

SULFUR GASES PRODUCED BY THE DECOMPOSITION OF SULFIDE MINERALS: APPLICATION TO GEOCHEMICAL EXPLORATION

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ABSTRACT

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We have evaluated the potential application of sulfur gas analysis to exploration for buried sulfide mineral deposits by: (1) calculating by use of equilibrium thermodynamics, the relative abundances of gases that should be given off by decomposing sulfide minerals; and (2) determining experimentally the abundances of gases that are actually given off. The calculations indicate that the gases that should be given off by decomposing sulfide minerals are (in order of decreasing abundance) H_2S , COS , CS_2 , CH_3SH , $(CH_3)_2S_2$ or SO_2 or S_2 (depending on Eh and pH). In contrast, our experiments show that decomposing sulfide minerals evolve only CS_2 and COS , in order of decreasing abundance. Pyrite produces the largest amounts of sulfur gas. Moist (rather than saturated) and non-sterile (rather than sterile) conditions enhance gas generation from pyrite, although no large difference appeared between sterile and non-sterile experiments for other sulfide minerals. These experiments indicate that the sulfur gases CS_2 and COS could be useful indicators of buried metal sulfide deposits.

INTRODUCTION

The analysis of sulfur gases produced by the decomposition of metallic sulfide minerals could be used in geochemical exploration for concealed mineral deposits (Rose et al., 1979; Lovell et al., 1980). Several investigators have reported field measurements of H_2S and SO_2 over areas of sulfide mineralization (Elinson et al., 1970; Rouse and Stevens, 1971; Shipulin et al., 1973), but omitted full details of analytical procedures, making critical appraisal difficult. Carbonyl sulfide (COS) and carbon disulfide (CS_2) as well as H_2S have been reported over sulfide mineralization and geothermal areas

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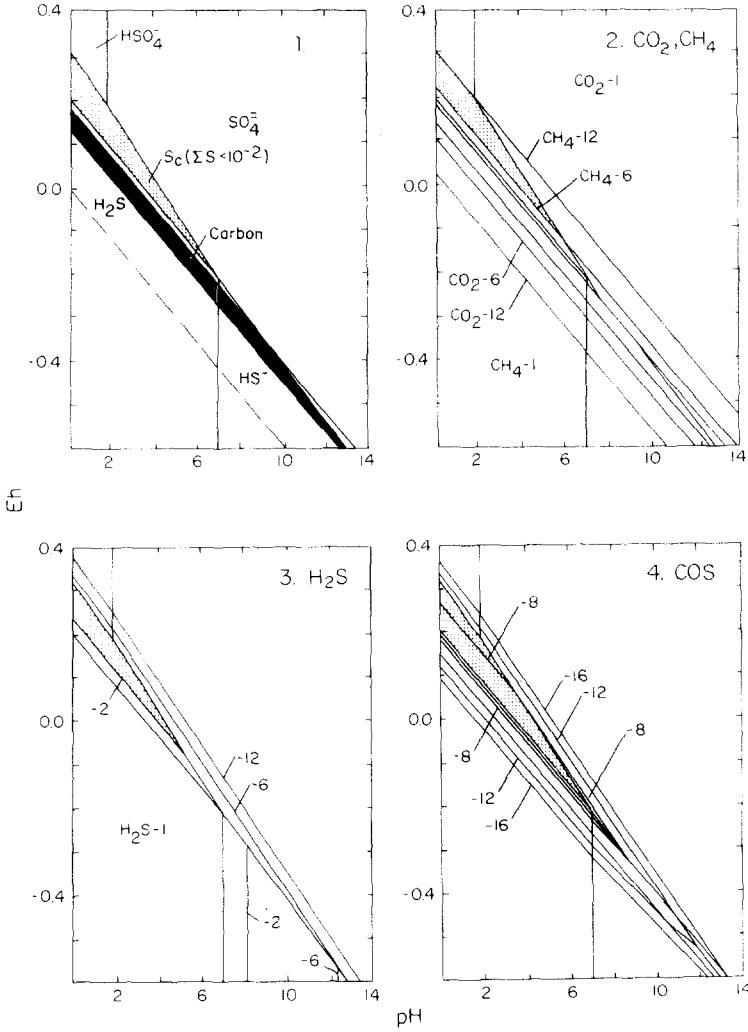


Fig. 1. Dominance fields for aqueous sulfur species. CO_2 is in equilibrium with all species above the carbon dominance field and CH_4 is in equilibrium with all species below the carbon field.

Fig. 2. Contours on logarithms of partial pressures of CO_2 and CH_4 . Limits of dominance fields of sulfur species from Fig. 1 are shown for reference.

Fig. 3. Contours on logarithms of partial pressures of H_2S . Limits of dominance fields of sulfur species from Fig. 1 are shown for reference.

Fig. 4. Contours on logarithms of partial pressures of COS . Limits of dominance fields of sulfur species from Fig. 1 are shown for reference.

(Hinkle and Kantor, 1978; Hinkle and Harms, 1978), although these gases were driven off collectors at high temperatures rather than being measured directly. In spite of these generally encouraging preliminary observations, sulfur gas analysis has not yet been widely applied in mineral exploration, in part because of the uncertainty over the gases that will be given off by decomposing sulfide minerals vs. those produced by microbial activity (cf. Zobell, 1963).

This study was designed to clarify these ambiguous aspects of sulfur gas geochemistry by: (1) prediction of the sulfur gases that would be generated by decomposing sulfide minerals, by use of equilibrium thermodynamic calculations (Garrels and Christ, 1965); and (2) direct measurement of sulfur gases generated by decomposing sulfide minerals in the laboratory. Our results show that sulfur gases generated by decomposing sulfide minerals can be distinguished from the other sulfur gases likely to be formed by microbial processes and thus offer the potential for being useful indicators of sulfide mineral deposits at depth.

EQUILIBRIUM CONCENTRATIONS OF SULFUR GASES

Results of the calculations

Figure 1 shows aqueous species of sulfur as well as the dominance fields for native or solid sulfur and for graphite. This figure serves as a reference to Figs. 2 through 10, which show the dependence on Eh and pH of the equilibrium partial pressures of CO_2 , CH_4 , H_2S , COS , SO_2 , CH_3SH , CS_2 , S_2 , and $(\text{CH}_3)_2\text{S}_2$ in contact with aqueous sulfur species in water at 25°C and 1 atmosphere total pressure. Free energies of formation used to calculate these diagrams were obtained from Wagman et al. (1968) and from Robie et al. (1978). These diagrams were calculated for systems with 10^{-2} molal total dissolved sulfur or the sum of the partial pressure of CO_2 and CH_4 equal to 10^{-1} atmospheres, or both. Activity and fugacity coefficients were neglected because at these concentrations negligible error is introduced.

The effect of changing the concentration of dissolved sulfur at $\text{pH} = 2.5$ can be seen in Fig. 11, which shows partial pressures of carbon and sulfur gases for total soluble sulfur of 10^{-1} , 10^{-2} , and 10^{-4} molal, and with partial pressure of CO_2 plus CH_4 equal to 10^{-1} atmosphere. For each gas, three concentration curves have been shown corresponding to the three soluble sulfur concentrations listed above. The field for carbon is also shown for the sum of partial pressures of carbon gases equal to 10^{-1} atm.

