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The Solubility of Sulphur in Hydrous Rhyolitic Melts

BEATRICE CLEMENTE, BRUNO SCAILLET AND MICHEL PICHAVANT

INSTITUT DES SCIENCES DE LA TERRE D'ORLEANS, CNRS, 1A RUE DE LA FEROLLERIE, F-45071 ORLEANS CEDEX 2, FRANCE

Experiments performed at 2 kbar, in the temperature range 800–1000°C, with fO2 between NNO-2.3 and NNO+2.9 (where NNO is the nickel-nickel oxide buffer), and varying amounts of sulphur added to hydrous metaluminous rhyolite bulk compositions, were used to constrain the solubility of sulphur in rhyolite melts. The results show that fS2 exerts a dominant control on the sulphur solubility in hydrous silicate melts and that, depending on fO2, a rhyolitic melt can reach sulphur contents close to 1000 ppm at high fS2. At fO2 below NNO+1, the addition of iron to a sulphurbearing rhyolite magma produces massive crystallization of pyrrhotite and does not enhance the sulphur solubility of the melt. For a given fO2, the melt-sulphur-content increases with fS₂. For fixed fO2 and fS2, temperature exerts a positive control on sulphur solubilities, at least for fO2 below NNO+1. The mole fraction of dissolved sulphur exhibits essentially linear dependence on fH₂S at low fO₂ and, although the experimental evidence is less clear, on fSO_2 at high fO_2 . The minimum in sulphur solubility corresponds to the redox range where both fH₂S and fSO₂ are approximately equal. A thermodynamic model of sulphur solubility in hydrous rhyolite melts is derived assuming that total dissolved sulphur results from the additive effects of H₂S and SO₂ dissolution reactions. The model reproduces well the minimum of sulphur solubility at around NNO+1, in addition to the variation of the sulphide to sulphate ratio with fO2. A simple empirical model of sulphur solubility in rhyolitic melts is derived, and shows good correspondence between model and observations for high-silica rhyolites.

KEY WORDS : sulphur; solubility; rhyolite; thermodynamics; *f*O₂; *f*S₂

INTRODUCTION

Sulphur species are the most abundant magmatic volatiles, after H₂O and CO₂. Sulphur is also a major component of magmatic solid and melt phases (e.g. pyrrhotite, anhydrite, Fe–S–O liquid). Experiments performed at 1 atm on a wide variety of silicate liquid compositions have shown that sulphur solubility is a function of fO2, f S2, temperature and melt composition (Fincham & Richardson, 1954; Richardson & Fincham, 1956; Abraham & Richardson, 1960; Abraham et al., 1960; Haughton et al., 1974; Katsura & Nagashima, 1974; Shima & Naldrett, 1975; Buchanan & Nolan, 1979; O'Neill & Mavrogenes, 2002). Experimental studies in which fO2 varied significantly have shown that a minimum in sulphur solubility occurs at around NNO to NNO+1 (NNO being the Ni–NiO solid buffer assemblage) (see Carroll & Webster, 1994). Experimental studies carried out at high pressure (Carroll & Rutherford, 1985, 1987; Luhr, 1990) on hydrous andesitic to dacitic compositions have also shown a minimum in sulphur solubility in this

redox range. The effect of temperature on sulphur solubility has been studied, mostly at 1 atm (Richardson & Fincham, 1954; St Pierre&Chipman, 1956; Nagashima & Katsura, 1973; Katsura & Nagashima, 1974; Buchanan et al., 1983). These studies showed that for a constant SO₂ input in 1 atm gas furnaces [or constant absolute value of fS₂ for the study by Buchanan et al. (1983)], and a constant absolute value of fO₂, the sulphur solubility increases with temperature under reducing conditions (below NNO-1) and decreases when temperature increases under oxidizing conditions. Luhr (1990) observed a positive dependence of sulphur solubility on temperature under oxidizing conditions at high pressure, but fS_2 was not kept constant in these experiments. In fact, with the exception of Luhr (1990), most highpressure sulphur solubility experiments have been performed without the precise and systematic control of fS2. This hinders the understanding of the control that fS_2 may have on sulphur solubility in hydrous silicate liquids, which, in turn, renders difficult any thermodynamic modeling of the sulphur solubility in silicate melts. To address this issue, we have determined the relationship between fO₂, fS₂, T (temperature) and XS (dissolved melt sulphur content) for rhyolitic compositions. We have used rhyolitic compositions primarily because itmakes it possible to work at relatively low temperatures (≤1000°C), where accurate control of critical parameters (namely T, fO_2 , fH_2O_1 , and fS_2) is comparatively easy. In addition, sulphur solubility data on rhyolitic melts are still scarce (Carroll & Rutherford, 1987; Luhr, 1990; Baker & Rutherford, 1996a; Scaillet et al., 1998), and our study aims at filling this gap. Rhyolitic melts represent important compositional end-members in the evolution of Srich intermediate to silicic magmas, such as those found in arc settings (e.g. Martel et al., 1998; Scaillet & Evans, 1999). Here, we present a detailed set of sulphur solubility data, acquired at between 800 and 1000°C at 2 kbar and under various fO₂ and fS₂. We emphasize how fS_2 , fO_2 and T control the solubility of sulphur in rhyolitic melts and we derive both a thermodynamic and an empirical model for the solubility of sulphur in hydrous rhyolite melts.

