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SOLUBILITY OF SULFUR AND SULFIDE IMMISCIBILITY IN SYNTHETIC THOLEIITIC MELTS AND THEIR RELEVANCE TO BUSHVELD-COMPLEX ROCKS

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ABSTRACT

Three synthetic tholeiitic melts have been examined experimentally at 1200°C under controlled oxygen and sulfur fugacities at one atmosphere total pressure. Runs were carried out over an oxygen fugacity range of –log 8.50 to –log 11.50 and a sulfur fugacity range of –log 1.00 to –log 4.00. In sulfur-undersaturated silicate melts the amount of dissolved sulfur increases with increasing sulfur fugacity and decreasing oxygen fugacity. Results obtained on starting composition DB/3 (SiO_2 47.6, Al_2O_3 14.8, CaO 8.1, MgO 11.1, total iron as FeO 17.8 wt. %) establish sulfur saturation in the silicate melt along the oxygen fugacity isobars of –log 10.50 and –log 11.50: sulfur fugacities are greater than –log 1.75 and –log 3.75 respectively. By running two additional compositions DB/8 and PAL–685, with FeO contents of 22.75 and 15.65 wt. % respectively, in the field of saturation, sulfur solubility as a function of oxygen fugacity and iron could be established. From Fick's 2nd law of diffusion and the determined sulfur profile a value of 5.6 x 10^{-8} was obtained for the apparent interdiffusion coefficient of sulfur in starting composition DB/3. The experimental results suggest that in the iron-rich melts present at the top of the Bushveld sequence where values of oxygen fugacity were probably close to the QFM buffer curve, values of sulfur fugacity greater than –log 1.00 would be required before an immiscible sulfide phase could be formed at temperatures of 1200°C. The large field over which the melt is saturated with sulfur at low oxygen fugacity, however, enables an immiscible sulfide to form at very much lower values of sulfur fugacity. This may be an important factor in the formation of sulfide concentrations in the magnesium-rich melts that were present at the base of the Bushveld sequence.

SOMMAIRE

Trois bains de tholéite synthétique fondue ont fait l'objet d'études à 1200°C, 1 atm, à fugacités d'oxygène et de soufre contrôlées, variant de –log 8.50 à –log 11.50 et de –log 1.00 à –log 4.00, respectivement. Dans les bains de silicate sous-saturés en soufre, la quantité de soufre en solution augmente lorsque la fugacité de soufre croît et que celle d'oxygène décroît. Pour une composition initiale "DB/3" (SiO_2 47.6, Al_2O_3 14.8, CaO 8.1, MgO 11.1, FeO (fer total) 17.8% en poids), la saturation en soufre du bain silicaté maintenu à des conditions isobariques de fugacité d'oxygène de –log 10.50 et –log 11.50 a été observée à des fugacités du soufre supérieures à –log 1.75 et –log 3.75, respectivement. Deux autres compositions, "DB/8" (22.75% FeO) et "PAL–685" (15.65% FeO), ont permis d'établir la solubilité du soufre en fonction de la fugacité d'oxygène et de la teneur en fer. A partir de la deuxième loi de diffusion de Fick et du profil des concentrations en soufre, nous obtenons une valeur de 5.6 x 10^{-8} pour le coefficient d'interdiffusion apparent du soufre pour la composition "DB/3". Nos résultats expérimentaux font penser que dans les bains riches en fer de la partie supérieure du complexe du Bushveld, où la fugacité d'oxygène a probablement été fixée par le tampon QFM, la fugacité du soufre a dû excéder –log 1.00 avant qu'une phase sulfurée immiscible ne puisse se former à 1200°C. La grandeur du champ de stabilité d'un bain saturé de soufre à faible fugacité d'oxygène permet la formation de sulfure immiscible à fugacité de soufre beaucoup plus basse. Ce peut être là un facteur important dans la formation de concentrations de sulfures dans les bains à forte teneur en magnésium situés à la base du complexe du Bushveld.

(Traduit par la Rédaction)

INTRODUCTION

When a silicate melt becomes saturated with sulfur, an immiscible sulfide melt forms, coexisting with the silicate liquid. Concentrations of such a sulfide liquid in natural rocks and its subsequent crystallization could lead to the formation of sulfide orebodies. The study of magmatic ore deposits in natural rocks is lim-

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ited, however, by the difficulty in obtaining reliable data for the intensive parameters at the time of their formation.

Temperature and oxygen fugacity estimates from magnetite-ilmenite pairs in Bushveld diorites from the Bethal area (Buchanan 1976) indicate that they had undergone extensive subsolidus re-equilibration along the QFM buffer curve. A range of temperature and oxygen fugacity of 590 to 685°C and $10^{-20.5}$ to $10^{-17.5}$ was established. As the upper stability limit of pyrite is 743°C, it is not possible to determine the sulfur fugacity of Bushveld rocks at liquidus temperatures from the composition of pyrrhotite in equilibrium with pyrite. It was hoped, however, that the minimum temperature and sulfur fugacity conditions in the Bushveld rocks could be established (Buchanan 1976). The highest temperature obtained was 680°C and the value of $10^{-0.4}$ established for the sulfur fugacity could not, therefore, reflect the chemical conditions prevailing during the precipitation of the sulfides.