Implications of the calculations

Figure 11 shows that the relative order of abundance of sulfur gases under equilibrium conditions is H_2S , COS , CS_2 , CH_3SH , etc. Figures 2 through 11 show that the sulfur gases are most abundant at low to intermediate oxida-

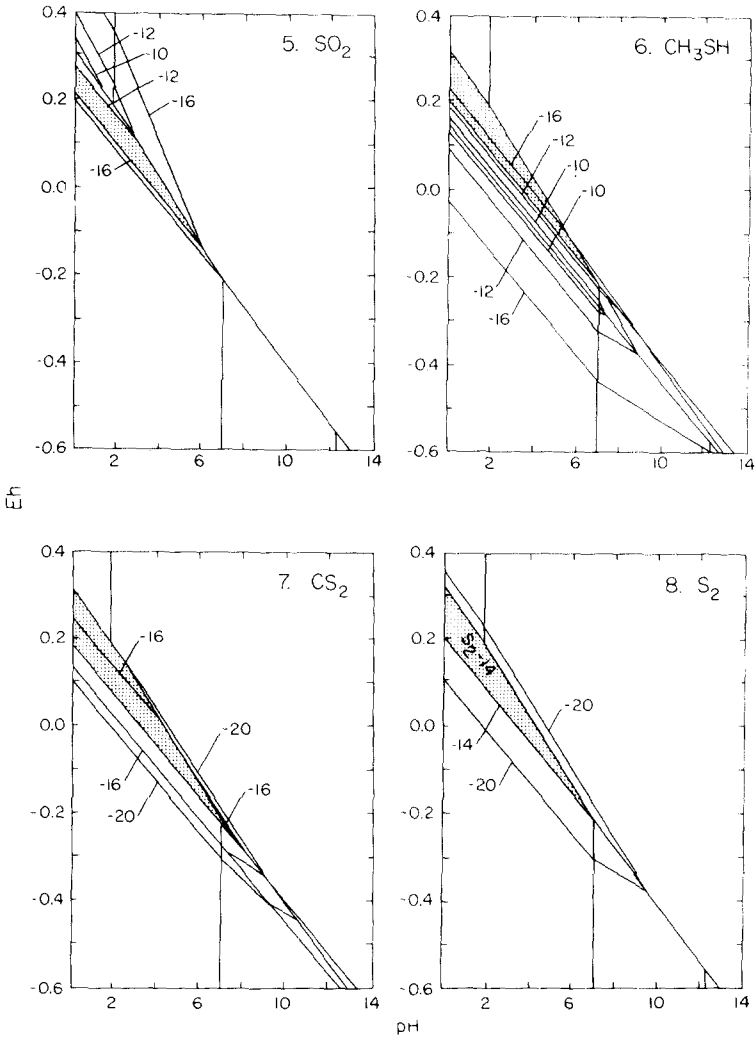


Fig. 5. Contours on logarithms of partial pressures of SO_2 . Limits of dominance fields of sulfur species from Fig. 1 are shown for reference.

Fig. 6. Contours on logarithms of partial pressures of CH_3SH (methyl mercaptan). Limits of dominance fields of sulfur species from Fig. 1 are shown for reference.

Fig. 7. Contours on logarithms of partial pressures of CS_2 . Limits of dominance fields of sulfur species from Fig. 1 are shown for reference.

Fig. 8. Contours on logarithms of partial pressures of S_2 . Limits of dominance fields of sulfur species from Fig. 1 are shown for reference.

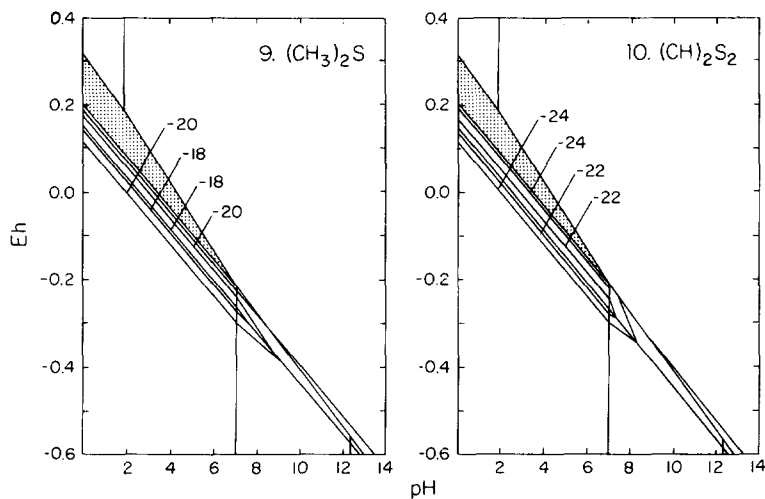


Fig. 9. Contours on logarithms of partial pressures of $(\text{CH}_3)_2\text{S}$ (dimethyl sulfide). Limits of dominance fields of sulfur species from Fig. 1 are shown for reference.

Fig. 10. Contours on logarithms of partial pressures of $(\text{CH}_3)_2\text{S}_2$ (dimethyl disulfide). Limits of dominance fields of sulfur species from Fig. 1 are shown for reference.

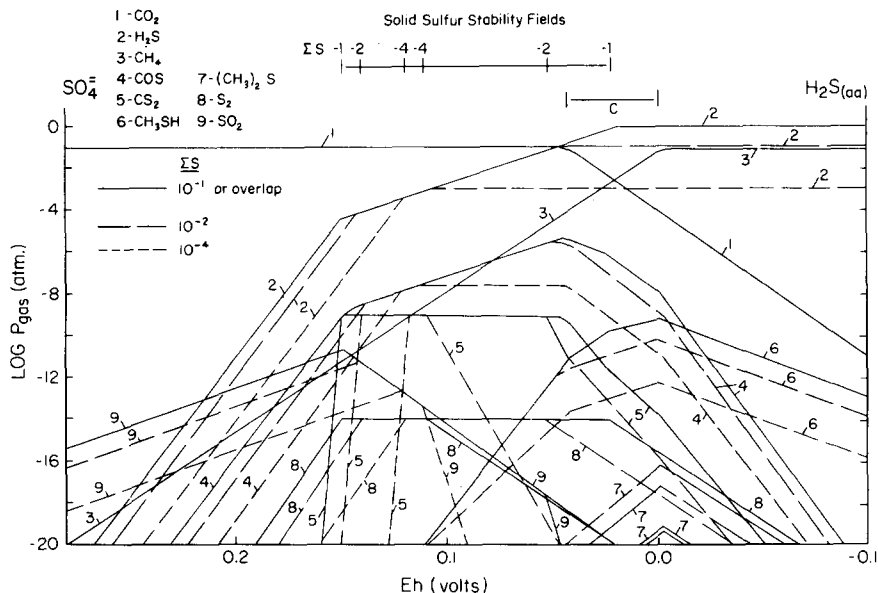


Fig. 11. Sulfur and carbon gases in equilibrium with aqueous sulfur species at $\text{pH} = 2.5$, $P_{\text{CO}_2} + P_{\text{CH}_4} = 10^{-1}$ atm, $\Sigma S = 10^{-1}$ m, 10^{-2} m, and 10^{-4} m.

tion potentials and neutral to low pH. Only H_2S should persist at significant partial pressures under very reducing conditions and at higher pH values. No sulfur gases should occur at significant equilibrium partial pressures under oxidizing conditions at intermediate to high pH.

