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Sulfide saturation of basalt and andesite melts at high pressures and temperatures

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Abstract

The solubility of sulfur in silicate melt coexisting with iron sulfide melt has been determined as a function of temperature and pressure for three silicate compositions: Mt. Hood andesite, Grande Ronde basalt and Goose Island basalt (FeO_t = 5.4, 11.1 and 17.0%, respectively). Experimental temperatures vary from 1300–1460° C and pressures vary from 12.5–30 kbar. The oxygen fugacity in the experiments is near that of the $C–CO–CO_2–O_2$ buffer (10^{-9} bar at P_t = 20 kbar) and the sulfur fugacity is buffered internally at a value above the iron–troilite equilibrium ($f_{S_2} \approx 1$ bar at P_t = 20 kbar).

Sulfur solubility decreases with increasing pressure and increases with increasing temperature and FeO_t content of the silicate melt; observed solubilities range from a low value of 0.05 wt.% at 30 kbar and 1420° C (andesite) to a high value of 0.26% at 12.5 kbar and 1420° C (Goose Island basalt). The FeO_t content of the coexisting sulfide melt decreases with increasing pressure (from a maximum of 5.5% at 12.5 kbar and 1420° C—Goose Island basalt), increases with FeO_t content of the silicate melt and does not appear to be dependent on temperature. With increasing pressure, the miscibility gap between natural silicate melts and sulfide melts expands and the ratio of $FeO_t^{\text{silicate melt}}/FeO_t^{\text{sulfide melt}}$ increases.

The sulfur solubility measurements establish a basis for evaluating the appearance of immiscible sulfide in erupted magmas, core segregation processes, and subsequent transition metal partitioning studies. Because of the strong negative pressure dependence of sulfur solubility in silicate melts, a magma may be sulfide-saturated in the source region but not on eruption until the late stages of crystallization.

Introduction

When the sulfur content of an Fe-bearing magma exceeds the saturation limit for the bulk composition, an immiscible iron sulfide melt fraction separates. Chalcophile elements, including many transition metals, partition preferentially into the sulfide melt (MacLean and Shimazaki, 1976; Fleet *et al.*, 1977; Medvedev and Al'mukhamedov, 1978; Rajamani and Naldrett, 1978; Fleet *et al.*, 1981) effecting major changes in the trace and minor element distributions of the silicate melt (Duke and Naldrett, 1978) and possibly generating metal-sulfide deposits (Naldrett, 1973; Campbell, 1977). Chalcophile element distributions will also be dependent on whether the silicate melts are sulfur-saturated at their source: Elimination of the residual sulfide (by dissolution in the silicate melt) is required for the entry of many elements (*e.g.*, the Pt-group elements) into the silicate melt. To understand the geochemistry of sulfur-bearing magmatic systems, better knowledge is required of the solubility of metal sulfide in silicate melt at its source, and how that solubility changes as a function of changing intensive and extensive variables. In this investigation, the sulfur saturation surface has been determined between 12.5 and 30 kbar and 1300–1460° C for three silicate melt compositions representing a range of SiO_2 and FeO_t (total iron calculated as FeO) compositions: Mt. Hood andesite (MHA), Grande Ronde basalt (GRB) and Goose Island basalt (GIB).

Measurements of sulfur content in sulfur-undersaturated silicate melts, determined at low pressure in simple synthetic systems (Fincham and Richardson, 1954; Richardson and Fincham, 1954; MacLean, 1969; Shimazaki and Clark, 1973) and in complex synthetic and natural systems (Haughton