Microprobe analysis of pyroxene pairs associated with sulfide mineralization in Bushveld rocks of the Bethal area has provided useful insight into the petrogenesis of the ore zone. Ca-rich pyroxene from this zone displays either reversed fractionation with respect to Fe, or replacement of Mg by Ca with Fe remaining constant (Buchanan *in press*). It was suggested that these trends arose from the precipitation of immiscible sulfide which depleted the magma in iron.

Experimental studies provide an alternative means by which the role of oxygen fugacity, sulfur fugacity, temperature and magma composition in the production of a sulfide phase in Bushveld-type magmas can be established. By integrating these studies with petrographic data that can reasonably be expected to reflect conditions present at liquidus temperatures, it should be possible to remove some of the uncertainty associated with the genesis of magmatic sulfide mineralization.

Experimental studies on silicate melts under controlled oxygen and sulfur atmospheres and at one atm total pressure have been completed by Haughton *et al.* (1974) who determined the sulfur solubility characteristics of a large range of rocks at 1200°C, as well as by Shima & Naldrett (1975) who carried out their work on a single ultramafic melt at 1450°C. In the former study the contribution of the oxide components to the sulfur-solubility characteristics of the silicate melt was established. Haughton *et al.* showed that the capacity of a silicate melt to dissolve sulfur is considerably increased in melts with a high content of FeO and TiO_2. Most of the runs were carried out in the field of sulfur saturation, *i.e.*, an immiscible sulfide phase was present in equilibrium with the silicate liquid. In the study by Shima & Naldrett, the field of sulfur saturation was clearly defined as a function of sulfur fugacity.

Naldrett (1969) has shown that at high temperatures an immiscible iron–sulfide liquid contains significant amounts of oxygen. On cooling, the iron-oxide component of the sulfide phase exsolves either magnetite or wüstite.

The present study was undertaken to establish more precisely the effect of oxygen as well as sulfur fugacity on the field of sulfide immiscibility and to apply the results to rocks of the Bushveld complex. In order to provide data compatible with the work of Haughton *et al.*, all runs were carried out at 1200°C. The compositions of the three synthetic starting materials examined in this study are given in Table 1.

PARTIAL EQUILIBRIA IN THE SILICATE MELT

According to Fincham & Richardson (1954), sulfur is soluble in silicate melts both as the sulfide and sulfate species. The two equilibria present can be represented by the following reactions:

$$\tfrac{1}{2}S_2 + O^{2-} \rightleftharpoons \tfrac{1}{2}O_2 + S^{2-} \qquad (1)$$

$$\tfrac{1}{2}S_2 + \tfrac{3}{2}O_2 + O^{2-} \rightleftharpoons SO_4^{2-} \qquad (2)$$

From their non-geological experimental melts they showed that for fixed partial pressures of sulfur in the gas phase, sulfide sulfur decreases as oxygen pressure rises and sulfate sulfur increases. At 1500°C minimum sulfur contents were obtained at oxygen partial pressures of about 10^{-15} atm.

Katsura & Nagashima (1974) showed that at 1200°C sulfur is principally held in basaltic melts as the sulfide species at oxygen partial

TABLE 1. COMPOSITIONS OF SYNTHETIC STARTING MATERIALS

	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	FeO	Total
DB/3	47.58	14.84	8.10	11.10	12.27	6.71	100.60
DB/8	48.88	5.43	9.31	11.88	17.89	6.65	100.04
PAL-685	58.58	13.00	7.93	4.12	10.91	5.83	100.37

Analyst: P. Watkins

pressures below 10^{-8} atm and as dissolved sulfate at oxygen partial pressures above 10^{-8} atm. Therefore, all experiments in this study were carried out in the oxygen fugacity range of –log 8.50 to –log 11.50 as sulfide is the predominant species in Bushveld rocks.

Shima & Naldrett (1975) have shown that sulfur is held in the melt by displacing oxygen atoms and forming sulfur–metal bonds, principally with ferrous iron. Bonding probably also occurs with titanium and to a lesser extent with calcium. The iron–sulfur solution reaction can be expressed as follows:

$$\tfrac{1}{2}S_2 + FeO \rightleftharpoons \tfrac{1}{2}O_2 + FeS \qquad (3)$$

which can also be expressed as the redox reaction in (1).

In addition to the sulfidation reaction, equilibrium has to be achieved between the oxidation states of iron and the partial pressure of oxygen according to the following reaction:

$$\tfrac{1}{2}O_2 + 2FeO \rightleftharpoons Fe_2O_3 \qquad (4)$$

which can be expressed as a redox reaction:

$$\tfrac{1}{2}O_2 + 2(Fe^{2+}) \rightleftharpoons O^{2-} + 2(Fe^{3+}) \qquad (5)$$

At constant oxygen fugacity the overall equilibrium for the system can be represented as follows. For reactions (3) and (4):

$$\tfrac{1}{2}S_2 + 3FeO \rightleftharpoons FeS + Fe_2O_3 \qquad (6)$$

and for reactions (1) and (5):

$$\tfrac{1}{2}S_2 + 2(Fe^{2+}) \rightleftharpoons S^{2-} + 2(Fe^{3+}) \qquad (7)$$

If the silicate liquid is *undersaturated with sulfur*, the Fe^{2+}/Fe^{3+} ratio as well as the FeO content of the silicate melt will remain constant and the amount of sulfur in the melt will increase as a direct function of increasing sulfur fugacity [reaction (7)]. The relative proportions of ferrous to ferric iron in basaltic melts have been determined by Hill & Roeder (1974). At 1200°C and for oxygen fugacity values between –log 8.50 and –log 11.50, between 90 and 95%, respectively, of the iron present will be in the divalent state. In sulfur-undersaturated melts at *constant sulfur fugacity*, any increase in the oxygen fugacity would decrease the amount of sulfide in the melt as the sulfide-sulfate minimum is approached. Any increase in the oxygen fugacity would also result in a decrease in the ferrous iron content in the melt [reaction (5)] which would further decrease the amount of sulfide that could be held in the melt [reaction (3)].