Significant partial pressure, or concentration, as used here means a concentration in the gaseous phase high enough to be detected analytically. For sulfur gases, analyses are most easily done with a gas chromatograph, which can detect concentrations of sulfur gas as low as several parts per billion without preconcentration techniques. One ppbv (parts per billion gas, volume per volume basis) corresponds to a gas pressure of 10^{-9} atmosphere. Thus, on Figs. 2 through 11, the calculated partial pressure of any sulfur gas species would have to be greater than 10^{-9} atmosphere for it to be detected analytically. Evaluation of the diagrams in light of this restriction indicates that equilibrium concentrations of H_2S_g under the conditions of these calculations should be detectable over a relatively wide range of Eh and pH, and COS should be detectable over a restricted range of Eh and pH.

These results can be further interpreted in relation to the ranges of Eh and pH observed in nature and the calculated dominance fields of iron sulfides

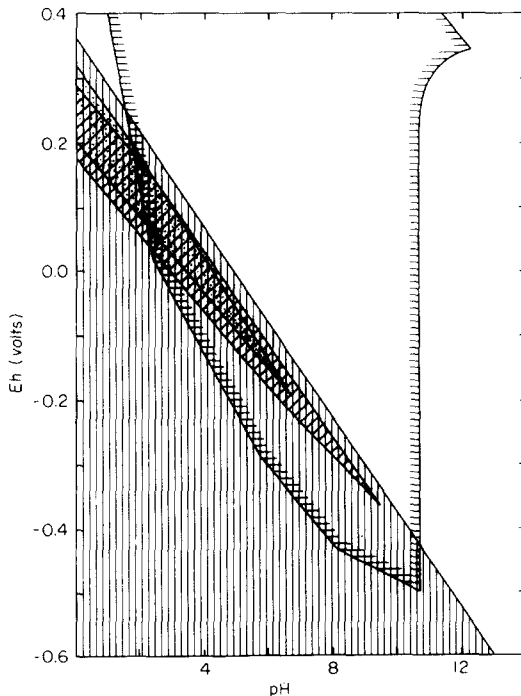


Fig. 12. Field in which $P_{\text{H}_2\text{S}}$ exceeds 10^{-9} atm (vertical ruling), field in which P_{COS} exceeds 10^{-9} atm (diagonal ruling), and field for solid sulfur (stippled) in relation to natural limits of Eh and pH (hachured line) (Baas-Becking et al., 1960). Total dissolved $\text{S} = 0.01$, $P_{\text{CO}_2} + P_{\text{CH}_4} = 0.1$ atm.

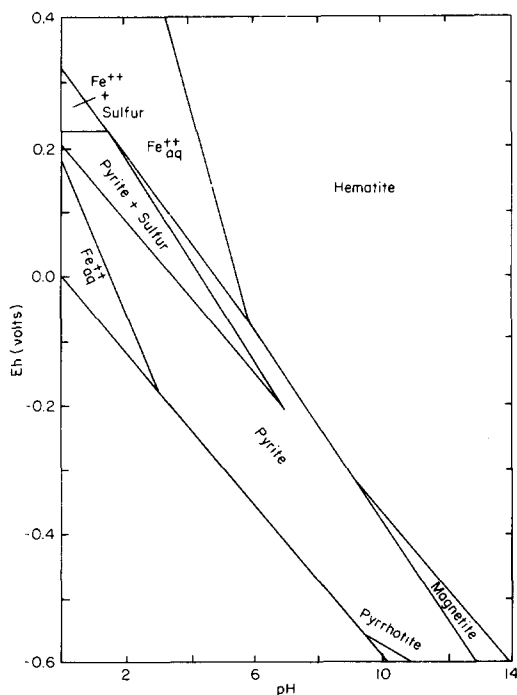


Fig. 13. Equilibrium relationship of iron sulfides and oxides in water at 25°C and 1 atm total pressure. $S = 10^{-2}$ m and total dissolved iron = 10^{-4} m. Siderite is not stable at $P_{CO_2} + P_{CH_4} = 10^{-1}$ atm for which this diagram was constructed.

and oxides. Baas Becking et al. (1960) have proposed limits of Eh and pH in the natural environment on the basis of numerous measurements of waters. Their suggested natural limits, which are superimposed in part on Fig. 12, further restrict the conditions under which sulfur gases can exist at equilibrium in nature. Figure 13 shows the calculated dominance fields of iron sulfides and oxides at a concentration of total dissolved iron equal to 10^{-4} molal and under the conditions previously specified for the sulfur gas diagrams. This figure shows the iron phases present in equilibrium with sulfur gases depicted in Figs. 2 through 10. Comparison of these figures with those previously presented suggests that the dominant iron-bearing phase that coexists with sulfur gases and aqueous sulfur species will be pyrite. Another possible phase, siderite, is not stable under the conditions considered in the calculations.

EXPERIMENTAL DETERMINATIONS OF SULFUR GASES

Introduction

Numerous authors have suggested that reactions involving sulfur at ambient temperature and pressure are very sluggish and that thermodynamic

equilibrium is seldom attained (Zobell, 1963; Goldhaber and Kaplan, 1974). For this reason, we conducted experiments designed to determine by direct measurement the sulfur gases that are generated by the decomposition of sulfide minerals. These experiments were performed under sterile and non-sterile conditions to evaluate biological effects on sulfur gas generation. Microorganisms are especially influential in mediating the transformation of sulfur from one valence state to another (Roy and Trudinger, 1970).

Experimental methods

In all experiments, 20 grams of 40–80 mesh crushed sulfide mineral (pyrite, chalcopyrite, galena, and sphalerite) were added to either of two types of glass vessels. The first type (Vessel A) has a volume of 280 ml and is separated into two compartments by a sintered glass filter disc of 5 micron porosity (Fig. 14). This vessel was used in experiments in which the sulfide mineral was kept moist with 10 ml of water but not saturated. Water was circulated through the crushed sulfide mineral via a peristaltic pump and Tygon tubing. The second type of experimental vessel (Vessel B) has a volume of 180 ml (Fig. 15) and was used in experiments in which the sulfide

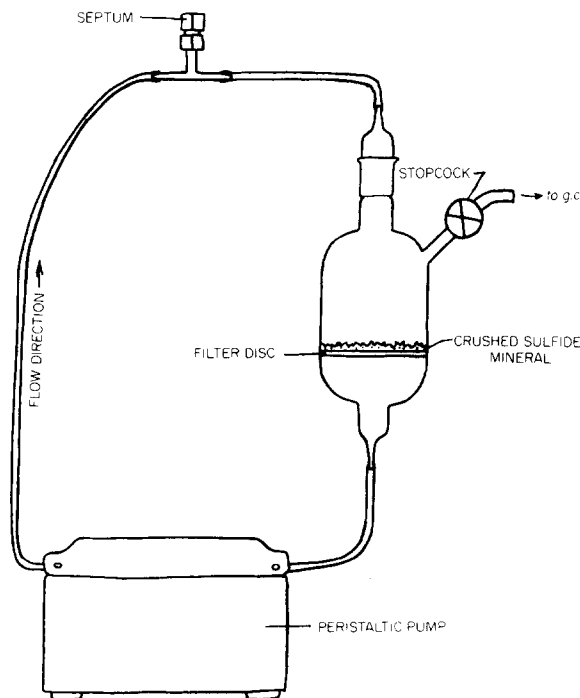


Fig. 14. Experimental vessel A. Note that water is pumped into top of vessel where it drips onto sulfide minerals on fritted glass filter disc. Gas (air, helium) pressure through the septum was used to force sample gas out the stopcock to the gas chromatograph.