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et al., 1974; Katsura and Nagashima, 1974; Shima and Naldrett, 1975; Buchanan and Nolan, 1979, Danckwerth *et al.*, 1979), have indicated a strong dependence on temperature and composition: A positive dependence of sulfur content on temperature, f_{S_2}, and TiO_2 and FeO content of the silicate melt and a negative correlation between sulfur content and f_{O_2}. Along the sulfide saturation surface, however, sulfur contents of silicate melts decrease with increasing f_{S_2} and decreasing f_{O_2} (Haughton *et al.*, 1974; Danckwerth *et al.*, 1979). Additionally, estimates of sulfur solubility in silicate melts have been made by analyzing sulfur contents of rapidly quenched basalts and dacites (Moore and Fabbi, 1971; Mathez, 1976; Czamanske and Moore, 1977; Ueda and Itaya, 1981), of differentiated siliceous melt in a Hawaiian lava lake (Skinner and Peck, 1969), and of glass inclusions trapped in crystals (Anderson, 1974). These data show a large degree of variability as one would expect of occurrences of variable composition which quenched at different rates, temperatures, and pressures.

Experiments involving sulfur at high pressures are few in number because of experimental difficulties, primarily those of encapsulation and of controlling f_{O_2} and f_{S_2}. Helz and Wyllie (1979) determined sulfur solubility in carbonatitic melts (iron-absent) at 1 kbar. Helz (1977) determined the first appearance of sulfide melt in natural basalts to 20 kbar. Experiments were done in Pt capsules without controlled f_{O_2} and f_{S_2}; although iron loss to the capsule was minimal (within approximately 3% of the original amount), sulfur mass balance was not reported. Huang and Williams (1980) investigated portions of the system Fe–Si–S–O to 32 kbar and demonstrated that the sulfide melt–silicate melt miscibility gap expands with pressure. Mysen (1977) presented preliminary results for SO_2 solubility in albite melt, but with no details on experimental technique. Mysen and Popp (1980) reported sulfur solubilities increasing markedly with pressure and only slightly with temperature in diopside and albite melt; however, applications of their results to natural systems are limited by the Fe-absent compositions they investigated. The current investigation was undertaken to reconcile the variable, and, in some instances, conflicting results of previous investigators and to establish a basis for future partitioning studies of platinum metals between sulfide and silicate melts.

Experimental methods

All experiments were done with a piston-cylinder apparatus using 1.27 cm talc-Pyrex furnace assemblies and a piston-out technique with a −5 kbar correction for friction as calibrated against the quartz–coesite transition. Nominal pressures were maintained at ±0.1 kbar. Temperatures were measured with Pt-Pt10Rh thermocouples and automatically controlled to ±2° C. No corrections for the effect of pressure on the emf of the thermocouple have been made.

Starting materials were 60% silicate and 40% pyrrhotite by weight. The compositions of the silicate fractions are shown in Table 1. The Mt. Hood andesite, Grande Ronde basalt, and Goose Island basalt were selected for the ranges of SiO_2 and FeO_t they encompassed. Melting phase relations of the andesite at high pressures have been determined by Eggler and Burnham (1973); those of the Goose Island basalt have been determined by Helz (1978). High pressure phase relations have not been established for the Grande Ronde basalt; however,

Table 1. Compositions of silicate starting materials

	MHA*	GRB**	GIB*
SiO_2	60.78	54.38	45.93
TiO_2	0.83	1.91	3.73
Al_2O_3	17.38	14.71	11.67
Fe_2O_3	2.24	n.d.	4.06
FeO	3.38	11.11***	13.36
MnO	0.10	0.19	0.30
MgO	3.19	4.58	4.23
CaO	6.09	8.01	8.81
Na_2O	4.16	2.67	2.40
K_2O	1.20	1.14	1.28
P_2O_5	0.18	0.29	1.77
S	n.d.	n.d.	0.13
H_2O	0.44		1.03
Total	99.97	98.99	98.70

*Collected by G. E. Lofgren.
**Collected by P. Schiffman.
***Total iron determined as FeO.
Analyses determined by XRF at Johnson Space Center; Na_2O determined by INAA; FeO determined by titration.

Schiffman and Lofgren (1982) have determined the 1-atm relations at the QFM buffer. The silicate fractions were equilibrated at the QFM buffer at 900° C and 1-atm for two days prior to mixing with the sulfide fraction.