When the silicate melt becomes *saturated with sulfur*, an immiscible sulfide phase will form. Although the Fe^{2+}/Fe^{3+} ratios in the silicate melt [reaction (3)) and sulfur fugacity. oxygen fugacity, the iron sulfide melt will remove FeO and equilibrium has to be reached between FeO, the FeS "component" in the silicate melt [reaction(3)] and sulfur fugacity. The overall equilibrium for these components can be expressed by reactions of the type given in (6).

EXPERIMENTAL TECHNIQUES

Furnace atmosphere control

Mixtures of carbon dioxide, carbon monoxide and sulfur dioxide were used to provide controlled furnace atmospheres. Flow rates were controlled through conventional capillary flowmeters. Fugacities of sulfur and oxygen were calculated using the program GASES (unpubl., British Steel Corp.). Thermochemical data were taken from JANAF tables (Stull 1965). As the temperature of the experiments was at 1200°C and the total pressure close to one atm, the gases were considered as behaving ideally.

Furnace construction

Special precautions were necessary to prevent the buildup of condensed sulfur at the gas exit in the furnace used for experiments carried out under controlled sulfur atmospheres. Gas was introduced from the top of the furnace and a system of indirect suction *via* a small filter pump was constructed at the bottom of the reaction tube. The design provided effective extraction of the exhaust gases in spite of sulfur condensation in the exit tube. A flexible heating element maintained the temperature above the melting point of sulfur in that part of the reaction tube projecting below the furnace insulation. Condensed sulfur was collected in a conical flask at the base of the reaction tube.

Power was supplied to the furnace through a P.I.D. temperature control system which maintained the temperature to ±1°C of the set point. Temperatures were measured at regular intervals during the run by means of a Pt–Pt 13%, Rh thermocouple enclosed in a "gas-tight" alumina sheath and calibrated against the melting point of gold.

General procedure

The apparatus was tested for air leaks by checking the wüstite/magnetite buffer reaction (Darken & Gurry 1945) in a sulfur-free atmosphere at 1200°C. Pressed disks of the starting material 4 mm in diameter were suspended in the furnace using the bead technique of Donaldson *et al.* (1975). The disks were initially fused onto a platinum loop by passing a small current through before attaching them to the charge assembly. The sample was lowered into the hot zone of the furnace with the correct gas mixture flowing. At the completion of each run, with the gas still flowing, the bead was withdrawn quickly into the air and quenched in water.

Analysis of run products

Chemical analyses were obtained on a modified Cambridge Scientific Instruments "Geoscan". Elements were analyzed in pairs at 15 kV and corrections to the raw data were made using the program written by Mason *et al.* (1969). Sulfur was analyzed using synthetic ZnS as a standard and a P.E.T. spectrometer crystal. An analysis from a single beam-position represents ten separate counting periods each of ten seconds both for peak and background spectrometer settings. This gave a detection limit for sulfur of 0.005 wt. % (calculated by taking the concentration equivalent in the standard of three times the standard deviation of the background count rate of the sample).

SILICATE AND SULFIDE CRYSTALLIZATION CHARACTERISTICS

Of the three starting compositions examined in the study, only PAL–685 was above its liquidus temperature at 1200°C. The only mineral phase present on the liquidus in DB/3 at 1200°C is olivine; it forms less than 20 vol. % of the bead. The composition of the olivine varies between $Fa_{22.7}$ and $Fa_{27.8}$, and is reflected in the depletion of MgO in the coexisting glass compared with the original starting material. Partition coefficients for iron and magnesium between olivine and glass are close to 0.30, in agreement with data from other studies. Pyroxene is the only mineral phase on the liquidus in DB/8; it forms about 25 vol. % of the bead.

Microscopic examination in reflected light of polished thin sections of charges saturated in sulfur indicates the presence of round immiscible sulfide droplets set in the silicate glass. Evidence of exsolution of the iron-oxide component in the sulfide phase can normally be seen under high magnification as a fine-scale eutectic-type intergrowth.

SULFUR DIFFUSION IN UNDERSATURATED SILICATE MELTS

The time taken for equilibrium to be achieved in beads undersaturated with sulfur depends on sulfur diffusion rates as well as the time taken for the strongly oxidized starting material (Table 1) to reach equilibrium according to reaction (5). During the early stages of a run, reaction (4) would be displaced to the right and it would be expected that as equilibrium was achieved oxygen would be released from the silicate melt. Evidence of degassing could be seen in beads run for 48 hours or less as they tended to be cloudy and vesicular. These beads were also characterized by concentration gradients for iron and sulfur (Fig. 1a) together with sulfide droplets which redissolved with longer run times. The metastable sulfide phase as well as the iron concentration profile are probably associated with nonequilibrium in the silicate melt with respect to reactions (4) and (5).

The sulfur-concentration profile (Fig. 1a) is more likely to be a function of diffusion rates; in order to establish these independently of reactions (4) and (5), beads of starting composition DB/3 were equilibrated for 48 hours in a sulfur-free atmosphere at the same oxygen fugacity and temperature as the intended run with sulfur. The results obtained on such a bead subsequently rerun for a short time in a sulfur atmosphere are shown in Figure 1b.

