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Sulfur speciation in hydrous experimental glasses of varying oxidation state: Results from measured wavelength shifts of sulfur X-rays

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ABSTRACT

The geochemical behavior of sulfur may be affected by magmatic oxidation state because sulfur has the capacity to occur in multiple valence states. We have used the focusing geometry of an electron microprobe to measure the wavelength of S*Kα* X-rays [λ(S*Kα*)] from hydrous experimental melts synthesized at oxygen fugacities that range from near the iron-wüstite buffer to the magnetite-hematite buffer. Comparison of λ(S*Kα*) for sulfur dissolved in experimental melts with λ(S*Kα*) for FeS and $CaSO_4$ indicates that the proportion of dissolved sulfur present as sulfate increases, as might be expected, with increasing oxygen fugacity (f_{O_2}). At oxidation states 2 or more log f_{O_2} units above the fayalite-magnetite-quartz (FMQ) equilibrium, significant amounts (>50%) of sulfur are present as sulfate species in the melt. The change from sulfide-dominant to sulfate-dominant speciation occurs over the range of oxygen fugacity between the FMQ equilibrium and 2 log f_{O_2} units above FMQ (=FMQ + 2). In natural melts that have equilibrated at or below FMQ + 1, sulfur is probably present mainly as S^{2-}, or in the case of hydrous magmas, as HS^-, as has been suggested by others.

INTRODUCTION

Volcanic rocks contain measurable quantities of sulfur present as both sulfide and sulfate (Ricke, 1960; Schneider, 1970; Puchelt and Hubberton, 1980; Sasaki and Ishihara, 1979; Ueda and Sakai, 1984; Sakai et al., 1982, 1984). Ricke (1960) has also shown that sulfide and sulfate may be found in most common igneous minerals in concentrations at the several parts per million level. The relative proportions of sulfide and sulfate in analyzed rocks vary considerably, yet the effects of pressure, temperature, oxidation state, and melt composition on the redox state of sulfur in magmas remain poorly understood. In this paper we describe measurements of the wavelength of S*Kα* [λ(S*Kα*)] radiation from glasses synthesized at oxygen fugacities that range from relatively reducing (near the iron-wüstite buffer) to highly oxidizing (magnetite-hematite buffer). Our results provide new information concerning the effects of magmatic oxidation state on the relative proportion of dissolved sulfur present as sulfate and the possible effects of sulfur speciation changes on the geochemical behavior of sulfur.

Previous studies have shown that the wavelength of S*Kα* radiation in different compounds is sensitively dependent on the local electronic environment of sulfur in the compound of interest (Faessler and Goehring, 1952; Faessler and Schmid, 1954; Wilbur and Gofman, 1966; Chappell and White, 1968; Connolly and Haughton, 1972). Variations in the wavelength of S*Kα* radiation are directly related to changes in the oxidation state of sulfur because of the higher bond energies associated with oxidized sulfur species. These higher bond energies are reflected in the shorter wavelength of S*Kα* X-rays from oxidized sulfur. The work of Connolly and Haughton (1972) shows that sulfur in basaltic melt equilibrated at low oxygen fugacity is present mainly as S^{2-}. Little is known, however, about the speciation of sulfur at oxidation states greater than the FMQ buffer. Although the significance of near-surface oxidation remains to be evaluated (e.g., Christie et al., 1986) oxidation states greater than FMQ may be appropriate for many calc-alkaline magmas (Carmichael et al., 1974; Haggerty, 1976; Gill, 1981).

EXPERIMENTAL METHODS

Details of the experimental techniques used to make the glasses examined in this study are given in Carroll and Rutherford (1985, 1987). Reference samples with sulfur of known valence state include synthetic FeS (S^{2-}), natural anhydrite ($CaSO_4$; S^{6+}), and a natural sulfur-bearing meionite scapolite (mainly S^{6+}; Jarosewich et al., 1979).

Measurement of λ(S*Kα*) was accomplished using the focusing geometry of a three spectrometer Cameca electron microprobe. A PET crystal was used on each spectrometer so that three independent measurements of the S*Kα* wavelength shift could be determined at one time. For each unknown measured, the wavelength of S*Kα* radiation from synthetic FeS was also determined, and all wavelength shifts reported are given relative to FeS. Operating conditions were varied according to the concentration of sulfur in the sample analyzed. Conditions for the experimental glasses (0.05 to 0.3 wt% S) were 15 keV accelerating voltage, 30–40-nA beam current, 10–30 μm beam diameter, and 60–200-s