Pyrrhotite was synthesized in evacuated silica glass tubes at 700° C for 18 hours using Fe wire (99.95% purity) and S (99.999+% purity). The iron sulfide composition, determined by the X-ray diffraction technique of Toulmin and Barton (1964), is $Fe_{0.985}S$. The desired mixtures of silicate:sulfide (60:40, by weight) were prepared by grinding in alcohol to less than 3 μm grain size and drying at 120° C in an evacuated oven.

The capsule configuration in all the experiments involved loading 5–10 mg of the starting mixture into a graphite capsule which was then loaded into a Pt capsule (3 mm diameter) and sealed. This design provided a closed system, buffered the oxygen fugacity at a known value, and prevented iron and sulfur loss to the precious metal capsule. All experiments were at pressures and temperatures above the liquidus of the bulk composition except for one run at 20 kbar and 1300° C involving the GRB in which approximately 2% crystals were detected. Two immiscible liquid phases, one predominantly silicate and the other sulfide, were observed in all runs. The sulfide melt typically segregated to form a single spherical bleb at the bottom of the charge and quenched to a fine grained pyrrhotite aggregate. The silicate melts quenched to glass.

Compositions of the coexisting melts were determined by electron microprobe analysis using troilite and basalt glass standards. Within the limits of resolution, no solution of silicate melt components in the sulfide melt, with the exception of iron, was detected. Multiple analyses of iron and sulfur in the silicate melt and sulfide melt were obtained and the data averaged; values are presented with $\pm 1\sigma$ errors.

The oxygen fugacity in the experiments must have been near the C–CO–CO_2–O_2 buffer (French and Eugster, 1965; French, 1966). The initial redox state of the silicate component was at QFM; thus, a slight excess of oxygen was available at run conditions. The C–CO–CO_2–O_2 buffer is about 1 log unit more oxidizing than the IW buffer at all run conditions.

The sulfur fugacity in the experiments was buffered internally by the bulk composition and varies with pressure and temperature. The lower limit of possible values of f_{S_2} is constrained by the iron–troilite buffer: Using the free energy data for liquid FeS of Sharma and Chang (1979) and extrapolated molar volume data for sulfur liquid from West (1950) and Toulmin and Barton (1964), the minimum $\log f_{S_2}$ at 20 kbar and 1420° C is about −0.5, and probably changes less than 1 log unit in either direction between 12.5 and 30 kbar. The upper limit on f_{S_2} values in the experiments can be no greater than the total pressure ($\log f_{S_2} = 4.3$ at 20 kbar) and is probably much less.

Experimental results

In Table 2, the experimental conditions and sulfur contents of the silicate melts are summarized. Experiments were at 12.5, 20, and 30 kbar and a temperature range of 1300–1460° C. The temperature and pressure dependences of sulfur contents in silicate melts are plotted in Figures 1 and 2, respectively. Sulfur saturation shows a negative pressure dependence and a positive temperature dependence for all three silicate compositions. Lowest solubilities are observed in the MHA which has high SiO_2 and low FeO_t contents; highest solubilities occur in the GIB which has low SiO_2 and high FeO_t. There is no basis for claiming linear temperature and pressure dependences other than noting that a straight