From Fick's 2nd law of diffusion and the determined sulfur profile, diffuson coefficients were calculated using the equation derived for diffusion into a sphere at short run times. The calculation assumes that (1) the melt is in equilibrium with the gas phase at the gas–melt interface, (2) there is a constant surface concentration and (3) there is no convection. A value of 5.6×10^{-8} was obtained for the apparent interdiffusion coefficient.

The slow diffusion rate established for sulfur is reflected in the results obtained from pre-equilibrated beads run at different time intervals (Fig. 2). Total sulfur in beads run for less than 48 hours and characterized by sulfur gradients was estimated by graphic integration of the diffusion profile. It can be seen from the lower curve that at least 72 hours are required to achieve equilibrium in pre-equilibrated beads.

It is more convenient to carry out runs in a sulfur atmosphere using the original oxidized starting material; a series of experiments was carried out at different time intervals under these conditions. The results, also plotted in Figure 2, define a trend shown by the top curve in which sulfur in the melt rises to a maximum after 60 hours, and falls off sharply

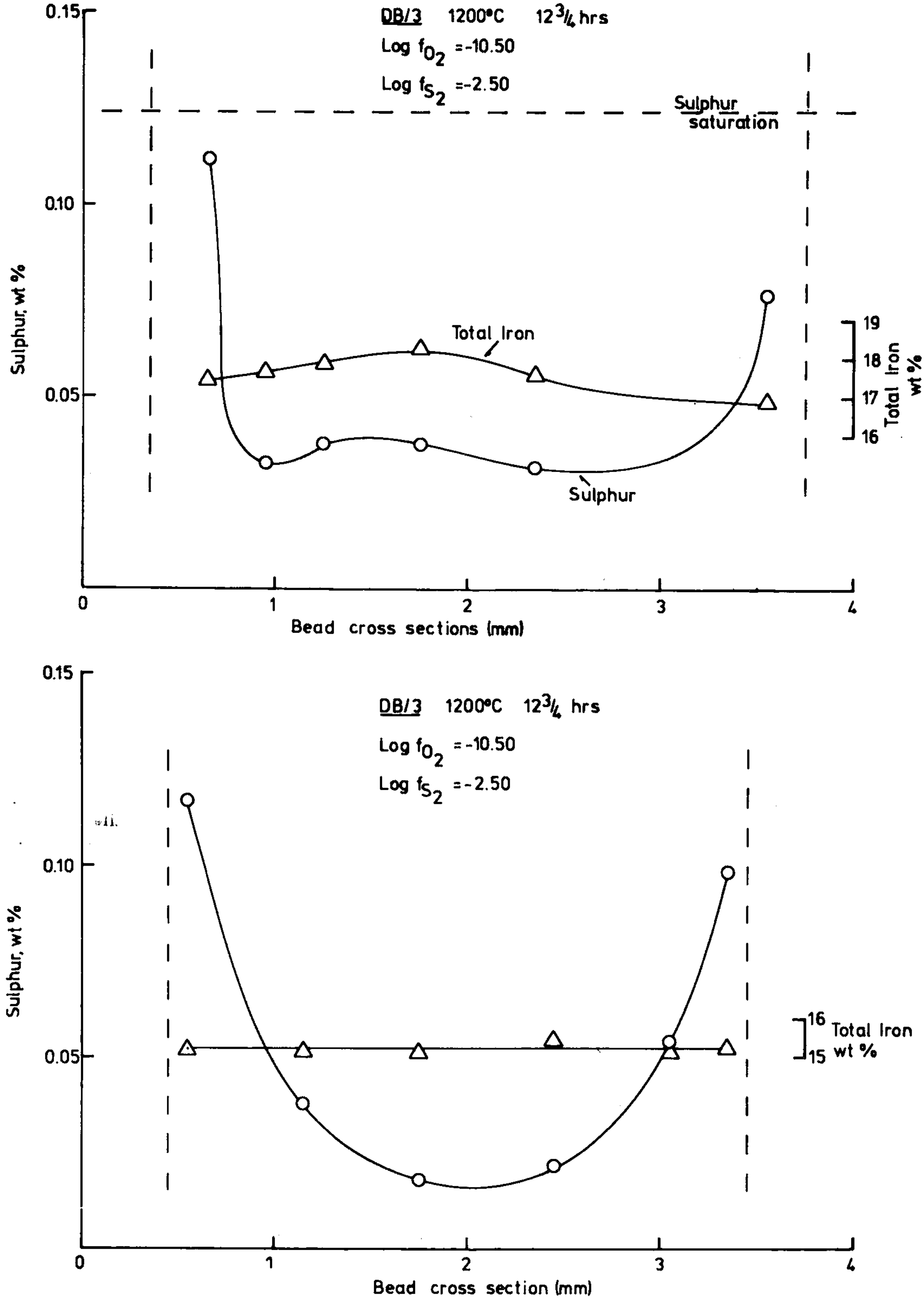

FIG. 1. Microprobe analyses of sulfur in the silicate glass from two beads of starting composition DB/3 obtained from the same run. Fig. 1a shows the diffusion profile present in oxidized starting material after 13¾ hours run time; Fig. 1b shows the diffusion profile present in starting material that had been pre-equilibrated.

