Biogeochemistry 1: 375–383 (1985).

The effects of heat and stannous chloride addition on the active distillation of acid volatile sulfide from pyrite-rich marine sediment samples

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Key words: iron monosulfide, acid volatile sulfide, pyrite, stannous chloride, sediments

Abstract. Iron monosulfides are important intermediates in pyrite formation, and are operationally defined as sulfides soluble in concentrated hydrochloric acid. A number of variations are currently employed in their isolation and quantification. In this study, the active distillation of acid volatile sulfide from sediment samples was studied to determine the effects of stannous chloride and heat. The addition of $SnCl_2$ caused recovery of sulfide to increase by 20% during distillations performed at room temperature. If distillations with $SnCl_2$ were then heated and boiled, recovery increased by up to 100%. Tests with 98% pure pyrite and elemental sulfur showed that these compounds were reduced to sulfide in solutions of 15% and 20% $SnCl_2$ in boiling 6N HCl, and that these reactions were grain size dependent. The compounds were not significantly reduced by solutions of $SnCl_2$ at room temperature, or by boiling 6N HCl not containing $SnCl_2$.

Introduction

Iron monosulfides are important intermediates in pyrite formation in marine sediments and exist in a variety of crystalline forms (Goldhaber and Kaplan, 1974). Operationally, iron monosulfides are defined as solid phase sulfides soluble in HCl whereas the iron disulfides, pyrite and marcasite are insoluble (Kaplan et al., 1963, Berner, 1964). Typical analytical procedures involve sediment acidification and evolution of the resulting H_2S via a nitrogen gas stream into a silver nitrate trap (Goldhaber and Kaplan, 1980). However, different investigators have carried out the acidification step under conditions where heat has been applied to the acid-sediment slurry (Berner, 1964, Berner et al. 1979), and at room temperature (Goldhaber and Kaplan, 1980, Westrich, 1983, Aller, 1977). Performing the distillation at room temperature may cause the underestimation of iron monosulfides because some well-crystallized forms (e.g. greigite) may not dissolve in a short period of time except when heat is applied (Berner, personal communication cited in Westrich, 1983).

Furthermore, the procedure is known to underestimate acid volatile sulfide because the acidification step also liberates ferric iron which reacts with sulfide to produce elemental sulfur (Berner, 1974, 1964). To prevent this oxidation and obtain quantitative recovery of iron monosulfides in the presence of iron oxides, Pruden and Bloodfield (1968) suggested that the acidification step be carried out in the presence of stannous chloride, which acts to reduce ferric iron and thus protects the dissolving sulfide.

The study presented below was conducted to examine the effects of stannous chloride addition on pyrite and elemental sulfur present in acidified sediment slurries. Previously, Pruden and Bloomfield (1968) had noted that pyrite reacted slowly with stannous chloride while elemental sulfur did not, but it was not clear from their discussion how much the reduction of pyrite might interfere with measurement of acid volatile sulfide in pyrite rich marine sediments.

Methods

Acid volatile sulfide was determined by active distillation of frozen sediment cakes which had been recovered from pore water pressure squeezers. The procedure followed was that of Goldhaber and Kaplan (1980). The outer brown oxidized portion of the frozen sediment was scraped away to reveal black sediment which was subsampled for sulfide and percent water measurements. Sulfide samples were put into large test tubes and flushed with deoxygenated nitrogen or argon. Subsequently anaerobic 6N HCl or 6N HCl containing 15 or 20% $SnCl_2$ (weight to volume) was added through a three-way stop-cock. The acid-sediment slurries were vortex mixed for one minute and the evolved sulfide was removed to a 0.1 M $AgNO_3$ trap with the inert gas stream. A trap containing pH 4 phosphate buffer was placed in line before the silver nitrate trap to protect it from chloride interference. Heat was applied by placing the acid-sediment slurry containing tubes in flasks containing water and heating them from below with a gas burner. The reactions were continued for one hour and the resulting AgS was collected on a pre-weighed nuclepore filter, dried, and weighed; Results were calculated as mg S per gram of dry sediment.

Similar measurements were performed on 98% pure (Goldhaber, 1983) pyrite from the Climax Molybdenum mine. When indicated, this pyrite was purified by boiling it in anoxic 6N HCl for 30 min and in anoxic acetone for 100 min. Elemental sulfur was prepared by the acidification of sodium thiosulfate. The elemental sulfur precipitate was collected on a filter, washed with water, and recrystallized from acetone.

A long term pyrite experiment was run in a round bottom flask equipped with a condensor, heating mantle and magnetic stirrer. This reaction was bubbled with inert gas and sulfide stripped away into a silver nitrate trap as described above.