Table 2. Results of experiments

Run number	P (kbar)	T (°C)	duration (hr)	S solubility (wt%)*
	(Mt. Hood Andesite)$_{60}$(Fe$_{.985}$S)$_{40}$			
740	12.5	1420	6	0.14 ± 0.014
745	20	1340	7	0.05 ± 0.010
734	20	1380	6.5	0.07 ± 0.020
735	20	1420	5	0.09 ± 0.013
744	20	1460	4.75	0.12 ± 0.011
736	30	1420	6	0.05 ± 0.012
	(Grand Ronde Basalt)$_{60}$(Fe$_{.985}$S)$_{40}$			
741	12.5	1420	6	0.19 ± 0.009
709	20	1300	6	0.09 ± 0.009
747	20	1380	6	0.14 ± 0.012
737	20	1420	6	0.15 ± 0.007
746	20	1460	4	0.17 ± 0.010
717	30	1420	7.25	0.11 ± 0.016
	(Goose Island Basalt)$_{60}$(Fe$_{.985}$S)$_{40}$			
753	12.5	1420	4	0.26 ± 0.017
755	20	1340	9.33	0.17 ± 0.009
757	20	1380	15.75	0.19 ± 0.012
759	20	1420	8.5	0.22 ± 0.014
751	20	1460	4.5	0.25 ± 0.019
749	30	1420	5	0.18 ± 0.010

*Errors are ± 1σ.

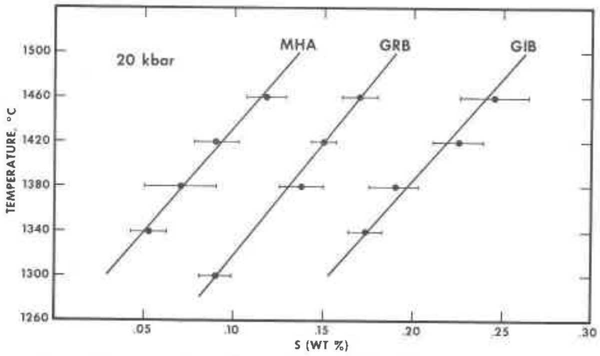

Fig. 1. Temperature dependence of sulfur saturation in Mt. Hood andesite (MHA), Grande Ronde basalt (GRB) and Goose Island basalt (GIB) at 20 kbar. The brackets are ±1σ.

line fits the limited number of points; in fact, Richardson and Fincham (1954) and Haughton *et al.* (1974) have shown that a log sulfur concentration *vs.* reciprocal temperature plot defines a straight line.

Figure 3 shows sulfur *vs.* FeO_t contents of the silicate melts at 1420° C for three pressures, to emphasize the opposing effects of pressure and FeO_t content on sulfur saturation. At constant pressure and temperature, the sulfur fugacity and the oxygen fugacity are fixed and, thus, the ferric/ferrous ratio is approximately constant for the three melt compositions. Between 12.5 and 30 kbar, sulfur contents in the silicate melts decrease by less than 0.1 wt.% for all melts. The ferric/ferrous ratio also decreases with increasing pressure but by only a slight amount as the oxygen fugacity associated with the $C–CO–CO_2–O_2$ buffer increases at a lesser rate than that associated with the I-W buffer. Increasing FeO_t content of the silicate melt is accompanied by an increase in the sulfur content of about 0.12 wt.%.

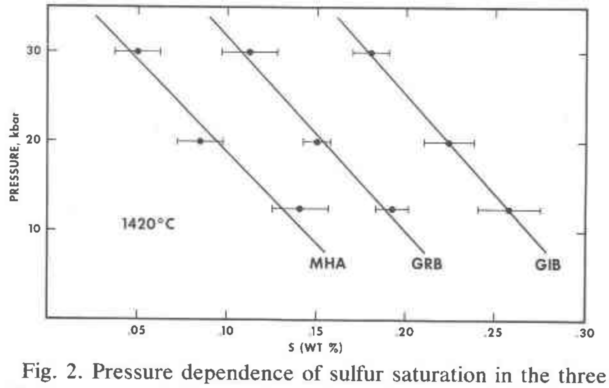

Fig. 2. Pressure dependence of sulfur saturation in the three silicate melts at 1420° C. Brackets are ±1σ.

