan-Shui River at 0–5 cm depth (0.26 mmol Fe(III)/g, dry weight basis) were placed into each of the four 250-ml flasks. The flasks were closed and purged with a pure N_2 gas. Two treatments with duplication were (1) 2 ml 1 M AA solution and (2) 2 ml O_2-free distilled water (control). Sequential AVS, CRS and ES diffusion procedures were followed. Similar experiments were also conducted on the Dan-Shui River sediment collected at 5–10 cm depth (0.18 mmol Fe(III)/g, dry weight basis) and the low ferric NTU ditch sediment. Additional treatment of 20 mg ferric oxides powder on the NTU ditch sediment was also included to determine the effect of different levels of acid-soluble Fe(III) on sulfide recoveries.

3.4. The effectiveness of AA to reduce Fe(III) after 48 h in 6 M HCl

A 10-mM ferric solution as $FeCl_3$ was prepared in O_2-free water. Equal amounts of 2 M AA and 12 M HCl solutions were mixed to generate a solution of 1 M AA in 6 M HCl. The AA/HCl solution was stored in a transparent bottle and a dark brown bottle, respectively, to simulate the lighted and dark conditions, because we suspected that light might have something to do with the reactions. After 48 h, 20 μl of the AA/HCl solution was added to 5 ml of the 10 mM ferric iron solution. The mixture was then diluted (1:9) with distilled water and the remaining Fe(III) in the solution was determined by the ab-

sorbance at 375 nm (Hsieh and Hsieh, 2000). The effectiveness of the aged AA solution to reduce Fe(III) was expressed as a percentage relative to that of a freshly prepared AA solution. The experiment was duplicated.

3.5. Statistical analysis

Statistical analysis of comparison of means was carried out using the procedure provided by the SAS PC-version computer software package (SAS Institute, 1990).

4. Results

4.1. Recovery of ZnS in the presence of ferric oxides

The average recovery of AVS from ZnS in the control (ZnS only, no ferric oxides) was 98.7% (Table 1). In the presence of 30 mg ferric oxides (0.31 mmol acid-soluble Fe(III)), the average AVS recovery was only 72%. The difference between the control and the ferric oxides-treated sample was highly significant ($p < 0.01$) indicating that the ferric oxides did interfere with the AVS analysis. With the AA amendment, the average AVS recovery in the presence of 30 mg ferric oxides was improved to 92.9%. The difference between the control and the ferric oxides with AA treatment was not significant ($p > 0.05$). With the $SnCl_2$ amendment, the recovery of ZnS in the presence of 30 mg ferric oxides was only 69%. The difference between the control and the ferric oxides plus $SnCl_2$ treatment was highly

significant ($p < 0.01$) indicating that $SnCl_2$ amendment did not prevent the ferric interference. The missing AVS was recovered mainly as ES, apparently being oxidized by Fe(III). Only 3–8% of the AVS was unaccounted for (Table 1).

4.2. Effect of ferric oxides on pyrite during a sequential diffusion procedure

After a normal overnight (18 h) AVS diffusion procedure and in the presence of 30 mg ferric oxides, the pyrite-S was underestimated by 9% ($p < 0.05$) as CRS in comparison to the control (Table 2). After a 48-h AVS diffusion procedure in the presence of 30 mg ferric oxides, the pyrite-S was underestimated by 35% ($p < 0.01$) as CRS in comparison to the control. The missing pyrite-S was not recovered as AVS or ES indicating that it might be oxidized to a form not recoverable by the diffusion procedure, possibly sulfur oxides. With the AA amendment, pyrite-S was fully recovered as disulfide after a 48-h AVS pretreatment in the presence of the ferric oxides.

4.3. Effect of AA on recovery of sulfides from sediments containing ferric iron

In the Dan-Shui sediments that contained high acid-soluble ferric iron (0.18–0.26 mmol/g), the AVS recoveries without the AA amendment were 36–54% less than ($p < 0.01$) those with the AA amendment (Table 3). In the NTU ditch sediment that contained low acid-soluble ferric iron (0.005 mmol/g), the average AVS recovery without the

Table 1
Effect of ferric oxides on the recovery of synthetic ZnS by the diffusion method
The values in parentheses indicate the range of two measurements. Although CRS was also determined in the experiment, none had been detected.

Sample weight (ZnS-S, mg)	Treatment	AVS		ES	
		mg	% Expected	mg	% Total S
3.26	Control	3.22(0.04)	98.7	Trace	Trace
3.21	FeOOH	2.31(0.16)	72.0	0.81	25.0
3.09	FeOOH + AA	2.87(0.14)	92.9	0.18	5.8
3.34	FeOOH + SnCl$_2$	2.28(0.22)	68.3	0.98	29.3

FeOOH: 30 mg; AA: 2 ml 1 M ascorbic acid solution.

Table 2
Effect of ferric oxides on the recovery of pyrite-S following a sequential AVS/CRS diffusion procedure
The values in parentheses indicate the range of two measurements.

Sample weight (Pyrite-S, mg)	Treatment	AVS	Disulfide		ES (mg)
			mg	% Expected value	
3.22	None	ND	3.17(0.07)	98.5	ND
3.08	FeOOH, 18 h	ND	2.81(0.11)	91.2	Trace
3.20	FeOOH, 48 h	ND	2.05(0.09)	64.1	Trace
3.45	FeOOH + AA, 48 h	ND	3.38(0.08)	98.0	ND

FeOOH: 30 mg; AA: 2 ml 1 M ascorbic acid solution; ND: not detected.