EXPERIMENTAL TECHNIQUES

Apparatus

All experiments were performed in an internally heated pressure vessel (IHPV), working vertically using Ar–H₂ mixtures as the pressurizing medium (Scaillet et al., 1992). For reducing conditions and at 800 and 930°C, we used a Shaw membrane to measure the f H2 (Shaw, 1963; Scaillet et al., 1992), connected to a Protais gauge (accurate to 0.1 bar). For experiments performed at 1000°C, the experimental fH_2 was measured using Ni–Pd-based solid sensors [Taylor et al., 1992; Pownceby & O'Neill, 1994; see Scaillet & Evans (1999) for additional details]. Sensor capsules were prepared using Pt tubes, lined with ZrO₂ to prevent reaction between Pt and the sensor material. The sensors were sealed. For each experiment, we used two starting sensor compositions with different bulk Ni/Pd ratios. In all cases, both sensors gave nearly identical final compositions, tightly bracketing the experimental fO_2 (or fH_2). Temperature was measured with three sheathed chromel–alumel thermocouples, calibrated at 1 atm against the melting point of NaCl and is accurate to within $\pm 5^{\circ}$ C. Pressure was monitored by a factory-calibrated Heise gauge, accurate to within 20 bar. All experiments were performed at 2 kbar, with run durations of between 6 and 9 days.

Quenching was accomplished by turning off the furnace power, with quench rates of around 100°C/min between 800 and 250°C.

Starting materials and capsule preparation

The experiments were performed with crushed anhydrous glasses of rhyolitic composition (Table 1), obtained by fusion of a synthetic gel at 1400°C and 1 atm. The compositions correspond to that of the interstitial glasses of the recent Mont Pelée andesites (P1 Plinian eruption, dated at 650 BP; Martel et al., 1998) and that of Mt Pinatubo 1991 dacite (Table 1). Experimental charges were prepared by weighing finely ground glass and elemental sulphur (S) into Au capsules. Between 5 and 6 wt% deionized and distilled H₂O was added, so as to reach conditions slightly below H₂O saturation for a system without sulphur under our experimental conditions. A preliminary study showed that the starting form of sulphur in the experimental charge (as elemental, pyrrhotite or anhydrite) has no detectable effect on the stability of sulphur-bearing phases. The addition of sulphur as anhydrite or pyrrhotite can, however, lead to an increase of the FeO_{tot} and CaO contents of the melt, eventually resulting in the crystallization of a silicate or oxide phase. Therefore, to avoid significant modifications of the starting glass composition as a result of the addition of elements other than sulphur, we used mainly elemental sulphur as starting material. Different concentrations of sulphur were used to generate different fS_2 . In some charges, synthetic pyrrhotites of differing starting compositions (i.e. Fe/S atomic ratio) were used as a sulphur source, with the purpose of monitoring the kinetics of attainment of equilibrium fS_2 . In addition, to investigate the role of iron on sulphur solubility in hydrous silicic melt, some charges were doped with magnetite. The bulk compositions of these magnetite-added charges are listed in Table 1. After quenching, the capsules were re-weighed, to check for leaks. They were then pierced under a binocular microscope, in order to detect a fluid phase, and any H₂S smell was noted. After complete opening, glass chips were mounted in epoxy resin and polished using diamond solutions for SEM and electron microprobe analyses.

Control of fO_2 and fS_2

Oxygen fugacity was varied between NNO-2.3 and NNO+2.9, by varying the fH_2 and fH_2O of the experiment. The sample capsules were always positioned near the Shaw membrane or near the sensor capsules. The fO_2 of any given charge was calculated through the water dissociation reaction

$$\mathbf{K}_{\mathbf{w}} = \frac{f\mathbf{H}_2 \times f\mathbf{O}_2^{1/2}}{f\mathbf{H}_2\mathbf{O}}.$$

We determined the fH_2O in each charge from the water content of the glass, using the model of Burnham (1979).