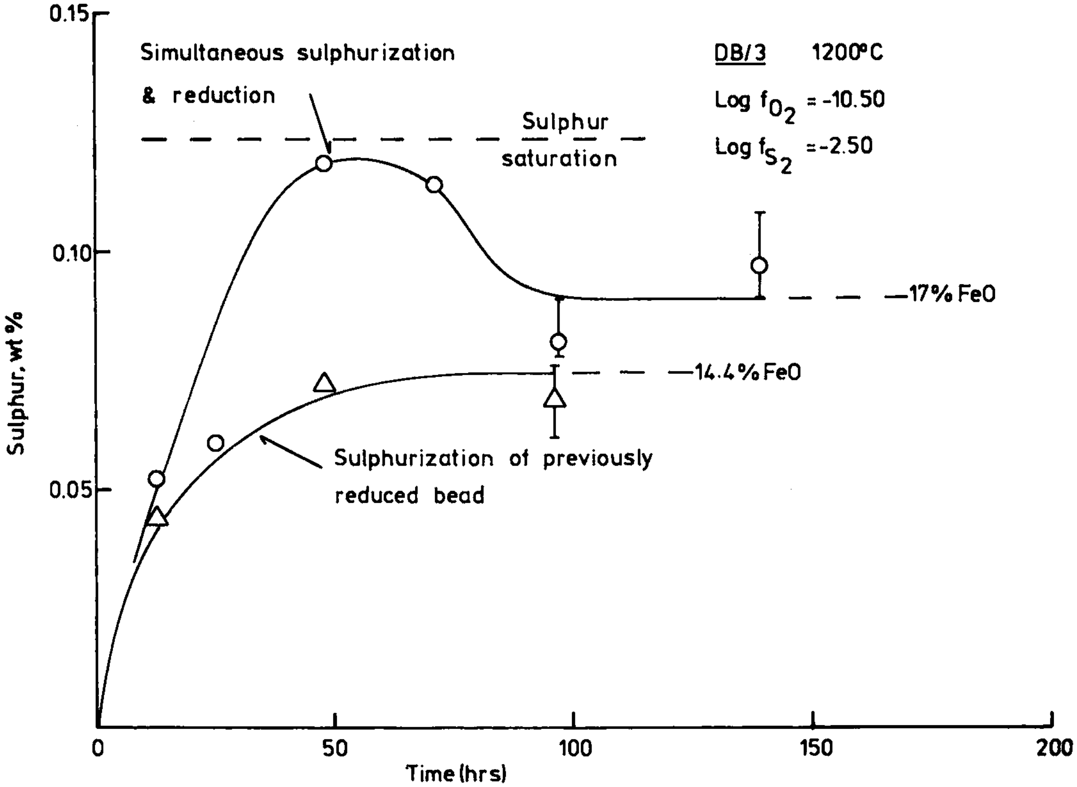

FIG. 2. Microprobe analyses of sulfur in silicate glass showing sulfidation curves obtained from both pre-equilibrated and oxidized starting composition DB/3. Vertical bars represent the range of values present in beads characterized by an overall flat diffusion profile.

as equilibrium is achieved after 90 hours. Sulfur present in the silicate melt in excess of equilibrium values in runs of 60 hours or less may possibly arise from the early formation of metastable sulfate species in the oxidized starting material. Reduction of the sulfate species takes place once the Fe^{2+}/Fe^{3+} ratio in the silicate melt reaches equilibrium according to reaction (5).

Turkdogan & Pearce (1963) report a maximum similar to that shown in Figure 2 during the sulfidation of highly reduced melts. They argued that reaction (1) is faster than reaction (5), with the result that the sulfur content of the melt reaches values above equilibrium owing to high concentrations of ferrous iron. As the oxidation of iron in the melt continues, the Fe^{3+}/Fe^{2+} ratio increases; as the partial pressure of sulfur in the gas is kept constant, the sulfur content of the melt must decrease as dictated by reaction (7).

SOLUBILITY OF SULFUR AS A FUNCTION OF FUGACITY AND MELT COMPOSITION

In order to ensure that equilibrium had been achieved, most runs were left in the furnace for at least 90 hours. The results from these series of experiments are listed in Tables 2a, 2b and 2c. Variation in sulfur solubility as a function of fugacity in starting material DB/3 has been plotted in Figure 3.

Experiments run at oxygen fugacities of greater than –log 10.00 all fell in the field of sulfur undersaturation and were found to give good agreement with the behavior predicted for sulfur by reaction (7) and discussed previously. Experiments carried out at oxygen fugacities of –log 10.50 and –log 11.50 reached saturation at sulfur fugacities of –log 1.75 and –log 3.75, respectively. On the –log 11.50 oxygen fugacity isobar the amount of sulfide formed can be estimated from the microprobe analyses of the coexisting silicate melt, which becomes depleted in FeO. From Table 2c (run 46) it can be seen that starting compositions DB/3 and DB/8, which are free of a sulfide phase, contain 15.67 and 21.21 wt. % FeO, respectively. FeO contents are reduced by up to 1.22 and 2.48 wt. %, respectively, in the field of sulfur saturation. PAL–685 contains 15.13 wt.% FeO in the field of undersaturation on the –log 10.50 oxygen isobar (run 71, Table 2b), which is reduced by 3.49 wt. % when starting material is run in the field of sulfur saturation on the –log 11.50 isobar (run 70, Table 2c). As the immiscible sulfide melt formed consists of about 60 wt. % iron (Naldrett 1969), the sulfide phase must form less than five wt. % of the beads in this study. At the higher oxygen fugacity isobar of –log 10.50 even at sulfur fugacities as high as –log 1.25 (run DB/3–81, Table 2b) the sulfide phase nucleates very slowly and only isolated blebs are present.