AA amendment was not significantly different ($p < 0.05$) from that with the AA amendment. When additional 20 mg ferric oxides powder was added to the NTU ditch sediment (combined acid-soluble Fe(III) was 0.21 mmol/sample), the average AVS recovery without the AA amendment was 39% less than ($p < 0.01$) that with the AA amendment. The missing AVS without the AA amendment was later recovered mainly as ES, an evidence of AVS oxidation by Fe(III) (Table 3). The disulfide (CRS) recoveries were not significantly different ($p < 0.01$) between the AA amendment and the control. Appar-

ently, during the regular (18 h) AVS diffusion procedure, the ferric iron had little effect on the analysis of disulfides of the sediments.

4.4. Effectiveness of AA to reduce ferric iron after being aged in 6 M HCl

After 48 h in 6 M HCl, AA lost 13% and 24%, respectively, of its effectiveness to reduce Fe(III) in the dark brown and transparent bottles. When freshly prepared, 1 mol of AA reduces 2 mol of ferric iron in acid solutions (Hsieh and Hsieh, 1997). The re-

Table 3
Effect of ascorbic acid (AA) amendment on the recovery of AVS, disulfide and ES of two sediments containing acid-soluble ferric minerals
The values in parentheses indicate the range of two measurements.

Sample weight		Fe(III)	Treatment	AVS	Disulfide	ES	AVS + ES
Wet	Dry						
g		mmol/g		μmol/g			
Dan-Shui 0–5 cm							
3	1.5	0.26	+2 ml AA	44.8(4.8)	37.4(5.8)	3.2(0.8)	48.0
3	1.5	0.26	+2 ml H$_2$O	20.8(4.4)	43.8(4.6)	24.3(2.5)	45.1
Dan-Shui 5–10 cm							
3	1.6	0.18	+2 ml AA	98.9(5.2)	48.6(3.2)	0.9(0.0)	99.8
3	1.6	0.18	+2 ml H$_2$O	64.3(5.9)	45.4(5.5)	32.6(4.6)	96.9
NTU ditch							
5	1.4	0.005	+2 ml AA	14.7(2.2)	9.5(2.8)	1.0(0.0)	15.7
5	1.4	0.005	+2 ml H$_2$O	13.8(2.1)	9.2(2.5)	1.8(0.2)	15.6
NTU ditch + 20 mg FeOOH each							
5	1.4	0.21[a]	+2 ml AA	15.0(2.0)	9.3(1.4)	3.7(1.1)	18.7
5	1.4	0.21[a]	+2 ml H$_2$O	9.1(2.1)	9.4(1.1)	6.2(0.8)	15.3

[a] Including the 20 mg FeOOH added to each sample.

sults indicate that 1 M AA solution retained most of its reducing power even after 48 h in 6 M HCl. A dark brown bottle is better than a transparent bottle to preserve the effectiveness of AA. The results indicate that at least 3–4 mmol Fe(III), or its equivalence, could be reduced by 2 ml 1 M AA during the diffusion procedure.

5. Discussion

This study indicates that the AVS diffusion procedure underestimated AVS in the presence of acid-soluble ferric iron. The missing AVS was mainly recovered as ES by the diffusion procedure, a result similar to that of the hot distillation procedure (Rice et al., 1993). The AA amendment of the diffusion procedure largely prevented the interference of acid-soluble Fe(III) on AVS in the synthetic ZnS while $SnCl_2$ did not. Although both AA and $SnCl_2$ can reduce Fe(III) in acidic conditions, the latter is much less soluble. Since only soluble Sn(II) can provide protection to AVS, the low solubility of $SnCl_2$ seriously limits its protective function in the diffusion procedure. Use of AA in the AVS diffusion procedure does not cause dissolution of disulfides (Hsieh and Shieh, 1997), probably because AA is a milder reducing agent than $SnCl_2$.

The concentration of acid-soluble Fe(III) in a sediment also affects the degree of interference on the AVS recovery. For example, at a 0.005-mmol/g Fe(III) level, the AVS in the NTU ditch sediment was not significantly underestimated while at a 0.21-mmol/g Fe(III) level (i.e., one order of magnitude higher than that of AVS), the AVS was underestimated by 39% (Table 3).

The presence of 0.27–0.39 mmol acid-soluble Fe(III) interfered little on the recovery of disulfide during a normal 18-h AVS diffusion procedure. Prolonging the AVS diffusion procedure beyond 18 h, however, may risk the chance of disulfide oxidation by Fe(III). Ferric interference on disulfide during a sequential cold AVS/CRS diffusion procedure may be more significant than that in a sequential hot AVS/CRS distillation procedure. Rice et al. (1993) reported that only 3–5% of pyrite could be oxidized by ferric iron in a hot distillation procedure, whereas this study found the interference was 9–35% using

the diffusion procedure. Hot AVS distillation usually is much shorter (< 1 h) procedure than a cold AVS diffusion (12–18 h). Longer contact with acid beyond 18 h increases the chance of disulfides being oxidized by Fe(III). AA amendment, however, protects disulfide from oxidation even in a prolonged (48 h) diffusion procedure. The results of this study indicate that the AA amendment of the diffusion procedure is an effective solution to the AVS analysis of modern sediments in the presence of significant amount of acid-soluble ferric minerals.

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