A trend of increasing FeO_t contents of the silicate melts with increasing pressure for a given bulk composition is also evident in Figure 3 (emphasized by the dashed control lines). Such trends cannot be explained by the assumption that all iron is divalent. Even if all the iron were calculated as ferric, the difference would not account for the "lost" iron in the silicate melt at 12.5 kbar. Nor can it be surmised that iron is being incorporated into the sulfide melt to compensate for the deviation from stoichiometric troilite: for the amount of sulfide present, the addition of only 0.4 wt.% Fe is needed to satisfy the stoichiometry. The likely explanation is that FeO is dissolving in the sulfide melt preferentially at lower pressures. A similar decrease in FeO solubility in FeS-rich melts with increasing pressure in the system Fe–S–O was reported by Wendlandt and Huebner (1979).

To test the suggestion that Fe-loss in the silicate melts is related to FeO gain in the sulfide melt, mass balance calculations for iron in the sulfide melt were made (summarized in Table 3). Averaged iron and sulfur analyses of the sulfide melts at 12.5 and 30 kbar and 1420° C indicate iron in excess of that needed for a stoichiometric FeS melt. When oxygen is added to the excess iron in the amount appropriate for FeO, the summed weights are comparable to the FeO_t deficits observed in the silicate melts, suggesting that there can be appreciable FeO solubility in the sulfide melts at the lower pressures. High FeO contents of the silicate melt correlate

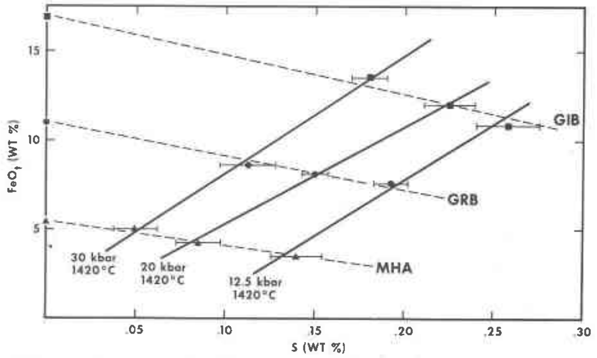

Fig. 3. Effect of FeO_t content of the silicate melt on the saturation sulfur content of the silicate melt at constant pressure and temperature for the three melts (solid lines). At fixed pressure and temperature the f_{O_2} and f_{S_2} are fixed; thus, the Fe^{3+}/Fe^{2+} ratio is approximately constant. Dashed lines show the loss of FeO_t component from the silicate melt at low pressure (discussed in the text). Changing temperatures at fixed pressure for a given composition (not shown) alters the sulfur content but not the FeO_t content of the silicate melt.

Table 3. Calculated FeO solubility in sulfide melt

Run number	P (kbar)	T (^oC)	X_{Fe}* (mol)	X_S* (mol)	Excess Fe (wt%)	Calculated O with excess Fe (wt%)	Calculated FeO solubility (wt%)	FeO deficiency in silicate melt
				Goose Island Basalt - $Fe_{.985}S$				
753	12.5	1420	1.1276	1.0495	4.36	1.25	5.61	6.14
749	30	1420	1.1277	1.0770	2.83	0.81	3.64	3.62
				Grand Ronde Basalt - $Fe_{.985}S$				
741	12.5	1420	1.1327	1.0912	2.32	0.66	2.98	3.50
717	30	1420	1.1335	1.1084	1.40	0.40	1.80	2.49
				Mt. Hood Andesite - $Fe_{.985}S$				
740	12.5	1420	1.1442	1.1277	0.92	0.26	1.18	1.95
736	30	1420	1.1259	1.1306	(-0.26)	(--)	(--)	0.41

**Molar proportions of Fe and S in sulfide melt.*

with high FeO contents in the sulfide melt. Because the calculation assumes stoichiometric troilitic melt, which would only occur in equilibrium with iron metal, minimum estimates of FeO solubility in sulfide melt are obtained.

