Lawrence Berkeley National Laboratory

Recent Work

Title

GEOCHEMICAL AND COSMOCHEMICAL CYCLES INVOLVING SULFUR, SULFIDE, SULFITE, AND SULFATE

Permalink

<https://escholarship.org/uc/item/3jb1c1qd>

Author

Meyer, B.

Publication Date

1979-07-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA, BERKELEY, CA

Materials & Molecular Research Division

Submitted to Geochimica Cosmochimica Acta

GEOCHEMICAL AND COSMOCHEMICAL CYCLES INVOLVING SULFUR,
SULFIDE, SULFITE, AND SULFATE

B. Meyer, L. Peter and M. Ospina

July 1979

RECEIVED
LAWRENCE
BERKELEY LABORATORY

JUL 30 1979

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782*

LBL-9396 C.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

GEOCHEMICAL AND COSMOCHEMICAL CYCLES INVOLVING SULFUR, SULFIDE, SULFITE AND SULFATE

B. Meyer,* L. Peter and M. Ospina

Department of Chemistry
University of Washington
Seattle, Washington 98195

and
Molecular and Materials Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

Raman spectra of aqueous systems containing sulfur dioxide, elemental sulfur and sulfate indicate that the equilibrium between these species is catalyzed by elemental sulfur. Therefore, dynamic equilibrium can be expected under conditions prevalent on Venus, on Io and in epigenic sulfur deposits.

Sulfur, sulfuric acid, sulfur dioxide and water are in contact with each other in a variety of systems such as planetary atmospheres (Knollenberg, 1979; Nelson, 1978; Oyama, 1979; and Stewart, 1979), bio-epigenic sulfur deposits (Rucknick, 1979) as well as in industrial SO₂ recovery systems in coal burning power plants (Meyer, 1977).

The reactions and equilibria between elemental sulfur, sulfur dioxide, sulfuric acid and water can be summarized in two over-all equations:

At room temperature pure liquid SO₂ in contact with water is stable for many years. Likewise, elemental sulfur, water and sulfuric acid do not readily react. However, contrary to the widely held belief, this sulfur system is not inert. Priestley, 1790, heated sulfur dioxide in a sealed tube and observed the reaction over a period of several months and observed crystals which he identified as elemental sulfur. Boehm, 1882, studied reaction Eq. II. Bichowsky, 1922, studied both systems carefully and discovered that the reactions are reversible. Despite its importance and practical applications, the chemistry of this system has not been studied in more than half a century, even though Thode's pioneering work on isotope fractionization (Monster, 1965) stimulated interest among earth scientists (Ellis, 1971; Oana, 1966; Oana 1971; and Robertson, 1973). Unfortunately, thermodynamics are only of limited help, because of the uncertainty about the variety of states in which the various sulfur species can appear. We report here some qualitative data based on experiments in which we used high purity elemental sulfur and *in situ* observation techniques. Neither was available to earlier authors.

At room temperature, we confirm that the pure chemicals in reaction (I) do not react noticeably over a period of at least five years. However, in the presence of ammonia or other suitable catalysts, reaction commences within weeks (Meyer, 1979), elemental sulfur precipitates from tubes containing sulfur dioxide within one to three years, and the resulting

XBL 793-8912

Fig. 1. Raman spectra of sulfur systems: (a) SO_2 and H_2O after 27 hours at 80°C , (b) elemental sulfur and water after 24 hours at 190°C , (c) elemental sulfur, SO_2 and H_2O after 12 hours at 120°C , and (d) SO_2 and water with 0.1 M BaCl_2 after 12 hours at 25°C .

solution contains dithionate and other sulfur oxyacids as transient species, in addition to sulfate which constitutes the most stable end product. Figure 1a shows the Raman spectrum of the aqueous phase in a sealed pyrex tube 6 mm diam. x 6 cm containing 0.2 ml. H_2O and 0.2 ml liquid sulfur dioxide at 25°C after it was heated for 27 hrs at 80°C . The liquid remained clear and colorless. The broad peaks at 470 cm^{-1} and 800 cm^{-1} are characteristic for colloidal sulfur; the weak shoulders at 980 cm^{-1} and $1,050 \text{ cm}^{-1}$ are due to sulfate and bisulfate, respectively. The strongest peak at $1,144 \text{ cm}^{-1}$, due to unreacted sulfur dioxide, is not shown. The Raman band intensities can be evaluated by comparison with the internal water standard (Meyer, 1979) and correspond to 0.25 M sulfate and 0.30 M bisulfate solutions. Our observations are consistent with Bichowsky's equilibrium studies (Bichowsky, 1922), however, we have found that at 80°C reaction (I) proceeds about halfway in one day or less, while Bichowsky observed that at 312°C equilibrium in the opposite direction required at least three to seven days.