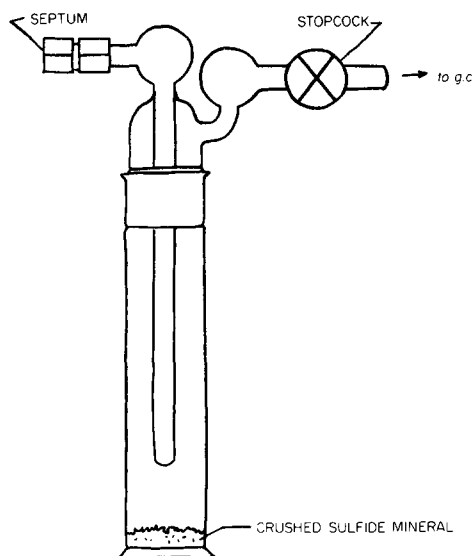


Fig. 15. Experimental vessel B. Sample gas was forced from this vessel in a manner similar to that used in vessel A.

mineral was allowed to decompose either dry or completely saturated with 10 ml of water. Gases were sampled from the headspaces of the experimental vessels through glass side stems connected to Teflon-plug stopcocks. A 20 ml injection of air through a septum connected to the experimental vessel forced a sample into the gas chromatograph for analysis. For sterile experiments the apparatus, minerals, and water were autoclaved, and precautions taken to preserve sterility during set-up and sampling. In a further effort to evaluate biological effects, one set of experiments was performed in which sterile and nonsterile soil (10 grams of 80 mesh dry soil) was added to 10 ml of water and 20 grams of 40–80 mesh crushed pyrite. The experimental vessels were sampled daily for a period of time ranging from 9 to 15 days. At the end of an experiment, Eh and pH of the final solutions in the experiments were measured on a Corning Model 10 pH meter. Experimental reliability was assessed by performing all experiments in duplicate.

The headspace samples and standards were analyzed on a Tracor 560 gas chromatograph with a Model 700A Hall electrolytic conductivity detector operated in the sulfur mode (Gluck, 1981). The column oven was temperature programmed from 50°C to 80°C. The column oven program held the temperature at 50°C for four minutes before heating at a rate of 15°C/min for two minutes. After the column had reached 80°C, the program maintained this temperature until all gases had been eluted. The reactor temperature for the detector was kept at 820°C and reactor base was held at 200°C. Helium carrier gas flow, air flow to the detector, and methanol

solvent flow were 25 ml/min, 50 ml/min, and 0.5 ml/min, respectively. A 180-cm glass column packed with 60–80 mesh Carbopack B treated with 1.5% XE-60 resin and 1.0% H_3PO_4 was used to separate the sulfur gases (Supelco, Inc., Bellefonte, PA). Under these operating conditions and using this column, all sulfur gases were separated from one another except dimethyl sulfide and dimethyl disulfide used as standards (Fig. 16). A Carle six-port switching valve (Carle Instruments, Inc., Fullerton, CA) was used to inject gas samples from a two ml glass sample loop onto the analytical column.

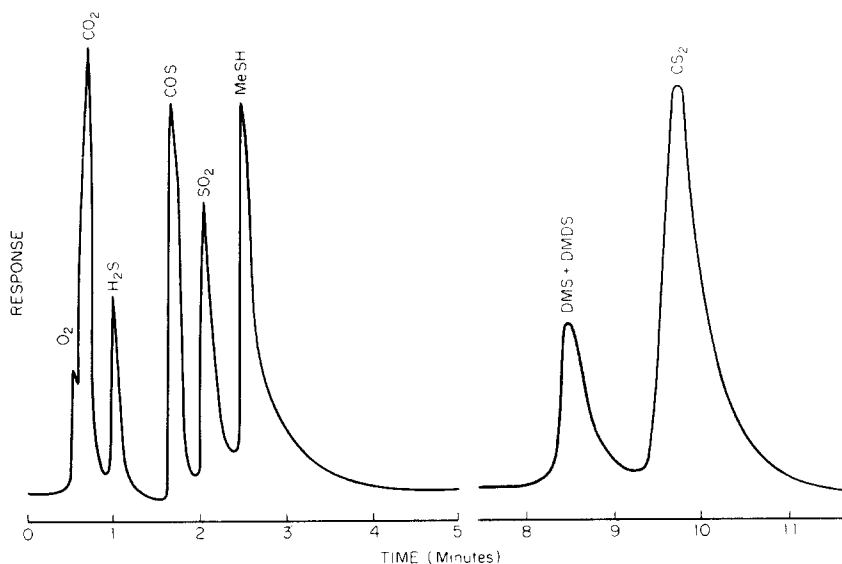


Fig. 16. Chromatogram of sulfur gases used as standards. Note broken time axis.

A permeation tube calibration system provided standard concentrations of H_2S , COS , SO_2 , CH_3SH (methyl mercaptan, MeSH), $(\text{CH}_3)_2\text{S}$ (dimethyl sulfide, DMS), and CS_2 . Permeation tubes were kept in a water bath held at $35^\circ\text{C} \pm 0.1^\circ\text{C}$ to insure constant permeation rates. Laboratory air provided continual flow over the permeation tubes. When standard concentrations were desired, laboratory air was first passed through a multi-bed absorbent filter (Farwell et al., 1979a) to remove trace water vapor or sulfur gas before passing over the permeation tubes. Diluent air flow was measured with a calibrated Gilmont flowmeter (VWR Scientific, Inc., Detroit, MI).

Experimental results

Table I lists our experiments and briefly summarizes our results. Eh and pH measurements of final solutions from the experiments are recorded in Table II. We further elaborate on the results of our experiments, in order of what we believe to be their significance, as follows:

TABLE I

Experiments performed

Sulfide mineral sample ¹	Conditions ²	Sulfur gases detected ³
Non-sterile pyrite	M	CS ₂ , COS
	S	CS ₂ , COS
Sterile pyrite	M	CS ₂ , COS
	S	CS ₂ , COS
Non-sterile chalcopyrite	M	CS ₂ , COS
	S	CS ₂ , COS
Sterile chalcopyrite	M	CS ₂ , COS
	S	CS ₂ , COS
Non-sterile galena	M	CS ₂ , COS
	S	CS ₂ , COS
Sterile galena	M	CS ₂ , COS
	S	CS ₂ , COS
Non-sterile sphalerite	M	CS ₂ , COS
	S	COS ₄
Sterile sphalerite	M	CS ₂ , COS
	S	COS ₄
Non-sterile pyrite + soil	S	CS ₂ , COS
Sterile pyrite + soil	S	CS ₂ , COS
Non-sterile pyrite ⁵	D	CS ₂ , SO ₂ , COS
Non-sterile galena ⁵	D	CS ₂ , SO ₂ , COS

¹ Each experiment was duplicated.

² 10 ml of pH = 6.5 water was added to the crushed sulfide mineral in which the mineral was kept either moist (M) with water in Vessel A or saturated (S) with water in Vessel B. Dry (D) experiments contained the sulfide which had been dried overnight at 110°C and then added to Vessel B.