Owing to the slow precipitation of a sulfide phase, it is probable that iron is removed in amounts well short of the equilibrium values that should be reached between the FeO and FeS components in the silicate melt and sulfur fugacity [reaction (6)]. By plotting total FeO analyzed in saturated beads of all starting compositions as a function of sulfur in the glass (data plotted in Fig. 4 are taken from Tables 2b and 2c), however, a reasonable fit is obtained on the oxygen isobars. This suggests that

TABLE 2a. MICROPROBE ANALYSES OF SILICATE MELTS FROM STARTING COMPOSITION DB/3 IN EQUILIBRIUM WITH THE -LOG 8.50, -LOG 9.50 AND -LOG 10.00 OXYGEN FUGACITY ISOBARS

TEMPERATURE = 1200°C. KEY TO "PHASES PRESENT" : ol = olivine, gl = silicate glass, sp = abundant immiscible sulfide developed, (sp) = minor immiscible sulfide developed, px = pyroxene.

LOG f_{O_2}	= -8.50		LOG f_{O_2} = -9.50				LOG f_{O_2} = -10.00		
LOG f_{S_2}	-1.40	-2.00	-1.00	-2.00	-3.00	-4.00	-1.50	-2.00	-3.00
RUN NO.	43	38	41	35	36	37	49	47	48
SO_2 CC/MIN	98.76	62.88	45.77	9.71	2.98	0.69	14.91	5.92	1.19
CO_2 CC/MIN	4.85	86.20	32.54	120.26	164.62	133.82	89.32	108.47	117.81
CO CC/MIN	16.40	10.91	61.69	30.03	32.40	25.49	55.77	45.61	41.01
TOTAL CC/MIN	120.01	159.99	140.00	160.00	200.00	160.00	160.00	160.00	160.01
TIME (HOURS)	77	99	101	95	96	112	90	99	95
Phases Present	ol+gl	ol+gl	ol+gl	ol+gl	ol+gl	gl+ol	ol+gl	ol+gl	ol+gl
Mol. % Fa	25.50	25.10	25.42	25.79	25.09	25.65		24.84	
NUMBER OF ANALYSES IN AVERAGE	5	5	5	5	5	5	5	5	5
SiO_2	48.26	48.32	49.12	49.15	48.66	49.28	49.22	48.33	49.68
Al_2O_3	15.92	16.02	16.18	15.59	16.14	15.91	15.00	15.76	14.96
CaO	8.76	8.88	8.99	8.68	8.92	8.82	8.15	8.88	8.42
MgO	8.82	9.09	8.86	8.61	8.97	8.91	9.16	9.07	9.15
FeO	17.05	16.65	16.37	16.97	16.19	16.66	17.13	16.60	16.77
TOTAL	98.81	98.96	99.52	99.00	98.88	99.58	98.66	98.64	98.98
WEIGHT PERCENT SULFUR									
AVERAGE	0.027	0.009	0.059	0.027	0.015	0.011	0.070	0.062	0.025
RANGE	0.021-0.034	0 005-0.015	0.054-0.062	0.018-0.036	0.010-0.22	0.006-0.016	0.062 0.074	0.057-0.067	0.021-0.028

equilibrium has been achieved between the amount of sulfur dissolved in the silicate melts and its FeO content as indicated by reaction (6). The data of Haughton *et al.* (1974) have also been plotted in Figure 4 in cases where their gas-mixing ratios fell in the field of sulfur saturation defined by Figure 3. Their data show good agreement with the trends established from the present study, provided data for combined FeO and TiO_2 are used.

TABLE 2b. MICROPROBE ANALYSES OF SILICATE MELTS FROM STARTING COMPOSITIONS DB/3 AND PAL-685 IN EQUILIBRIUM WITH THE -LOG 10.50 OXYGEN FUGACITY ISOBAR. TEMPERATURE = 1200°C

LOG f_{O_2} = -10.50							
LOG f_{S_2}	-1.25	-1.75	-2.00	-2.50	-3.00	-3.50	-4.00
RUN NO.	81	69	31	42	33	71	34
SO_2 CC/MIN	22.11	8.08	5.01	2.04	0.90	0.43	0.30
CO_2 CC/MIN	50.60	82.32	89.20	95.79	98.26	99.26	139.51
CO CC/MIN	87.29	69.60	65.79	62.18	60.84	60.31	84.07
TOTAL CC/MIN	160.00	160.00	160.00	160.01	160.00	160.00	223.88
TIME (HOURS)		94	96	97	91	94	119
				DB/3			
PHASES PRESENT	ol,gl(sp)	ol,gl(sp)	ol+gl	ol+gl	ol+gl	ol+gl	ol/gl
MOL. % Fa			25.94	26.58	27.79		25.54
NUMBER OF ANALYSES IN AVERAGE		3	5	5	5	4	5
SiO_2	-	50.01	49.97	48.85	49.79	49.79	50.19
Al_2O_3	-	15.87	15.39	15.72	14.47	15.42	15.62
CaO	-	8.75	8.64	8.71	8.55	8.74	8.66
MgO	-	8.78	8.61	8.81	8.39	8.70	8.64
FeO	-	16.53	17.27	17.10	17.02	16.67	16.46
TOTAL		99.94	99.88	99.19	99.22	99.32	99.57
WEIGHT PERCENT SULFUR							
AVERAGE	0.114	0.136	0.123	0.081	0.039	0.068	0.020
RANGE	0.106-0.125	0.122-0.150	0 115-0.130	0.078-0.090	0.035-0.048	0.063-0.072	0.014-0.026
COMPOSITION		PAL - 685				PAL - 685	
PHASES PRESENT		gl				gl	
NUMBER OF ANALYSES IN AVERAGE		3				3	
SiO_2		56.32				55.87	
Al_2O_3		13.94				14.34	
CaO		9.59				9.56	
MgO		4.77				4.71	
FeO		15.04				15.13	
TOTAL		99.66				99.61	
WEIGHT PERCENT SULFUR							
AVERAGE		0.103				0.054	
RANGE		0.092-0.113				0.047-0.059	