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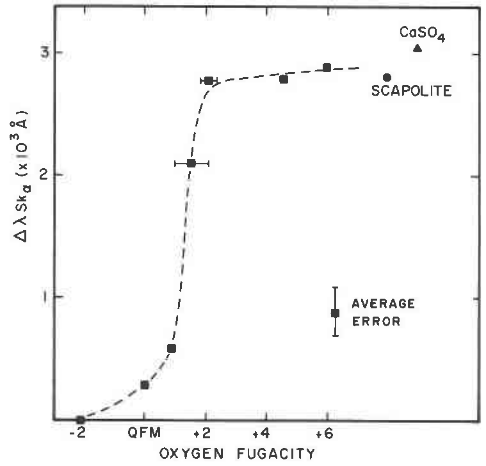

Fig. 1. Diagram showing the change in Δλ(S*Kα*) (× 10^3 Å, relative to FeS) as a function of experimental oxygen fugacity. Oxygen fugacities are shown relative to the synthetic fayalite-magnetite-quartz (FMQ) experimental buffer; thus +1 indicates an f_{O_2} that is 1 log unit more oxidizing than FMQ. Also shown are Δλ(S*Kα*) values for a sulfur-bearing meionite scapolite and anhydrite ($CaSO_4$). The estimated maximum error on each measurement, based on replicate measurements, is ±0.00020 Å.

counting time per spot. For the reference samples of FeS, anhydrite, and scapolite, the microprobe operating conditions were 15 keV, 20–40 nA, 5–10-μm beam diameter, and 15–60-s counting times. Once the approximate peak position was determined, a step-scan was made to include the peak and background. For each point in the step-scan the spectrometers were moved 0.00010 or 0.00005 sin θ units, with the smaller steps being taken over the central portion of the spectrum and covering the sin θ range corresponding to the peak width at half-maximum intensity.

The accumulated counts vs. sin θ data were fitted and smoothed using a modified Gaussian function and then plotted. Peak centers were measured at both one-half and two-thirds of the maximum peak height. The λ(S*Kα*) values from these two measurements, derived through the use of Bragg's law, were well within the estimated precision of the method for all cases, and the average value was used in calculating wavelength shifts. Each analysis session included measurement of λ(S*Kα*) for FeS before and/or after analysis of an experimental glass. Comparison of wavelength-shift values [Δλ(S*Kα*)] determined with each of the three spectrometers and duplicate analyses during different working sessions indicate that the peak-shift measurements quoted in this paper are reproducible to within approximately 0.00020 Å.

RESULTS

The conditions of synthesis for the glasses examined in this study and the measured wavelength shift of S*Kα* X-rays for each sample are given in Table 1. All wavelength shifts are reported relative to λS*Kα* from synthetic FeS. In Figure 1, the wavelength shifts are plotted as a function of the oxygen fugacity at which the experimental glasses were equilibrated. Oxygen fugacities in this diagram are given relative to the FMQ synthetic buffer curve, e.g., FMQ + 1 corresponds to 1 log f_{O_2} unit above the FMQ equilibrium.

The most notable result of the peak-shift measurements shown in Figure 1 is the dramatic increase in Δλ(S*Kα*) over the small range of oxygen fugacity between FMQ and FMQ + 2. Also shown in Figure 1 are the measured wavelength shifts for crystalline anhydrite and a sulfate-bearing meionite scapolite (Jarosewich et al., 1979). The peak-shift measurements show that sulfur in scapolite is present mainly as sulfate, in agreement with the findings of Chappell and White (1968). Anhydrite, as indicated by

TABLE 1. Synthesis conditions of experimental samples and measured S*Kα* peak shifts

Run	*T* (°C)	*P* (kbar)	Buffer*	Composition**	Run products†	log f_{O_2}††	Δλ(S*Kα*) (Å × 10^3)‡
HP-38	1150	4.50	C-CO-CO_2	DO8	Gl, FeS, Fe	FMQ − 2.1	−0.03 ± 0.05
C69a	1025	2.05	FMQ	MSH	Gl, FeS	FMQ	0.29 ± 0.12
C105b	955	2.02	NNO	EC224	Gl, FeS, Ox, (Q)	FMQ + 0.9	0.60 ± 0.14
C127a	974	1.16	C + CH_4 + Ar	EC224	Gl, FeS, (Anhy), Q, (r-Pl)	FMQ + 1.4	2.12 ± 0.07
C143a	953	2.03	C + CH_4 + Ar	EC224	Gl, Anhy, (FeS), Ox, Px, (Pl)	FMQ + 2.0	2.80 ± 0.21
C63b	1025	1.06	MNO	MSH	Gl, Anhy, Ox	FMQ + 4.5	2.80 ± 0.10
C75b	1025	2.90	MNO	VG-D64	Gl, Anhy, Ox	FMQ + 4.5	2.95 ± 0.11
C102b	920	1.95	MNO	EC224	Gl, Anhy, Ox, Pl	FMQ + 4.5	2.78 ± 0.20
C77b	1025	2.90	MH	MSH	Gl, Anhy, Ox	FMQ + 5.9	2.91 ± 0.09
				Scapolite			2.86 ± 0.18
				Anhydrite			3.06 ± 0.08