³ Detection limits for COS = 5 ppb and for CS₂ = 30 ppb. Detection limits for H₂S, SO₂, and MeSH = 5 ppb and for DMS and DMDS = 30 ppb.

⁴ The fact that COS was detected and CS₂ was not probably reflects the higher detection limit of CS₂ and its low concentration in these experiments.

⁵ The experiments were discontinued after one day of analysis.

(1) The sulfur gases emitted by the decomposition of sulfide minerals under moist and saturated conditions are exclusively, in order of increasing abundance, CS₂ and COS. Figure 17 shows a typical chromatogram of a gas sample from a vessel containing pyrite. H₂S was conspicuously absent from this and all other analyses of gases formed by decomposing sulfide minerals.

(2) The greatest amounts of sulfur gas are produced by the decomposition of pyrite. Chalcopyrite also yields relatively large amounts of sulfur gas, but galena and sphalerite emit very little. Figure 18 shows this result for experiments conducted under saturated conditions. Under moist conditions, pyrite and chalcopyrite also yielded greater amounts of sulfur gas than galena and sphalerite.

TABLE II

Eh-pH measurements of final solutions from experiments

Experiment	Condition	Eh (mvolts)	pH
Sterile-1 pyrite	S	824	3.0
	M	894	3.5
Sterile-2 pyrite	S	790	3.7
	M	944	3.4
Non-sterile-1 pyrite	S	970	3.1
	M	974	3.2
Non-sterile-2 pyrite	S	914	3.4
	M	934	3.4
Sterile-1 chalcopyrite	S	524	5.7
	M	844	4.7
Sterile-2 chalcopyrite	S	459	5.3
	M	794	4.5
Non-sterile-1 chalcopyrite	S	504	5.5
	M	864	4.5
Non-sterile-2 chalcopyrite	S	534	5.7
	M	924	4.1
Sterile-1 galena	S	774	6.2
	M	704	4.8
Sterile-2 galena	S	724	6.0
	M	744	4.9
Non-sterile-1 galena	S	684	5.9
	M	734	5.6
Non-sterile-2 galena	S	704	6.0
	M	694	5.6
Sterile-1 sphalerite	S	804	4.7
	M	849	4.5
Sterile-2 sphalerite	S	834	5.3
	M	864	4.6
Non-sterile-1 sphalerite	S	854	4.8
	M	854	4.0
Non-sterile-2 sphalerite	S	884	5.0
	M	844	4.4
Sterile-1 pyrite + soil	S	674	6.4
Sterile-2 pyrite + soil	S	674	6.6
Non-sterile-1 pyrite + soil	S	674	6.5
Non-sterile-2 pyrite + soil	S	694	6.6

In view of the thermodynamic calculations the evolution of carbon-sulfur gases under sterile conditions is surprising. The carbon may have come from CO₂, which was not effectively excluded from reaction vessels. Because of the possibility of minute amounts of organic compounds having been adsorbed from laboratory air, or being present in the original pyrite, one

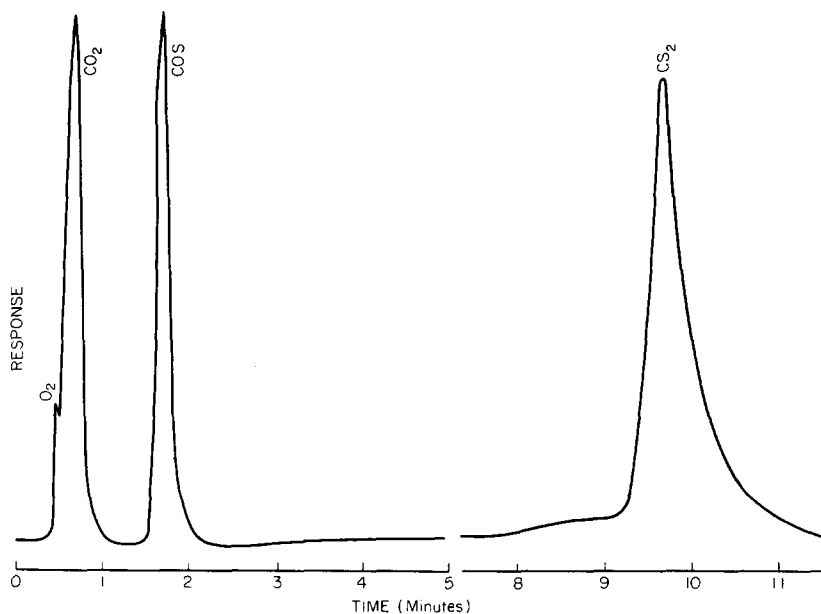


Fig. 17. Chromatogram of sulfur gases formed by the decomposition of pyrite under water saturated conditions.

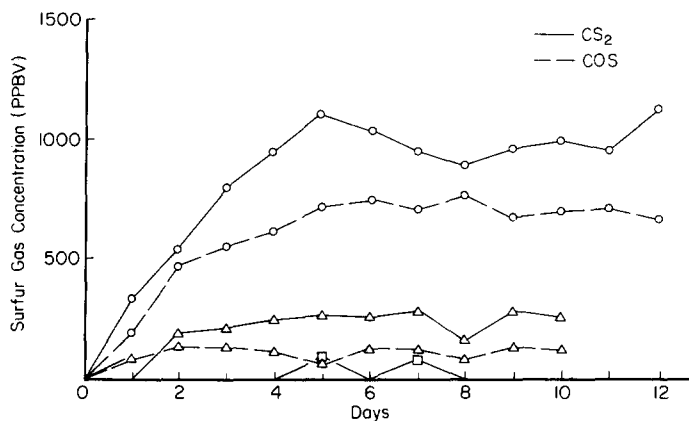


Fig. 18. Sulfur gas concentrations (parts per billion gas, volume per volume basis) from the decomposition of 20 grams of 40–80 mesh pyrite (\circ), chalcopyrite (Δ), and galena (\square) under water saturated conditions. Concentrations of sulfur gas less than 100 ppbv have not been plotted for the sake of clarity. The concentration of CS₂ in the galena experiment shown reached 100 ppbv only twice. Concentrations of CS₂ and COS never reached 100 ppbv in any sphalerite experiments.

experiment was performed using pyrite precleaned with heptane and methanol to remove natural organic material. This test showed no significant difference from otherwise similar experiments. The source of the carbon will be the subject of further investigation.