TABLE 2c. MICROPROBE ANALYSES OF SILICATE MELTS FROM STARTING COMPOSITIONS DB/3, PAL-685 AND DB/8 IN EQUILIBRIUM WITH THE -LOG 11.50 OXYGEN FUGACITY ISOBAR. TEMPERATURE = 1200°C.

LOG f_{O_2} = -11.50					
LOG f_{S_2}	-1.20	-2.00	-3.00	-3.50	-4.00
RUN NO.	44	40	45	70	46
SO_2 CC/MIN	25.17	5.76	1.01	0.49	0.40
CO_2 CC/MIN	0.12	47.00	53.09	54.25	87.65
CO CC/MIN	134.71	120.02	105.91	105.27	167.95
TOTAL CC/MIN	160.00	172.78	160.01	160.01	256.00
TIME HOURS	95	95	95	96	122
			DB/3		
Phases Present	ol,gl+sp	ol,gl(sp)	ol,gl+sp	ol,gl+sp	ol+gl
Mol. % Fa	22.70	25.28	22.49-25.66		24.07
NUMBER OF ANALYSES IN AVERAGE	5	5	4	5	5
SiO_2	48.62	49.43	49.24	50.68	49.14
Al_2O_3	16.04	15.97	16.43	16.63	15.59
CaO	8.81	8.94	8.97	9.06	8.89
MgO	9.47	8.77	9.82	8.74	9.40
FeO	15.54	16.04	14.45	14.82	15.67
TOTAL	98.48	99.15	98.91	99.93	98.69
WEIGHT PERCENT SULFUR					
AVERAGE	0.159	0.140	0.145	0.156	0.049
RANGE	0.155-0.163	0.130-0.152	0.138-0.157	0.148-0.170	0.041-0.059
COMPOSITION	DB/8		DB/8	PAL - 685	DB/8
PHASES PRESENT	px,gl(sp)		px,gl+sp	gl+sp	px+gl
NUMBER OF ANALYSES IN AVERAGE	2		3	2	4
SiO_2	52.74		51.41	57.27	51.10
Al_2O_3	8.39		7.81	15.05	7.53
CaO	12.10		11.77	10.39	11.80
MgO	7.54		7.98	5.28	7.78
FeO	18.73		19.50	11.64	21.21
TOTAL	99.50		98.47	99.63	99.42
WEIGHT PERCENT SULFUR					
AVERAGE	0.281		0.317	0.107	0.115
RANGE	0.278-0.284		0 314-0.322	0.097-0.117	0.110-0.121