Using the experimental data for sulfur solubility in silicate melt and the calculated data for FeO solubility in sulfide melt, a FeS–SiO_2–"FeO" diagram, projected from the remaining components, can be constructed. Figure 4 depicts the tielines between the coexisting melts at 1420° C and 12.5 and 30 kbar for the three bulk compositions. The expansion of the miscibility gap with increasing pressure is evident in the SiO_2-rich region; the expansion is a consequence of decreased sulfur solubility in silicate melt at high pressure. Huang and Williams (1980) previously noted an expansion of the miscibility gap in the system Fe–Si–S–O with increasing pressure. Also with increasing pressure the ratio of FeO_t in sulfide melt to FeO_t in silicate melt decreases, causing a counter-clockwise rotation of the tielines. Because a similar sense of rotation is observed for all three compositions it is likely that the neglected components have little impact on the phase relations, although they represent a compositional variable which is not evaluated in this study. For example, Thornber *et al.* (1980) have demonstrated that the ferric/ferrous ratio of melts is affected by bulk composition, particularly alkali contents, at constant *P*, *T* and f_{O_2}.

Discussion

Sulfur saturation of silicate melts

A comparison of existing data with the results of this investigation is difficult because of different experimental conditions and melt compositions. In this study it was observed that sulfur solubility at saturation increased with temperature and FeO contents of the silicate melt and decreased with increasing pressure. Because f_{O_2} and f_{S_2} increase with increasing pressure in the experimental design, it is impossible to separate their relative effects; that is, to claim that the increase in sulfur solubility is only a pressure effect. Although calculations of f_{S_2} and f_{O_2} at run conditions (discussed earlier) suggest only slight changing of these variables between 12.5 and 30 kbar, Haughton *et al.* (1974) showed that at 1-atm an increase of f_{S_2} by 1 log unit decreases the sulfur solubility at saturation by approximately 1/2

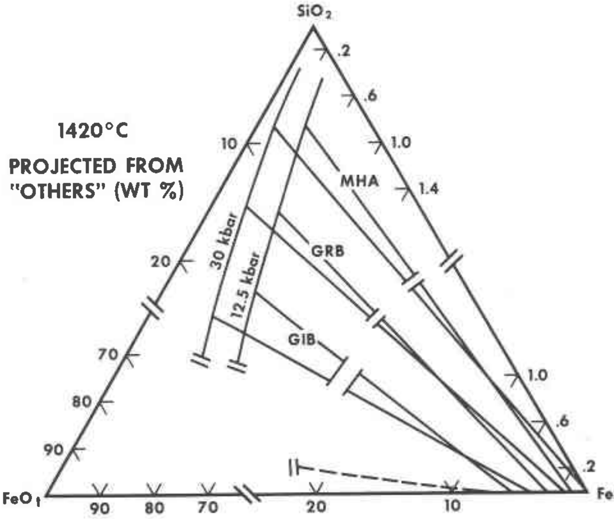

Fig. 4. Tie lines between coexisting immiscible sulfide and silicate melts at 1420° C and 12.5 and 30 kbar. Melt compositions are projected onto the FeS–FeO–SiO_2 surface from the other components.

log unit, which is well within the range of variation deserved in this study (*e.g.*, for GRB, log S concentration is −0.72 at 1420° C and 12.5 kbar, and −0.96 at 1420° C and 30 kbar). Opposing this effect of increasing f_{S_2} is the experimental observation that increasing f_{O_2} enhances the sulfur solubility at saturation (*e.g.*, Haughton *et al.*, 1974). The magnitude of sulfur solubilities determined in this study (0.05–0.25 wt.%) overlap analyses of solubilities in natural occurrences (approximately 0.1 wt.%) as well as ranges of values determined in 1-atm experiments (0.04–0.32 wt.%).