Results and discussion

Figure 1 shows the results of parallel room temperature distillations of acid volatile sulfide made on a core with and without 20% stannous chloride in the HCl used for acidification. On average, 21.6% higher yields resulted from

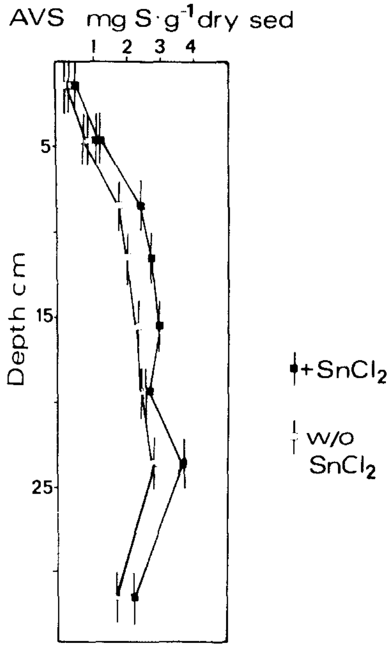

Figure 1. Results of acid volatile sulfide (AVS) distillations from a core collected on 2 May 1982 at Cape Lookout Bight, N.C., U.S.A. Closed Symbols represent measurements performed at room temperature and included SnCl$_2$, open symbols represent measurements which did not contain the reagent. Since these distillations were performed at room temperature, the lower yields in distillations without stannous chloride are interpreted to be due to oxidation of sulfide by ferric iron liberated by the acid treatment.

adding the reagent to the acid, presumably because this addition prevented the oxidation of sulfide by ferric iron which was liberated by the acid treatment. Recently, Howarth and Jørgensen (1984) found the oxidation of acid volatile sulfide by ferric iron to lower their recovery of labeled sulfur in the acid volatile phase by up to 7.8% in surficial samples and less in deeper samples.

Table 1 shows that in samples from Cape Lookout Bight, N.C., U.S.A. and from sediments of the North Carolina continental slope (900 m water depth) sulfide yields were increased dramatically when heat was applied after the distillations with SnCl$_2$ had run for an hour at room temperature or at 50°C. In the slope samples, yields of acid volatile sulfide increased by over 100% when the samples were held in boiling water baths, while in Cape Lookout samples they increased by 16 and 74%. The pyrite content (operationally defined as aqua regia soluable sulfur remaining after a room temperature or 50° distillation) at these stations was 112.3 ± 21.8 and 265.1 ± 46.8 μmoles S g dry sed^{-1} respectively. The additional amount of sulfide liberated upon boiling the samples with SnCl$_2$ represented 0.8 to 1.0% of the aqua regia soluable sulfur in the slope samples and 5 to 20% in the Bight samples.

Figure 2 presents the results of an experiment which tested the effects of

Table 1. Results of sulfide distillations of natural samples treated in series

Slope samples	Yield: μmoles S · g dry sed^{-1}	Yield: mg S · g dry sed^{-1}
H5-A (samples treated in series)		
warm (50°C) + $SnCl_2$	1.02	0.033
boiled + $SnCl_2$	1.09	0.035
Total yield	2.11	0.068
H5-B		
warm + $SnCl_2$	0.43	0.014
boiled + $SnCl_2$	0.85	0.027
Total yield	1.28	0.041
Cape Lookout Bight samples		
3–6 cm		
room temp. (25°) + $SnCl_2$	96.3	3.09
boiled + $SnCl_2$	15.1	0.48
Total yield	111.4	3.57
18–21 cm		
room temp. + $SnCl_2$	73.5	2.36
boiled + $SnCl_2$	54.6	1.75
Total yield	129.9	4.11

heat and $SnCl_2$ addition on distillations of 98% pure pyrite from the Climax mine, continental slope sediment and elemental sulfur. The successive hourly treatments referred to in the figure are listed in the figure caption. The results (Figure 2) show that sulfide was evolved at a much greater rate during the hot-acid, stannous chloride containing step (treatment 4) than in any of the preceding treatments, which suggests that pyrite and elemental sulfur may have been reduced. However, small quantities of sulfide were evolved in each treatment, possibly due to impurities in the pyrite or slight dissolution of the pyrite in the hot acid. Curiously, the purified pyrite appeared to show greater reactivity in the $SnCl_2$-free HCl than did the non-purified pyrite. This result may have been due to the removal of organic film coatings during the acetone extraction. More importantly however, both purified and non-purified pyrite reacted at least a factor of three times faster under the conditions of treatment 4 (hot acid $SnCl_2$) than in any other treatment (Figure 2).