	MP natural ¹	MP synthetic ²	MP15VII ³	MP16VII ³	MP17VII ³	MP18XII ³	MP19XII ³	Pinatubo ⁴
SiOn	75:65	75:92	70-43	71.60	71-47	72-06	72.06	78-29
Al ₂ O ₃	12.97	13.10	12.15	12.35	12.33	12.43	12.43	12.85
FeO	2.15	2.00	9.09	7.59	7.75	6-99	6-99	1.06
MgO	0-34	0.32	0.29	0-29	0.29	0-29	0-29	0-20
CaO	2.26	2.58	2.39	2.43	2.43	2.45	2.45	1.31
Na _z O	4-34	4-14	3-84	3-90	3.93	3-93	3-93	3-29
K ₂ O	1.94	1.94	1.80	1.83	1.83	1-84	1-84	2.85
FeO/(FeO+MgO)	0-86	0.87	0.97	0.96	0.96	0.96	0.96	0-84

The compositions are recalculated to 100% anhydrous. Total iron is given as FeO.

¹Natural interstitial glass composition of Mt Pelée andesite erupted in 1929 (Martel *et al.*, 1998). It also contains 0.26 wt % TiO_2 and 0.08 wt % MnO. Dry synthetic glass used in all non magnetite-doped charges.

³Magnetite-doped charges, obtained by mechanical mixture between the dry MP synthetic glass and stoichiometric magnetite.

Dry synthetic glass similar to the Pinatubo 1991 dacite interstitial glass (Scaillet & Evans, 1999). It also contains 0.15 wt % TiO₂.

Table 1: Starting compositions (wt %)

For experiments performed with a Shaw membrane, the oxygen fugacity of a given charge was computed from equation (2), knowing the fH₂ of the experiment, the fH₂O of the charge and the equilibrium constant of the reaction, Kw (Robie et al., 1979). For experiments with solid sensors, the prevailing fH_2 was first computed from equation (2), using the sensor composition and the model of Pownceby & O'Neill (1994) and assuming that fH_2O in the sensor was that of pure H_2O . Then, the fO_2 of the charge was calculated with fH₂ and fH₂O from the model of Burnham (1979). It should be noted that the above approach in controlling fO₂ does not require the presence of a fluid phase in the charge. Equilibrium (1) can be either homogeneous, with all components dissolved in the melt, or heterogeneous, with components either in the melt or fluid phases. The uncertainty in fO_2 calculation depends on the uncertainties in temperature, fH_2 and fH_2O . Errors arising from uncertainties attached to either fH_2 (± 0.1 bar) or temperature (±5°C) measurements are minor, i.e. less than 0.01 log fO₂. In contrast, the uncertainty attached to fH₂O is the main source of error, as it depends both on the uncertainty of the determination of the melt H₂O content, which is, here, estimated using the by-difference method (see below), and on the accuracy of the thermodynamic model used to calculate H_2O fugacities from melt H_2O contents. An error of ± 0.5 wt%in the melt H_2O content, which corresponds to the analytical uncertainty of most charges, translates into an error of c. 10% in *f*H₂O using the model of Burnham (1979), which, in turn, translates into an uncertainty of c. 0.2 log units in fO₂, if all other parameters are held constant. The error associated with the thermodynamic model is more difficult to evaluate. In this study, all melt compositions are rhyolitic (see below), with SiO2 contents in the range 75–79 wt % (anhydrous basis) and are, therefore, in a compositional domain that is well covered by existing thermodynamic models of H₂O solubility in silicate melts (see Zhang, 1999). Although it is well known that the Burnham model does not properly account for the actual water species in the melt, a recent compilation by Zhang (1999) has shown that, in terms of bulk water solubility, the Burnham model yields water contents almost identical to those obtained using speciation models (e.g. Stolper, 1982), at least up to 3 kbar. Thus, besides the speciation of water in silicate melt, the use of either model (Burnham- or Stolper-type) makes no difference in terms of f H₂O calculations that we are interested in. The Burnham model is based on the thermodynamic properties of pure water, as determined by Burnham et al. (1969), which were also used to derive the a and b parameters used in the MRK equation of state (EOS) of H₂O by Holloway (1977). In the updated version of the Stolper model, provided by Zhang (1999), the EOS of Pitzer & Sterner (1994) is used to calculate *f*H₂O. As explained below, the MRK-EOS of Holloway (1977) is used for the calculation of *f*S₂. Therefore, for the sake of internal consistency, the Burnham model has been used in this work. Standard error propagation formalism of analytical or experimental sources of error through equation (2) yields an uncertainty in *f*O₂ that is always less than 0.6 log units and with an average ($\pm 1\sigma$) of 0.18 log units for all charges. All experimental *f*O₂ are referenced to the NNO buffer (Holloway et al., 1992).