This study documents an apparent negative pressure dependence for sulfur solubility as previously suggested by Helz (1977) and Huang and Williams (1980). Mysen and Popp (1980) reported much higher sulfur solubilities (up to 1.4 wt.% S) in iron-absent melts of diopside and albite compositions in addition to solubilities that increased with increasing pressure. Their observations are difficult to reconcile with those of this study; however, it must be noted that the oxygen fugacity of their experiments was buffered by the boron nitride inner capsule of their assembly at a value several log units below the IW buffer (Wendlandt *et al.*, 1982), and not near the C–CO–CO_2–O_2 buffer as intended. The low f_{O_2}, in conjunction with high f_{S_2} of their experiments, probably stabilizes the association of sulfide with calcium in the silicate melt, accounting for the enhanced solubilities. Furthermore, because Mysen and Popp's (1980) experiments involve iron-absent systems, increases in f_{S_2} relative to f_{O_2} with increasing pressure probably enhance the sulfur solubility in the silicate liquid. The effect would be analogous to that observed in iron-bearing systems before separation of an immiscible FeS-rich liquid. Therefore, whereas the experimental results of Mysen and Popp (1980) and this investigation are apparently discrepant, in fact, the differences can be explained adequately in terms of the different experimental systems, and specifically, by the absence or presence of an immiscible iron sulfide fraction.

Whether silicate melts are sulfur-saturated in their source regions and/or when sulfide saturation occurs during magma ascent remain significant unknowns in our understanding of sulfur-bearing magmatic systems. A thorough understanding requires, among other things, knowledge of sulfur solubilities and the sulfur saturation surface for silicate melts as a function of *P*, *T*, and melt composition, as well as knowledge of sulfur abundances in melt source regions. The latter information is model dependent, sulfur abundances and distributions being a function of earth accretion and core segregation processes in addition to such variables as the f_{O_2} conditions of the protoearth. Sulfur contents of mantle xenoliths are probably not reliable indicators of sulfur abundances in the upper mantle because much of the sulfide in xenoliths can be interpreted as having been introduced or remobilized by late stage processes (Pasteris, 1981).

Helz (1977) suggested, on the basis of pervasive textural evidence of immiscible sulfide melts in eruptive basalts coupled with the experimental observation of sulfide saturation defining a *P–T* surface parallel to and very close to volatile-absent basalt liquidi, that sulfide liquid is probably present during melt formation and that sulfide remains as a residual phase in the source region. The results of this study confirm sulfur saturation isopleths roughly paralleling anhydrous basalt liquidi (*e.g.*, Thompson, 1972). Depending on the *P–T* trajectory of an ascending magma, however, it is conceivable that a magma may be saturated with respect to sulfur in the source region but not on eruption until the late stages of crystallization. For example, a liquidus influenced by the presence of volatiles, H_2O and/or CO_2 will have a steeper slope, dP/dT, than the sulfur solubility isopleths determined in this study for anhydrous basalt melts. Accordingly, a magma initially sulfur-saturated at its source would be undersaturated throughout an ascent that paralleled the slope of its liquidus or was in any way steeper than an anhydrous basalt liquidus. Perhaps the only direct evidence of sulfide-saturated silicate melt at elevated pressures is that reported by Roedder (1981): He observed sulfide-saturated melt inclusions in olivine of dunite inclusions in basalts from Loihi seamount and estimated (using *P–V–T* data for CO_2 extrapolated to 1200° C) that the inclusions were trapped at 10–18 km depth (3–5.5 kbar). Whereas these depths are above the magma source region, the evidence is supportive of sulfide-saturation at pressures at least intermediate between the source region and the surface.

Residual sulfide in the source region will influence chalcophile element abundances in a magma by acting as a sink for the chalcophile elements and preventing their enrichment in the silicate partial melt. Inasmuch as higher Ni contents of Archaean mafic rocks relative to modern basalts for a given Mg-number have been ascribed to the influence of transition metal monosulfides in the source regions of the older rocks (Arculus and Delano, 1981), it may also be necessary to stipulate that partial melting eliminated sulfide as a residual phase in the source region.