(3) The formation of CS_2 and COS from the decomposition of sulfide minerals occurs by inorganic reactions, as indicated by the generation of these gases under sterile as well as non-sterile conditions. Furthermore, in many experiments the amounts of sulfur gas produced by non-sterile experiments was not appreciably different from amounts produced by sterile experiments, which indicates that sulfur gases formed in the reactions are produced dominantly by inorganic processes. Figure 19 shows results of sterile and non-sterile experiments on pyrite and Fig. 20 shows results of similar experiments on chalcopyrite. Note that the patterns of sulfur gas evolution in sterile and non-sterile experiments are very similar. (If there were biological effects manifested in sulfur gas generation, a much greater rate of sulfur gas evolution in the non-sterile experiments would be expected.) Biological effects on sulfur gas generation cannot be completely ruled out, however. In saturated pyrite experiments, the average concentration of COS produced by the decomposition of sterile pyrite for each 12 days of analyses was less than the average concentration of COS in non-sterile ex-

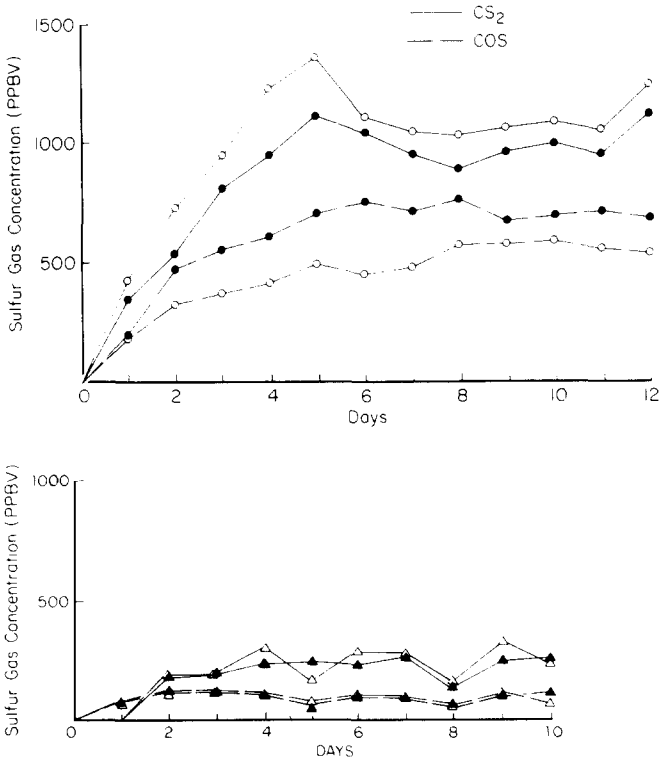


Fig. 19. Sulfur gas concentrations from the decomposition of 20 grams of 40-80 mesh pyrite in sterile (\circ) and non-sterile (\bullet) experiments under water saturated conditions.

Fig. 20. Sulfur gas concentrations from the decomposition of 20 grams of 40-80 mesh chalcopyrite in sterile (Δ) and non-sterile (\blacktriangle) experiments under water saturated conditions.

periments. The average concentration of COS in sterile experiments ranged from 49% to 77% of the average concentration in non sterile experiments. For CS₂, the average concentration in sterile experiments was less in 9 out of 12 days of analyses. For these 12 days, the average CS₂ concentration in sterile experiments ranged from 87% to 107% of the average CS₂ concentration in non-sterile experiments. These comparisons offer the best evidence suggesting biological effects on sulfur gas generation. Table III lists analytical data for both sterile and non-sterile experiments. Note that although the saturated pyrite experiments suggest biological interaction, other experiments do not. For example in the saturated chalcopyrite experiments, the average concentration of COS in sterile experiments was lower than the average concentration in non-sterile experiments only 6 out of 10 days of analyses. The average concentration of CS₂ in sterile experiments was less than the average concentration in non-sterile experiments only one out of 10 days. Thus, the data suggest but do not completely prove a biological enhancement of sulfur gas production.

In an effort to obtain more biologically active media than just the non-sterile sulfide mineral, non-sterile soil was added to pyrite. Corresponding sterile pyrite + soil experiments were also performed. Figure 21 shows the results of these experiments. Note the resemblances of the patterns of sulfur gas generation and the amounts of CS₂ in both experiments. This suggests that there was no significant biological effect on sulfur gas generation in this preliminary experiment. Curiously, COS was not generated in great amounts in sterile experiments. Comparison of Fig. 21 with Fig. 19 shows that levels of sulfur gas concentrations in the pyrite + soil experiments were

TABLE III

Data analyses of sterile and non-sterile experiments

Experiments	No. of days A < B	Range of values for ratio* A/B	No. of days C < D	Range of values for ratio* C/D
Saturated pyrite	12/12	0.49-0.77	9/12	0.87-1.07
Moist pyrite	12/15	0.49-1.25	11/15	0.59-2.61
Saturated chalcopyrite	6/10	0.60-1.54	1/10	0.93-3.15
Moist chalcopyrite	2/11	0.97-1.25	10/11	0.73-1.22
Saturated galena	5/12	0.33-1.00	2/12	0.33-1.00
Moist galena	0/10	1.00-1.75	0/10	2.0
Saturated sphalerite	4/9	—	—	—
Moist sphalerite	8/10	0.22-1.00	3/10	0.50-1.20
Saturated pyrite + soil	0/10	12.0-35.5	3/10	0.73-1.52

A: Average concentration of COS in sterile experiments.

B: Average concentration of COS in non-sterile experiments.

C: Average concentration of CS₂ in sterile experiments.

D: Average concentration of CS₂ in non-sterile experiments.

*Ratio computed for each day of analyses. Does not include values of zero in numerator or denominator.

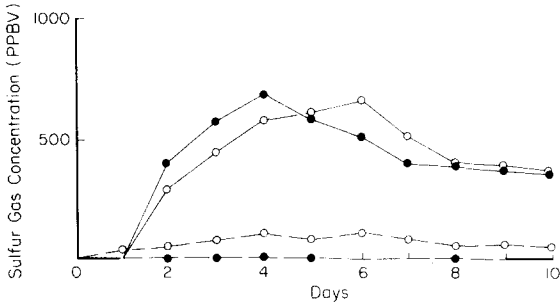


Fig. 21. Sulfur gas concentrations from the decomposition of 20 grams of 40–80 mesh pyrite + 10 grams of –80 mesh soil in sterile (○) and non-sterile (●) experiments under water saturated conditions.

lower than in the similar pyrite experiments shown in Fig. 19. We interpret this to mean either adsorption of the sulfur gases onto the soil or reaction of the gases with the soil.

(4) A greater amount of sulfur gas is produced when sulfide minerals are moist than when completely water saturated. Experiments conducted with moist sulfide mineral in Vessel A consistently produced more sulfur gas than experiments with water saturated sulfide mineral in Vessel B. It is noteworthy, however, that measureable amounts of sulfur gases were detected above completely submerged sulfide minerals.

(5) Sulfur dioxide was detected in completely dry samples of the sulfide minerals studied, but very small amounts of water inhibited SO_2 emissions.

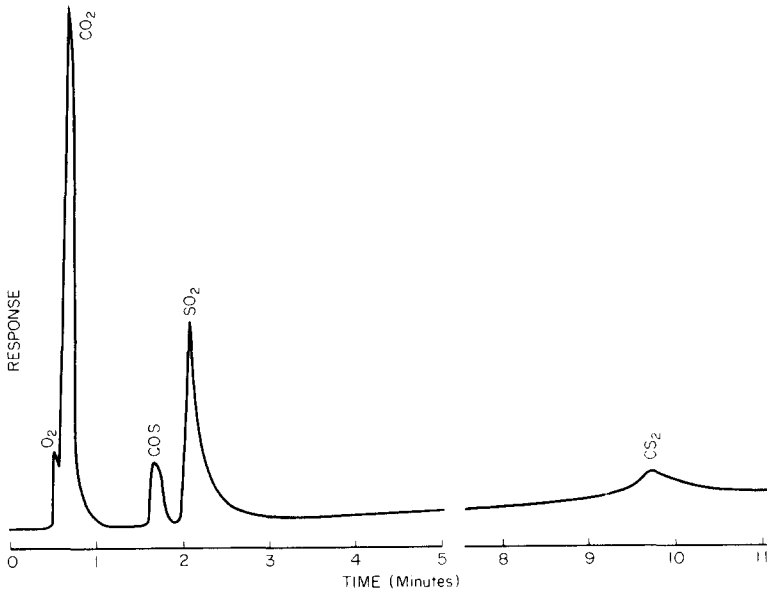


Fig. 22. Chromatogram of sulfur gases formed by the decomposition of galena under dry conditions.