* Experimental buffers: C-CO-CO_2 = graphite-CO-CO_2 equilibrium (French and Eugster, 1965); FMQ = Fe_2SiO_4-Fe_3O_4-SiO_2 buffer; NNO = Ni-NiO buffer; MNO = MnO-Mn_3O_4 buffer; MH = Fe_3O_4-Fe_2O_3 buffer. C + CH_4 + Ar indicates buffering method whereby a small measured amount of CH_4 is added to the predominantly Ar pressure medium. Sample and an assemblage of magnetite + ilmenite solid solutions are enclosed in adjacent unsealed tubes. Analysis of the Fe-Ti oxide assemblage at the end of the run provides an f_{O_2} value for the experiment. See Carroll and Rutherford (1987) for additional details regarding experimental methods.

** Natural samples used as experimental starting materials include DO8, a tholeiitic basalt; MSH, a dacite from the 1980 eruption of Mount St. Helens; EC224, a trachyandesite from the 1982 eruption of El Chichon volcano, Mexico; VG-D64, an oceanic andesite from the Galapagos rift.

† Run products: Gl = glass, Fe = Fe metal, FeS = pyrrhotite or an FeS-rich immiscible sulfide liquid, Anhy = anhydrite, Ox = Fe-Ti oxide phase(s), Pl = plagioclase feldspar, Px = Ca-rich pyroxene, Q = quench crystals, r- = interpreted as relict phase. Phases in parentheses indicate small or trace amount present.

†† Log oxygen fugacity (f_{O_2}) values are all reported relative to the FMQ buffer; thus FMQ + 2, for example, means 2 log f_{O_2} units above the FMQ buffer.

‡ All wavelength shifts for S*Kα* radiation are reported relative to FeS, i.e., Δλ(S*Kα*) = wavelength of S*Kα* radiation from FeS minus the wavelength of S*Kα* radiation from the unknown sample. Quoted wavelength shifts refer to sulfur dissolved in the glass portion of the experimental run products.

stoichiometry, has sulfur present only as sulfate. These results suggest that the observed increase in $\Delta\lambda(SK\alpha)$ of experimental glasses with increasing oxidation state reflects an increasing proportion of dissolved sulfur present as sulfate. Although the peak-shift observed for scapolite is close to that for anhydrite, it is slightly lower. The similarity in ionic size for S^{2-} and Cl^{-} (Holloway, 1981) and the common presence of Cl in scapolite suggest that the slightly lower $\Delta\lambda(SK\alpha)$ value measured for scapolite could be due to a small proportion of sulfur present as S^{2-}.

The results shown in Figure 1 provide qualitative information on the effects of oxygen fugacity on the speciation of dissolved sulfur in the experimental glasses. If we assume that $\Delta\lambda(SK\alpha)$ is proportional to the fraction of dissolved sulfur present as sulfate, then it is possible to calculate how the percentage of sulfur in solution as sulfate varies with oxygen fugacity. Taking $\Delta\lambda(SK\alpha)$ for $CaSO_4$ to represent 100% sulfur as sulfate, we obtain the proportionality

$$\%\ \text{sulfate in total sulfur} = \Delta\lambda(SK\alpha)_{\text{glass}}/\Delta\lambda(SK\alpha)_{\text{anhydrite}} \times 100. \qquad (1)$$

In Figure 2a the calculated fraction of sulfur present as sulfate is plotted as a function of oxygen fugacity, relative to the FMQ buffer. The results show sulfate abundances that vary from near 0% at FMQ to nearly 100% sulfate at 2 to 3 $\log f_{O_2}$ units above FMQ. For comparison, Figure 2b shows wet-chemical analyses of sulfide and sulfate abundances in $Na_2O \cdot 2SiO_2$ and tholeiitic basalt melts equilibrated at 1250 °C and 1-atm pressure with CO_2-H_2-SO_2 gas mixtures (Nagashima and Katsura, 1973; Katsura and Nagashima, 1974). Despite the differences in melt compositions and conditions of synthesis, the three data sets all show that the fraction of total sulfur present as sulfate increases from near 0% at FMQ to near 100% at 2 to 3 $\log f_{O_2}$ units above FMQ.