The continental slope sample results are somewhat different from the other results in this figure since this sample was known to contain acid volatile sulfide at the initiation of the experiment. This sulfide was either released or oxidized during treatment 1. Treatment 2 (boiling without $SnCl_2$) showed that only traces of greigite were present in this sample. In treatment 4 a large amount of pyrite or elemental sulfur was reduced and stripped away. The rate of this release was similar to the rate of release in the preceding pyrite experiments (Figure 2) when the results were normalized to the amount of pyrite present in each experiment. The slope sediment experiment contained 4.5 g of sediment which had an aqua regia soluable sulfur content of 3.6 mg S · dry sed^{-1}. Thus this experiment contained 30% of the sulfur

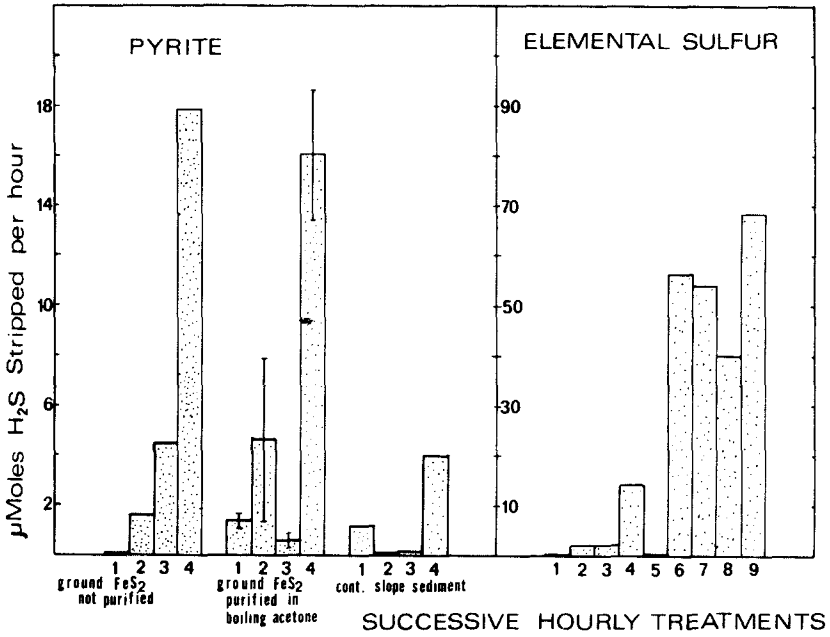

Figure 2. In pyrite and continental slope sediment experiments sequential hourly treatments were as listed in below. 100 mg of pyrite, 4.5 g of sediment and 10 mg of elemental sulfur was used in each experiment.

Sediment and pyrite experiments:

1. Material placed in 6N HCl and stripped with purified N_2.
2. Above reaction heated to boiling and stripping continued.
3. Reaction cooled. Stannous chloride added to make a 20% solution. Stripped for one hour at room temperature.
4. Above reaction heated to boiling and stripped for one hour.

Elemental sulfur experiment:

1. 10 mg of large crystals were placed in 6N HCl and stripped at room temperature for one hour.
2. The above reaction was gently boiled for one hour, stripping continued.
3. Reaction cooled to room temperature and stannous chloride added to make a 15% solution. Stripping continued at room temperature.
4. Reaction gently boiled for one hour, stripping continued.
5. Reaction cooled. 5 mg of ground sulfur crystals added. Stripped for one hour at room temperature.

6–9. Reaction boiled and stripped. $AgNO_3$ trap changed at hourly intervals.

contained in the 2 pyrite experiments (100 mg pyrite = 53.4 mg S) and released sulfide at approximately 25% of their rate.

In the slope sediment experiment of Figure 2, it is possible that some of the sulfide released in treatment 4 was elemental sulfur formed from acid volatile sulfide during acidification in step 1 (Figure 2) since the reactivity of elemental sulfur under the hot-acid reducing conditions is also shown in this

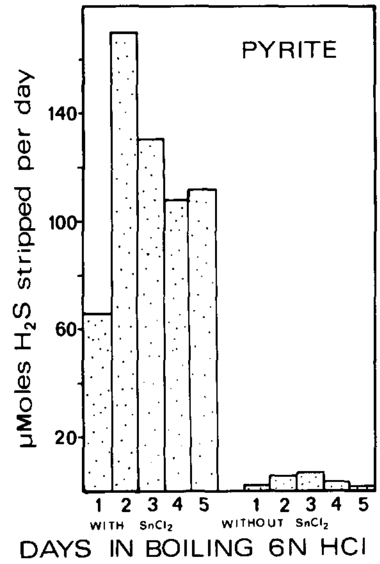

Figure 3. These results show significant pyrite reduction by stannous chloride in boiling HCl. With $SnCl_2$ 48% of the initial pyrite (72 mg) reacted. Without $SnCl_2$ only 2% of the pyrite was reduced to sulfide. Purified pyrite was used in this experiment.