Figure 22 is a chromatogram of a gas sample from Vessel B containing galena. This preliminary experiment was discontinued because we felt completely dry conditions are rare in environments in which sulfide mineral decomposits decompose. We noted that no SO_2 was detected when small amounts of water (less than one ml) were present. We interpret this to reflect the high solubility of SO_2 in water.

(6) If the sulfur gases evolve at a constant rate, concentrations in the head spaces of the reaction vessels should reach a steady value during the course of about two weeks because the daily sampling would eventually remove sulfur at the same rate. However, the approach to a steady state from this cause alone would be far less abrupt than that observed, indicating either that the rate of evolution decreases within the first 3 or 4 days, as would arise from diffusion through a thickening oxidized surface boundary layer on the mineral, or that sulfur gases are lost in other ways, such as by further oxidation of the gas to SO_2 .

DISCUSSION

Comparison of equilibrium thermodynamic calculations and experimental results

Our equilibrium thermodynamic calculations predict that the decomposition of sulfide minerals will at equilibrium produce, in order of abundance, H_2S , COS , CS_2 , etc. These calculations show also that only H_2S and COS should form at levels high enough to be detected analytically, and that the Eh-pH fields of importance for these gases are relatively restricted. These predictions show little resemblance to the actual distribution of sulfur gases observed to form by decomposing sulfide minerals. H_2S was not detected in any of the experiments. COS was formed in high enough levels to be detected analytically, as was CS_2 . Furthermore, as Fig. 23 illustrates, CS_2 and COS were formed in the experiments under oxidizing conditions at Eh and pH conditions far from those predicted in Figs. 4, 7, and 11 as being most nearly stable. This indicates that disequilibrium occurs in the experiments performed, even after periods as long as two weeks. Thus the calculated equilibrium concentrations of sulfur gases provide a basis for assessing the occurrence and magnitude of disequilibria in our systems, but do little to predict the sulfur gases likely to be generated in natural settings in which disequilibria are the rule.

The experiments indicate that sulfide mineral deposits can be expected to generate CS_2 and COS by the decomposition of sulfide minerals. The results also suggest that deposits containing pyrite will produce more gas than similar deposits that do not contain pyrite. The generation of CS_2 and COS when sulfide minerals are moist or completely saturated implies that they can be very useful indicators of sulfide mineral deposits under a variety of conditions. SO_2 was found to form from sulfide minerals in completely dry

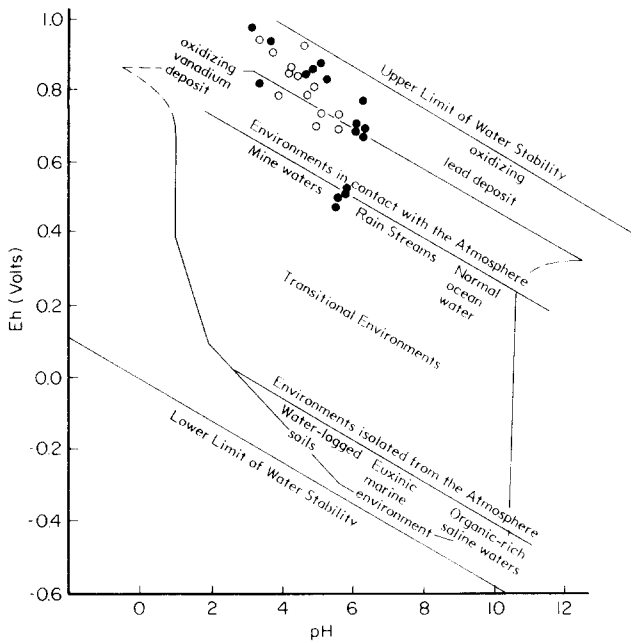


Fig. 23. Eh-pH measurements of final solutions from moist (○) and water saturated (●) sulfide mineral experiments in which CS_2 and COS were detected. Outlined area depicts natural limits of Eh and pH suggested by Baas Becking et al. (1960). Environments indicated are from Garrels and Christ (1965).

experiments, but the high solubility of SO_2 in water makes its detection unlikely in all but the most arid environments. Therefore, SO_2 is a much less favorable indicator of sulfide minerals than CS_2 and COS . For CS_2 and COS to be truly indicative of sulfide mineral decomposition, it must be shown that these gases are unlikely to be generated in great amounts by other processes in nature.

Other possible sources of sulfur compounds

Other possible sources of volatile sulfur compounds, in addition to sulfur gases that are produced by the decomposition of sulfide minerals, include the decomposition of sulfur-containing organic compounds in soil and microbial reduction of sulfate to produce H_2S . Volatile sulfur compounds are released from soils largely by microbial degradation of sulfur-bearing organic compounds. Volatile sulfur compounds formed from aerobic soils include dimethyl sulfide (DMS, $(\text{CH}_3)_2\text{S}$), dimethyl disulfide (DMDS, $(\text{CH}_3)_2\text{S}_2$), methyl mercaptan (MeSH , CH_3SH), and COS , whereas anaerobic soils produce DMS, DMDS, MeSH , CS_2 , and COS (Kadota and Ishida, 1972; Banwart and Bremner, 1974, 1975, 1976a, 1976b; Bremner and Steele, 1978.) Banwart and Bremner (1976) have demonstrated that when normally

aerobic soils are saturated with water, approximately 10 times more sulfur gases are emitted than before saturation. Out of 25 Iowa soils, Banwart and Bremner found only four soils that would emit detectable levels of sulfur gas under aerobic conditions and all of this was DMS. When the same soils were saturated with water, 14 of them released volatile sulfur, mainly as DMS (average 90%) with some COS, CS₂, MeSH, and DMDS. H₂S has never been detected when normally aerobic soils become saturated (Bremner and Steele, 1978). Anaerobic soils with abundant sulfide present will emit relatively large amounts of H₂S and CS₂ (Farwell et al., 1979b). Such soils may be expected in restricted environments such as tidal marshes and swamps. These observations indicate that the detection of anomalous levels of CS₂ and COS relative to the other sulfur gases such as DMS will be indicative of sulfide minerals at depth and thus are a powerful exploration tool, provided that the exploration survey is not carried out over anaerobic soils (eg. samples are collected below these soils if they are present).