According to earlier work (Bichowsky, 1922) reaction (II) takes sixty days to reach equilibrium at 260°C. However, using high purity sulfur, we observed already after 24 hrs at 190°C the Raman spectrum in Figure 1b. The main peaks correspond to 0.01 M sulfate (SO_4^{-2}) and 0.03 M bisulfide (HS^{-1}). Upon further heating, the concentration of sulfuric acid does not increase rapidly, but hydrogen sulfide disappears, probably because sulfuric acid and elemental sulfur enter reaction (I), and the resulting sulfur dioxide consume hydrogen sulfide yielding elemental sulfur. The latter reaction is well known and was first described by Wackenroder, 1846. It involves the formation of intermediate species in intermediate oxidation states, including thiosulfate, tetrathionate, and other polythionates which are not stable under our conditions (Meyer, 1977). The existence of hydrogen sulfide in reaction (II) suggests that hydrogen sulfide might also occur as an intermediate in reaction (I). Unfortunately, this cannot be easily verified, because of the above mentioned Wackenroder reaction.

In further experiments, we added elemental sulfur to the reagents in reaction (I). Figure 1c shows the Raman spectrum of this system after it was kept for 12 hrs at 120°C. The peaks at 1,050 cm^{-1} and 980 cm^{-1} correspond to 1 M HSO_4^{-1} solution and 0.2 M sulfate. Obviously, this reaction is far faster than with SO_2 and water alone, as observed in the experiment shown in Figure 1a. We observed the behavior of this system over a range of temperatures between 20°C and 200°C, and conclude that it is catalyzed by solid as well as liquid elemental sulfur. We do not understand the mechanism, but the affinity between sulfur dioxide and elemental sulfur is consistent with our earlier observation that the solubility of elemental sulfur in SO_2 exhibits unusual temperature dependence (Meyer, 1971). The solubility and catalysis effects are both difficult to measure quantitatively, because sulfur undergoes a phase transition at 95°C and changes its allotropic composition above the melting point at 124°C. The catalysis appears to be inhibited by a factor of four in 1 M HCl, but this effect is due to the fact that HCl reduces the solubility of SO_2 in water.

In the last set of experiments we sealed SO_2 in a tube containing 0.1 M BaCl_2 . The solution promptly clouded at room temperature due to the formation of BaSO_3 which slowly precipitated. Figure 1d shows the Raman spectrum of the suspension after 9 hrs. The strongest peak at 960 cm^{-1} is due to barium sulfite. The peaks at 800, 490 and 460 cm^{-1} are due to orthorhombic elemental sulfur. The peak at 980 cm^{-1} corresponds to sulfate. Since barium sulfate has a solubility product (Cohen, 1940) of about 10^{-10} , our observation indicates that the sulfate ion concentration reaches at least 10^{-9} M in our system.

Our experiments show that the ubiquitous reactions (I) and (II) can proceed over a wide range of temperatures, and thus can take a dynamic role wherever elemental sulfur and sulfuric acid or sulfite and water are present. The Pioneer experiments (Knollenberg, 1979; Oyama, 1979; Stewart, 1979) have recently indicated that in the upper cloud layer in the atmosphere of Venus at 13°C, sulfuric acid (Knollenberg, 1979) and sulfur dust are present. In lower, hotter levels, 30 miles above the ground, sulfur dioxide (Oyama, 1979; Stewart, 1979) and water vapor at about 200°C are present. Our work suggests that under these conditions, a dynamic chemical equilibrium between the atmospheric layers can be expected. As a further example, the Voyager Project shows that active volcanoes exist on Io and that its surface contains elemental sulfur (Nelson, 1978). Again, the temperature of the effluents is high enough to enhance equilibrium among reaction products before they are condensed on the cold surface. Finally, it is quite possible that reactions (I) and (II) can participate in the formation of sulfur deposits under conditions found in bio-epigenic deposits.