The assumption that $\Delta\lambda(SK\alpha)$ is linearly proportional to the fraction of sulfur present as sulfate requires that S^{2-} and S^{6+} are the predominant forms of dissolved sulfur. The presence of other forms of oxidized sulfur cannot be discounted, but the observations and conclusions made in this paper will not be seriously affected if the oxidized sulfur is a mixture of, e.g., S^{4+} and S^{6+} species.

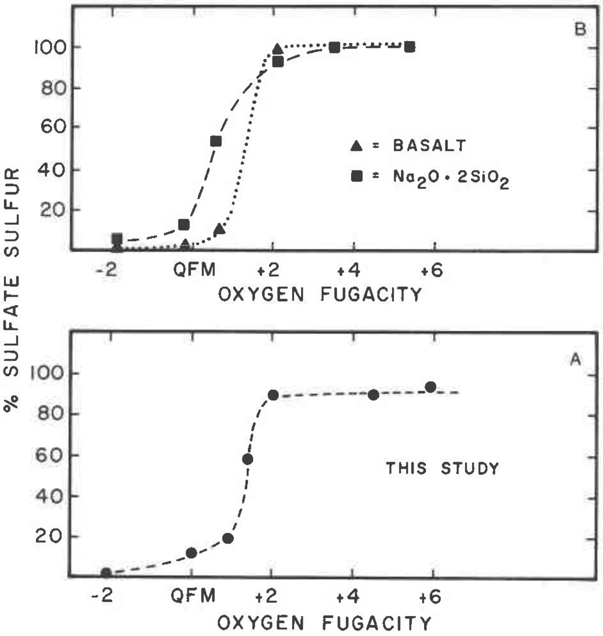

Fig. 2. Plot of percentage of total dissolved sulfur that is present as sulfate vs. experimental oxygen fugacity. (**a**) Results from this study based on data given in Table 1. The percentage of sulfate sulfur was estimated by assuming that measured $SK\alpha$ peak shifts are linearly proportional to the fraction of sulfur present as sulfate. The peak shift measured for anhydrite (0.00306 ± 0.00020 Å; relative to FeS) was assumed to indicate all sulfur present as sulfate. See text for further details. (**b**) Solid line shows results calculated from data of Nagashima and Katsura (1973), $Na_2O \cdot 2SiO_2$ melt, 1-atm pressure, 1250 °C. Dashed line shows results calculated from data of Katsura and Nagashima (1974) for a tholeiitic basalt at 1 atm, 1250 °C. Sulfide and sulfate sulfur abundances in the latter studies were determined by wet-chemical methods.

One additional point requiring comment is the fact that the peak-shift data collected for this study are for melt compositions varying from basalt to dacite synthesized over a range of pressure and temperature (1.06 to 2.90 kbar; 920 to 1150 °C; see Table 1). The measured wavelength shift of $SK\alpha$ radiation for a Galapagos andesite sample (VGD64; Byerly et al., 1976) run at 2.9 kbar, 1025 °C, MnO-Mn_3O_4 buffer is indistinguishable from the value determined for a Mount St. Helens dacite run at 1.06 kbar and the same temperature and buffer. This suggests that pressure variation between 1 and 3 kbar and melt composition variation between andesite and dacite do not have a measurable effect on the $\lambda(SK\alpha)$ values reported in this paper. This should not, however, be taken to indicate that the speciation of dissolved sulfur is unaffected by pressure and melt composition. It only means that the pressure and melt composition range covered by the quoted experiments does not change the speciation by a measurable amount (10% to 15% absolute).

A temperature difference of 100 °C also appears ineffectual in changing the relative concentrations of sulfide and sulfate in two MnO-Mn_3O_4 buffered experiments done at 925 and 1025 °C (C75b and C102b, Table 1). The measured $\Delta\lambda(SK\alpha)$ values for these experiments differ by 0.00017 Å and are identical within the estimated precision of the measurements (± 0.00020 Å). Calculations of fluid-phase equilibria in the H-O-S system suggest that oxygen fugacity will have the most significant effect on sulfide/sulfate ratios in magmas, with the effects of temperature being of secondary importance (Gerlach and Nordlie, 1971; Whitney, 1984). The 100 to 200 ppm sulfur concentrations in glasses synthesized below 900 °C would require extremely long counting times for peak-shift determinations, and such measurements were not attempted for this study.