The microbial reduction of sulfate and resultant production of H₂S is well established (Postgate, 1959; Zobell, 1963). Although H₂S was not shown to emanate directly from the sulfide minerals in our experiments, it might be argued that H₂S can be generated by microbial reduction of sulfate formed by an oxidizing mineral deposit. We think this is unlikely. The microbes responsible for the reduction of sulfate are strict anaerobes and can not tolerate high levels of acidity (Baas Becking et al., 1960; Goldhaber and Kaplan, 1974). Therefore, H₂S produced by sulfate reduction can only occur in environments that contain no dissolved oxygen have moderate to high levels of pH, and high concentrations of sulfate. Oxidizing mineral deposits in the subsurface are not likely to generate H₂S because of the associated high acidity and the oxygen content in ground water that is toxic to the microbes responsible for the reduction of sulfate. Furthermore, volatile H₂S will only be detected from environments with low levels of soluble iron and other cations capable of precipitating this reactive molecule (Ponnamperuma, 1972; Alexander, 1974). The high concentrations of metals in water near oxidizing mineral deposits further preclude the possibility of volatile H₂S generation from metallic sulfide deposits.

CONCLUSIONS

Equilibrium thermodynamic calculations predict that decomposing sulfide minerals will give off sulfur gases in the following order of abundance: H₂S, COS, CS₂, CH₃SH, (CH₃)₂S₂ or SO₂ or S₂. In contrast, experimental decomposition of moist and saturated sulfide minerals yields only CS₂ and COS, usually in that order of decreasing abundance. SO₂ was detected only over completely dry sulfide minerals. Of the sulfide minerals tested, pyrite generates the most gas, chalcopyrite the next largest amount and sphalerite and galena yield little or no gas. CS₂ and COS can also be derived from soils, but soils also yield large amounts of (CH₃)₂S₂, (CH₃)₂S and CH₃SH, which

are not given off by decomposing sulfide minerals. Thus, it appears likely that analysis of CS₂ and COS can be used to detect buried sulfide mineral deposits.

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REFERENCES

- Alexander, M., 1974. Microbial formation of environmental pollutants. *Adv. Appl. Microbiol.*, 18: 1-73.
- Baas Becking, L.G.M., Kaplan, I.R. and Moore, D., 1960. Limits of natural environment in terms of pH and oxidation-reduction potentials. *J. Geol.*, 68: 243-284.
- Banwart, W.L. and Bremner, J.M., 1974. Gas chromatographic identification of sulfur gases in soil atmospheres. *Soil Biol. Biochem.*, 6: 113-115.
- Banwart, W.L. and Bremner, J.M., 1975. Formation of volatile sulfur compounds by microbial decomposition of sulfur-containing amino acids. *Soil Biol. Biochem.*, 7: 359-364.
- Banwart, W.L. and Bremner, J.M., 1976a. Volatilization of sulfur from unamended and sulfate-treated soils. *Soil Biol. Biochem.*, 8: 19-22.
- Banwart, W.L. and Bremner, J.M., 1976b. Evolution of volatile sulfur compounds from soils treated with sulfur-containing organic materials. *Soil Biol. Biochem.*, 8: 439-443.
- Bremner, J.M. and Steele, C.G., 1978. Role of microorganisms in the atmospheric sulfur cycle. *Adv. Microbiol. Ecol.*, 2: 115-201.
- Elinson, M.M., Pashkov, Yu.N., Agabobov, G.M. and Ignat'eva, I.B., 1970. Research on gas aureoles around copper-molybdenum ore bodies. In: *Outline of the Geochemistry of Mercury, Molybdenum, and Sulfur in the Hydrothermal Process*. Nauka Publ., Moscow (In Russian). Engl. abstract in *Chem. Abstr.*, 74: item 5470.
- Farwell, S.O., Gluck, S.J., Bamesburger, W.L., Schutte, T.M. and Adams, D.F., 1979a. Determination of sulfur-containing gases by a deactivated cryogenic enrichment and capillary gas chromatographic system. *Anal. Chem.*, 51: 609-615.
- Farwell, S.D., Sherrard, A.E., Pack, M.R. and Adams, D.F., 1979b. Sulfur compounds volatilized from soils at different moisture contents. *Soil Biol. Biochem.*, 11: 411-415.
- Garrels, R.M. and Christ, C.L., 1965. *Solutions, Minerals, and Equilibria*. Harper and Row, New York, N.Y., 450 pp.
- Gluck, S.J., 1981. Performance of the Model 700A Hall electrolytic conductivity detector as a sulfur selective detector. *J. Chromatogr. Sci.*, 19: 235-238.
- Goldhaber, M.B. and Kaplan, I.R., 1974. The sulfur cycle. In: I.R. Goldberg (Editor), *The Sea*, Vol. 5. Wiley-Interscience, New York, N.Y., pp. 569-655.

- Hinkle, M.E. and Harms, T.F., 1978. CS₂ and COS in soil gas at the Roosevelt Hot Springs known geothermal resource area, Beaver County, Utah. *J. Res. U.S. Geol. Surv.*, 6: 571-578.
- Hinkle, M.E. and Kantor, J.A., 1978. Collection and analysis of soil gases emanating from buried sulfide mineralization, Johnson Camp Area, Cochise County, Arizona. *J. Geochem. Explor.*, 9: 209-216.
- Kadota, H. and Ishida, Y., 1972. Production of volatile sulfur compounds by microorganisms. *Ann. Rev. Microbiol.*, 26: 27-138.
- Lovell, J.S., Hale, M. and Webb, J.S., 1980. Vapour geochemistry in mineral exploration. *Min. Mag.*, pp. 229-239.
- Lucero, D.P., 1971. Performance characteristics of permeation tubes. *Anal. Chem.*, 43: 1744-1749.
- Ponnamperuma, F.N., 1972. The chemistry of submerged soils. *Adv. Agron.*, 24: 29-96.
- Postgate, J.R., 1959. Sulfate reduction by bacteria. *Ann. Rev. Microbiol.*, 13: 505-520.
- Robie, R.A., Hemingway, B.S., and Fisher, J.R., 1978. Thermodynamic properties of minerals and related substances at 298.15K and 1 bar (10⁵ pascals) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.*, 1452, U.S. Gov't Printing Office, Washington.
- Rose, A.W., Hawkes, H.E. and Webb, J.S., 1979. *Geochemistry in Mineral Exploration* Academic Press, New York, N.Y., pp. 490-517.
- Rouse, G.E. and Stevens, D.N., 1971. The use of sulfur dioxide gas geochemistry in the detection of sulfide deposits. *Ann. Meet. Am. Inst. Mining and Metall. Eng. New York*, March 3, 1971. *Abst. in Mining Eng.*, 1971: 22:65.
- Roy, A.B. and Trudinger, P.A., 1970. *The Biochemistry of Inorganic Forms of Sulfur*. Cambridge University Press, 400 pp.
- Shipulin, F.K., Genkin, A.D., Distler, V.V., Komarov, P.U., Malinovskii, E.P., Ozerova, N.A., Perel'man, A.I., Rekharskii, V.I., Roxanov, Yu. A., Filimonova, L.G., Chernyshev, V.F. and Elinson, M.M., 1973. Some aspects of the problem of geochemical methods of prospecting for concealed mineralization. *J. Geochem. Explor.*, 2: 193-235.
- Wagman, D.D., Evans, W.H., Parker, V.B., Harlow, I., Bailey, S.M. and Schumm, R.H., 1968. Selected values of chemical and thermodynamic properties. *National Bureau of Standards, Tech. Note 270-3*, 264 pp.
- Zobell, C.F., 1963. Organic geochemistry of sulfur. In: I.A. Breger (Editor), *Organic Geochemistry*. Pergamon, New York, N.Y., pp. 543-578.