Further study of these systems seems highly desirable, and would also directly benefit terrestrial pollution abatement processes, because the same chemicals occur in the liquor of several abatement systems used for capturing sulfur dioxide from coal burning electric power plants. In those systems a recurring key problem is the unreliable kinetics of conversion of sulfur (IV) to sulfate and/or elemental sulfur. It is amazing how little progress has been made in understanding the mechanism and the catalysis of reactions (I) and (II) since Priestley, 1970, or Wackenroder, 1846.

ACKNOWLEDGMENT

This work was partly supported by a contract from the Morgantown Energy Technology Center, U.S. Department of Energy.

REFERENCES

- BICHOWSKY F. R. (1922) Equilibrium in the reaction between sulfur dioxide and water. *J. Am. Chem. Soc.* 44, 116-134.
- BOEHM J. (1882) Die Reaktion zwischen Schwefel und Wasser. *Ber. Wien Akad.* 85, 554-557.
- COHEN E. and BLEKKINGH J.J.J.A. (1940) Einfluss des Dispersionsgrades auf die Löslichkeit Kristallisierter Stoffe. *Z. Phys. Chem.* 186A, 257-281.
- ELLIS A.J. and GIGGENBACK W. (1971) Sulphur hydrolysis in high temperature solutions. *Geochim. Cosmochim. Acta* 35, 247-260.
- KNOLLENBERG R.G. and HUNTEN D.M. (1979) Preliminary results of the Pioneer Venus nephelometer experiment. *Science* 203, 790-791.
- MEYER B. (1977) Sulfur, Energy, and Environment, Elsevier, Amsterdam.
- MEYER B., MULLIKEN B. and WEEKS H. (1979) The reaction of sulfur dioxide with ammonia. Phosphorus and Sulfur, in press.
- MEYER B., OSPINA M. and PETER L. (1979) Raman spectrometric determination of sulfur oxyacids. LBL Report 6599.
- MEYER B., AUSTIN J. and JENSEN D. (1971) Solubility of elemental sulfur in liquid sulfur dioxide. *J. Chem. Eng. Data* 16, 364-369.
- NELSON R.M. and HAPKE B.W. (1978) Spectral reflectivities of the Galilean satellites and Titan, 0.32 to 0.38 micrometers. *Icarus* 36, 304-329.
- OANA S. and ISHIKAWA H. (1966) Sulfur isotopic fractionation between sulfur and sulfuric acid in the hydrothermal solution of sulfur dioxide. *Geochem. J.* 1, 45-50.
- OANA S. and MIZUTANI Y. (1966) Sulfur isotopic fractionation between hydrogen sulfide and sulfur dioxide formed by the $4S + H_2S = 3H_2S + H_2SO_4$ reaction. *Symp. Geochem. Soc. Japan*. Nagoya.
- OYAMA V.I., CARLE G.C., WOELLER F. and POLLACK J.B. (1979) Venus lower atmospheric composition: analysis by gas chromatography. *Science* 203, 802-803.
- PRIESTLEY J. (1790) Experiments and Observations on Different Kinds of Air and Other Branches of Natural Philosophy, Vol. VI, pg. 333, J. Johnson, London.
- ROBERTSON B.W. (1973) Sulphur isotope equilibrium during sulphur hydrolysis at high temperature. *Earth Planetary Sci. Letters* 18, 443-450.
- RUCKMICK J.C., WINBERLY B.H. and EDWARDS A.F. (1979) Classification and genesis of biogenic sulfur deposits. *Econ. Geol.* 74, 469-474.
- STEWART A.I., ANDERSON D.E., Jr., ESPOSITO L.W. and BARTH C.A. (1979) Ultraviolet spectrum of Venus: initial results from the Pioneer Venus orbiter. *Science* 203, 777-778.
- WACKENRODER H. (1846) Ueber eine neue Säure des Schwefels. *Arch. Pharm.* 97, 272-290.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720