DISCUSSION

Oxidized sulfur in magmas

The results of this study suggest that oxidized forms of sulfur may comprise a significant fraction of the total dissolved sulfur occurring in natural magmas if oxidation states are higher than about 2 logf_{O_2} units above the FMQ buffer curve. These results are broadly consistent with the relative proportions of sulfate and sulfide measured in a variety of natural rocks. For example, analyses of fresh basalts from the Cayman Trough, the FAMOUS area, the Galapagos Ridge, and the Kilauea east rift by Sakai et al. (1984) show sulfate contents ranging from 0 to a maximum of approximately 25% (rarely) of the total sulfur present. Assuming that oceanic basalts are erupted at oxidation states mainly below FMQ, but with some as high as FMQ + 1 (Haggerty, 1976; Mathez, 1984; Carmichael and Ghiorso, 1986; Christie et al., 1986), the dominance of sulfide in these rocks agrees well with relations between f_{O_2} and sulfate abundances observed in this study.

Sulfate has also been found to comprise a significant fraction of the total sulfur in many I-type granitoids (1 to 100 ppm total S, with up to approximately 50% as sulfate: Ueda and Sakai, 1984). The higher fraction of sulfate in these rocks is consistent with their relatively oxidized nature compared to oceanic basalts. Perhaps the most striking reported examples of abundant sulfate in igneous rocks are the anhydrite-bearing trachyandesite erupted from El Chichon volcano in 1982 (Luhr et al., 1984; Rye et al., 1984) and the anhydrite-bearing lavas from Mount Lamington, Papua New Guinea (Arculus et al., 1983). For El Chichon, the relative modal abundances of anhydrite and pyrrhotite phenocrysts suggest that >90% of the sulfur in fresh pumices is present in oxidized form, indicating an f_{O_2} of crystallization at least 2 log units above the FMQ buffer curve.

Sulfur speciation and solubility behavior

The available data on H_2O and CO_2 solubility systematics and the chemical similarities between H_2O and H_2S and between CO_2 and SO_2 suggest that sulfur solubility in magmas should be influenced by sulfur speciation and the intensive or extensive variables that may affect sulfur speciation. In the case of hydrous magmas with oxygen fugacities near the FMQ buffer, our peak-shift measurements support the applicability of the reaction proposed by Burnham (1979) to describe the solution mechanism of H_2S,

$$H_2S_{(fluid)} + O^{2-}_{(melt)} = HS_{(melt)} + OH_{(melt)},$$

i.e., sulfur dissolves mainly as sulfide. However, for magmas with oxidation states 2 or more log f_{O_2} units above the FMQ buffer curve, our results show that it is also necessary to consider the solubility behavior of oxidized sulfur species. Work on the solubility of sulfur in hydrous melts staturated with anhydrite indicates that for identical melt composition, pressure, and temperature, the solubility of sulfate may be up to a factor of 10 greater than that observed for sulfide at pyrrhotite saturation (Carroll and Rutherford, 1987). Further work on sulfur speciation and solubility under relatively oxidizing conditions is necessary for understanding the solution mechanisms of sulfur present as sulfate; our results clearly demonstrate that it may comprise a significant fraction of the total sulfur in some natural rocks.

CONCLUSIONS

Measurements of the wavelength of S*Kα* radiation from hydrous andesitic to rhyolitic glasses synthesized over a range of oxygen fugacity show that the amount of dissolved sulfur present as sulfate is sensitively dependent on melt oxidation state. Our results and implications regarding the geochemical behavior of sulfur can be summarized as follows:

1. The proportion of dissolved sulfur present as sulfate in hydrous andesitic to dacitic melts synthesized at 920 to 1025 °C shows a strong dependence on oxygen fugacity, with the percentage of sulfate increasing from near 0% at the FMQ buffer to near 90% at 2 to 3 lof f_{O_2} units above FMQ. This rapid change in sulfur speciation occurs over an oxygen-fugacity range (FMQ to FMQ + 2 log units) considered typical for many calc-alkaline magmas more siliceous than andesite in composition.
2. The similarity between our results for hydrous melts and measured sulfide/sulfate ratios in experiments on dry basaltic and $Na_2O \cdot 2SiO_2$ melts synthesized over a range of f_{O_2} at 1250 °C, 1-atm pressure suggests that oxygen fugacity is a major factor affecting sulfur speciation in a wide variety of melt types. Temperature (920 to 1250 °C), water pressure (0 to several thousand bars), and melt composition (dry basalt, hydrous andesite, or dacite) appear to be of lesser importance in determining sulfur speciation in magmas. More extreme melt compositions, such as the silica-undersaturated alkali basalts studied by Schneider (1970), may favor the stabilization of sulfate, but our results do not allow us to comment on such effects (e.g., see Stormer and Carmichael, 1971).

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