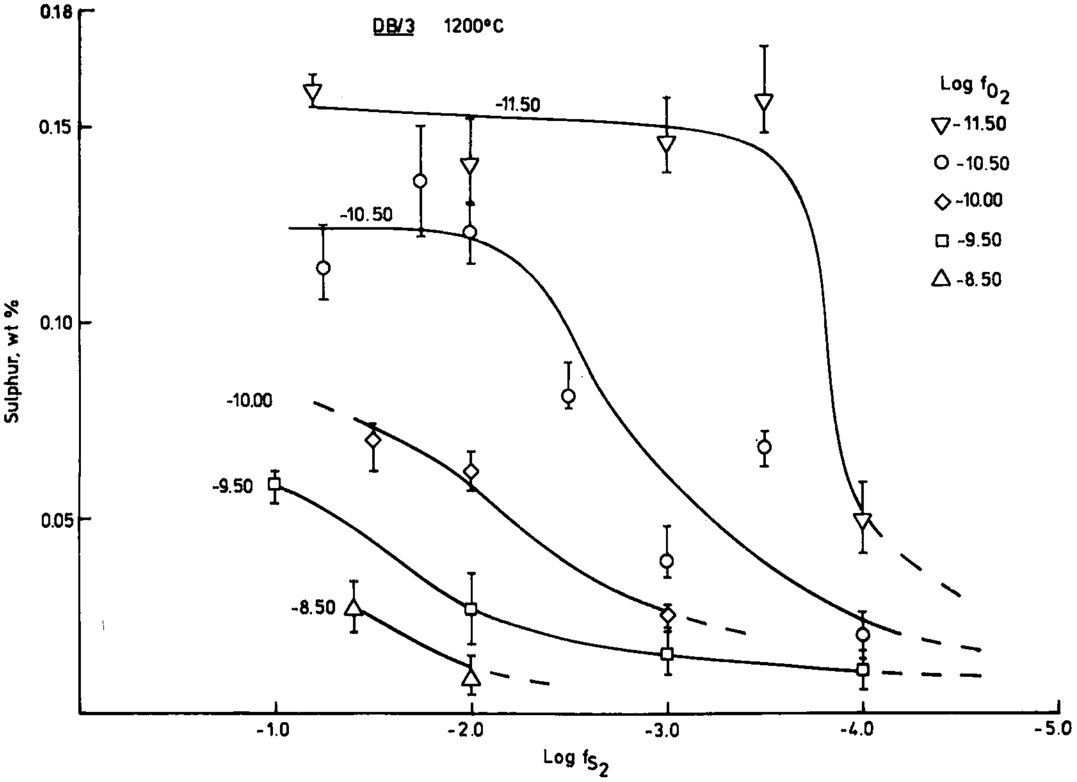

FIG. 3. Microprobe analyses of silicate glass from starting composition DB/3 as function of oxygen and sulfur fugacity. Data taken from Tables 2a, 2b, and 2c. Vertical bars represent the range of values present in the beads.

APPLICATION OF THE EXPERIMENTAL DATA TO BUSHVELD ROCKS

Diorites of the Upper Zone of the Bushveld, which formed from an iron-rich magma, normally contain disseminated sulfides, but significant concentrations are found only in association with magnetite-rich layers. The presence of disseminated sulfides suggests that the original magma was probably saturated with sulfur although only minor amounts of an immiscible sulfide phase were present. Any changes in the magma that would promote precipitation of magnetite would decrease the FeO content of the liquid and therefore decrease the capacity of a sulfur-saturated magma to dissolve sulfur (Fig. 4). These changes may ultimately lead to supersaturation of the magma in sulfur and so promote the formation of an immiscible sulfide phase.

The problem of establishing reliable oxygen fugacity data for the Upper Zone diorites from magnetite–ilmenite pairs has already been discussed. As oxygen fugacity apparently was close to the QFM buffer at subsolidus temperatures, the data of Wones & Gilbert (1969) can be used to calculate a value from the reaction at 1200°C. A calculated value of –log 8.47 would require, according to the data established in the present study (Fig. 3), values of sulfur fugacity greater than –log 1.00 before the magma could reach saturation.

It has already been shown that the nucleation of an immiscible sulfide phase in sulfur-saturated melts is inhibited at the higher values of oxygen fugacity. The value calculated from the QFM reaction is therefore consistent with the earlier suggestion that the Upper Zone magma would have to be supersaturated with sulfur before an immiscible sulfide phase could form.

Sulfur saturation can also be achieved on the –log 11.50 oxygen isobar at sulfur fugacity values as low as –log 3.75 (Fig. 3). Provided similar low-oxygen-fugacity conditions were present in the magma that gave rise to the magnesium-rich, magnetite-free rocks at the base of the Bushveld sequence, small increases in the sulfur fugacity would be sufficient to produce an immiscible sulfide phase. The overall amount of sulfur needed to saturate the magma would, however, be large (approximately 1500 ppm sulfur for a melt with 15% FeO at 1200°C: Fig. 4); the absence of widespread disseminated sulfides in rocks at the base of the Bushveld sequence argues against derivation from a magma saturated with sulfur. Only where sulfur was introduced into the magma from external sources is saturation likely to be achieved. Mobilization of sulfides in the underlying rocks in response to thermal metamorphism could, therefore, have played an important role in the formation of known sulfide concentrations in rocks at the base of the Bushveld sequence.

Whereas this study has focused on the effect of silicate melt composition and fugacity on sulfur solubility and sulfide immiscibility, temperature and pressure contributions have not been considered. B. Mysen (pers. comm.) has shown experimentally that sulfur solubility in silicate melts increases with increasing pressure. It would be expected, therefore, that an immiscible sulfide melt would separate from a magma during ascent from the mantle. Any reduction in temperature would also reduce the capacity of the melt to dissolve sulfur (Haughton *et al.* 1974) and could lead to the formation of a sulfide phase. Both factors may have contributed to the genesis of sulfide ore deposits associated with the Bushveld complex.

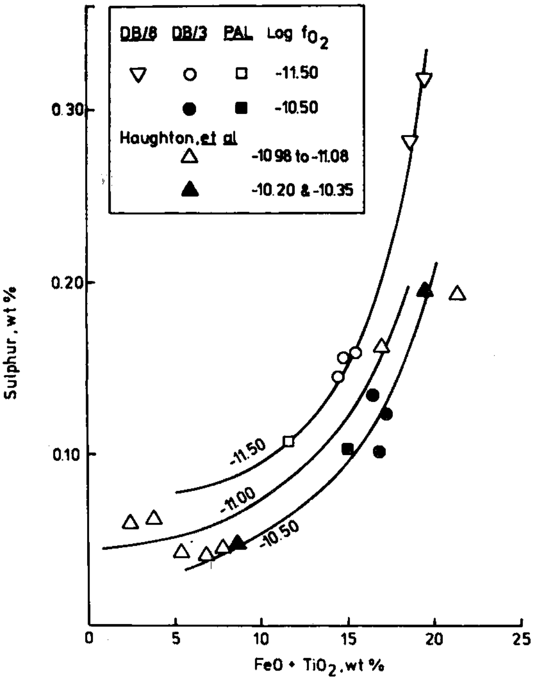

FIG. 4. Microprobe analyses for sulfur in silicate glass in equilibrium with an immiscible sulfide melt. Data are taken from Tables 2b and 2c as well as from Haughton *et al.* (1974).

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