figure. However, the results of Table 1 on a subsample of the same sediment showed that a hot $SnCl_2$ treatment following a warm $SnCl_2$ treatment liberated sulfur not reactive in the lower temperature reaction. Obviously this material was not greigite, as the hot acid treatment 2 of Figure 2 failed to liberate any greigite sulfur. The factor of 2 discrepancy observed between the warm and hot acid treatments of Table 1 could only have been caused by the reduction of some oxidized sulfur compound by $SnCl_2$ in the boiling acid. Since $SnCl_2$ was used in the first step of this experiment (Table 1) no elemental sulfur was formed upon initial acidification.

In the Bight samples (Table 1) the aqua regia soluable sulfur present was much more reactive to the boiling $SnCl_2$ solutions. This may have been due to a greater relative abundance of greigite and elemental sulfur, or the pyrite may have been more reactive due to grain size or crystal structure differences.

Figure 2 also shows that elemental sulfur is quite susceptible to reduction by $SnCl_2$ in boiling HCl. This result is in contrast to those of Pruden and Bloomfield (1968), who reported that elemental sulfur did not react under these conditions.

Figure 3 shows the results of boiling purified pyrite in 6N HCl for several days with and without 20% $SnCl_2$. In the presence of $SnCl_2$, 48% of the initial pyrite (72 mg) was converted to sulfide over the course of the experiment. Without the $SnCl_2$ only 2% of the initial pyrite reacted. This experiment conclusively demonstrated the reactivity of pyrite under the hot-acid stannous chloride conditions.

The inverse relationship between the reduction rate and particle size is demonstrated in the elemental sulfur results of treatments 5 and 6 (Figure 2) in which the addition of 5 mg of ground sulfur to the reaction system led to a dramatic increase in sulfide evolution. A similar experiment, run on ground pyrite which was qualitatively separated into three size fractions by successive decantation, showed that the relationship was inversely related to grain size in pyrite also. Unfortunately, no measurements were made of particle size. The experiment was conducted only to show that grain size was a factor in controlling pyrite reactivity.

Conclusions

Stannous chloride in boiling 6N HCl will reduce pyrite and elemental sulfur. If a natural sample is assayed for FeS by this method the result may be an overestimate. Pruden and Bloomfield (1968) provided no details, but noted this behavior for pyrite, but not for elemental sulfur. Troelsen and Jørgensen (1982) have shown that typical marine sediments have very low concentrations of elemental sulfur, so its reduction in the analysis of acid volatile sulfide may not lead to significant error. However, in marine sediments the principal form of sulfur is pyrite, so the reduction of a small percentage of the pyrite standing crop can cause serious error in the measurement of iron monosulfides.

If a natural sample contains recalcitrant FeS (which can only be dissolved by boiling HCl) in addition to ferric iron phases and pyrite, then there is at present no way to quantitatively separate the pyrite and the recalcitrant FeS in a single step. Because of ferric iron, stannous chloride should be used in the reaction, but if the reaction is heated to drive off all the FeS, then some pyrite will be reduced and driven off too. The method of choice for assaying for iron monosulfides may well depend upon how much greigite a sample contains. For recent marine sediments containing acid labile ferric iron, greigite and pyrite, the best method may be to add an additional procedure as did Howarth and Jørgensen (1984). In their study of subtidal sediments they performed a CS_2 extraction to measure elemental sulfur followed by a hot distillation without $SnCl_2$, followed by an additional CS_2 extraction to measure the elemental sulfur formed during the acidification step. The resulting residue can then be assayed for pyrite by either the aqua regia or chromium reduction technique. If a sample has little greigite, (for example, Kysing Fjord, H. Fossing, personal communication to Howarth and Jørgensen, 1984) than a room temperature distillation with $SnCl_2$ can be used.

Acknowledgements

We thank M. Goldhaber for supplying us with pyrite, R. Berner, D. Albert, and P. Crill for suggestions during the course of the study, and D. Burdige for criticism of the manuscript. Reviews by D. Postma, R. Howarth, and 2 anonymous reviewers were particularly helpful. Financial assistance was provided by the Marine Chemistry Program, Oceanography Section of the National Science Foundation through grant OCE 82-08666.

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