Oxygen content of sulfide melt

Naldrett (1969) has demonstrated that appreciable oxygen (7–8 wt.%) can dissolve in sulfide liquids in the system Fe–S–O at 1-atm. Wendlandt and Huebner (1979) subsequently showed that the solubility of oxygen in the same system at 30 kbar is less than 1 wt.%. Coupled with observations in this study, of decreasing FeO contents in sulfide melt with increasing pressure, it is suggested that the oxygen content of naturally occurring sulfide melts may be indicative of the depth of sulfur saturation or, at least, depth of equilibration.

Skinner and Peck (1969) noted that the sulfide-rich immiscible liquids coexisting with basalt in the Alae pit crater, Kilauea, contain about 4% oxygen by weight suggesting a near surface equilibration of silicate and sulfide melts. Mathez (1976) noted that the oxide content of immiscible sulfide blebs in a variety of submarine basalts was variable; occasionally coarse magnetite–sulfide intergrowths were observed with as much as 2.2% oxygen, but usually magnetite was very fine grained and often absent from the sulfide. The former textural occurrences could be interpreted as indicating shallow depths of origin whereas the latter imply attainment of sulfur saturation at high pressures, perhaps in the magma source region. If the oxygen content (as magnetite) of immiscible sulfide blebs is a reliable indicator of depth of saturation, then the identification of oxygen-poor blebs lends support to suggestions of residual sulfide in the mantle after anatexis and some melts may remain sulfur-saturated from source to surface.

A further application of the sulfide melt compositions observed in this study is to core segregation hypotheses. Because the density of the earth's core is approximately 10% less than that of Fe–Ni at the appropriate pressures and temperatures (Birch, 1964), the presence of as much as 20% of an additional element is required. Brett and Bell (1969) proposed that sulfur was a possibility by virtue of the low temperature of the Fe–FeS eutectic over a large pressure interval. Ringwood (1977 a,b) argued against sulfur as the light element in the core on the grounds that the earth would have had to accrete as much as one-half the primordial abundance. He argued instead that oxygen was a better candidate by virtue of presumed large oxygen solubilities in iron melt at core pressures and temperatures. Wendlandt and Huebner (1979), comparing the system Fe–S–O at upper mantle pressures with that at 1-atm (Hilty and Crafts, 1952; Naldrett, 1969), observed a decrease in oxygen solubility in the eutectic melt from about 8 wt.% at low pressure to less than 1 wt.% at 30 kbar. They surmised that if the system Fe–S–O was applicable then sulfur could not be discounted as the light element in the core. Huang and Williams (1980) investigated portions of the system Fe–Si–S–O at 30 kbar, showing that the miscibility gap between silicate and sulfide melts expands with pressure; they predicted that the sinking of a FeS-rich melt through the mantle would carry very little oxygen and silicon with it. The results of the current investigation in systems of greater geologic complexity support both previous observations. Although oxygen or silicon in the core cannot be discounted, if early terrestrial differentiation involved a magma ocean (*e.g.*, Anderson, 1981) then it is likely that a large reservoir of sulfur exists in the lower mantle if not in the core.

Conclusions

Analyses of coexisting immiscible sulfide and silicate melts quenched from experiments between 12.5–30 kbar and 1300–1460° C indicate that: (1) temperature and pressure have opposing effects on the sulfur contents of silicate melts at saturation; with increasing temperature sulfur contents increase whereas with increasing pressure (and increasing f_{O_2} and f_{S_2}) sulfur contents decrease; (2) high FeO_t contents of silicate melts enhance sulfur solubilities; and (3) the FeO solubility in sulfide melt decreases with increasing pressure.

These observations suggest that immiscible sulfide blebs occurring in erupted magmas may have segregated at either high or low pressures, or both: the *P–T* paths of ascending magmas and the slopes of the magmas' liquidi are important variables in determining when sulfur saturation occurs. A further implication of the data is that if planetary differentiation processes involve magma oceans, then it is likely that a reservoir of sulfide segregates into the lower mantle if not into planetary cores. This sulfide melt will be oxygen and silicon depleted at high pressures.

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