The fS_2 was determined from the composition of pyrrhotite, crystallized during the experiment (Froese & Gunter, 1976). The fS_2 of the experiments was thus not fixed by a standard buffer assemblage such as pyrite–pyrrhotite, but, instead, it was a function of the initial amount of sulphur in the charge and of the imposed experimental conditions. By changing the bulk sulphur content of the starting material, we changed the fS_2 of the

system. Sulphur fugacities calculated with pyrrhotite composition determined by XRD (see below) are known to within \pm 0.2 log units. However, under oxidizing conditions, pyrrhotite is not a stable phase and is replaced either by an Fe–S–O liquid (see below) or by anhydrite (Carroll & Rutherford, 1985, 1987; Luhr, 1990). In our experiments, progressive addition of sulphur leads to saturation of the hydrous silicate liquid with respect to a fluid phase. In such cases (i.e. fluid phase present), we used an MRK equation of state (e.g. Holloway, 1977, 1981, 1987) to determine fS_2 and the fluid phase composition.

The fluid phase can be described in the H–O–S system. By the phase rule, we have

$$v = 2 + C - \varphi$$

where *C* is the number of components, φ is the number of phases and *v* is the degree of freedom (4 in this case). The pressure, the temperature and the *f*H₂ are fixed in our experiments and we know the _fH₂O of each charge. Therefore, the system is invariant and we can calculate the fluid phase composition and, thus, the _fS₂. Note that this allows calculation of the fugacities of all S-bearing species in the fluid, even if none is known. In this study, we used the MRK equation of state (MRK-EOS) of Holloway (1977):

$$P = \frac{RT}{V-b} - \frac{a}{\sqrt{T} \left(V^2 + Vb \right)}$$

<i>i</i> is the pressure, <i>i</i> the temperature	P	s the	is	pressure,	Т	the	temperature
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where *P* is the pressure, *T* the temperature, *V* the volume, and *a* and *b* are two parameters as a function of temperature and/or pressure. For pure phases, *a* and *b* can be estimated from the critical pressure (*Pc*) and temperature (*Tc*) (Breedveld & Prausnitz, 1973; Ferry & Baumgartner, 1987). Calculation of the fluid phase compositions indicates that the major species under our experimental conditions are

H₂O, H₂, H₂S, SO₂ and S₂. H₂O is a polar molecule, the parameters *a* and *b* for water, taken from Holloway (1981). H₂S and SO₂ are also polar molecules but no P-V-T data are available under our experimental conditions. Therefore, we considered these molecules as non-polar, *a* and *b* being determined from *Pc* and *Tc*, as given by Shi & Saxena (1992). For S₂, *Pc* and *Tc* are not known and we used the estimated values of Shi & Saxena (1992). The full set of a and b parameters used in the MRK-EOS is listed in Table 2.

	$a~({ m atm}~ imes~{ m cm}^6{ m K}^{0.5}/{ m mole}^2)$	b (cm ³ /mole)
H ₂ ¹	3.56×10^6	15·15
H_2S^2	89.38×10^{6}	29.89
SO22	142.92 \times 10 ⁶	39-46
S22	25×10^{6}	20-57
	ao	b
H_2O^1	35×10^{6}	14-6

¹From Holloway (1981).

²From Shi & Saxena (1992).

Table 2: a and b parameters used in the MRK equation of state



Fig. 1. Comparison between fS_2 measured by the pyrrhotite composition [DFFS(po)] and fS_2 calculated from an MRK equation of state [DFFS(V)].

The MRK program was checked against the program of Connolly & Cesare (1993) and, for given *P*, *T*, fH_2 and fH_2O conditions, both methods were found to agree within 0.2 log fS_2 .

As discussed previously, for reducing conditions (fO2< NNO), fS_2 was calculated from the pyrrhotite composition. Some pyrrhotite-bearing charges that were saturated with a fluid phase provided a test of the validity of the MRK-EOS approach to compute fS₂ and fluid phase compositions. As shown in Fig. 1, the fS_2 given by the pyrrhotite composition and the fS_2 given by the fluid phase composition are usually found to agree with each other to within 1 log unit for most charges, which is considered encouraging, given our current poor knowledge of the thermodynamic behavior of the H–O–S fluids at magmatic conditions. Charges at an fO₂ above NNO+1 or at 1000°C are those for which the two methods yielded significantly different results (Fig. 1). This misfit could be due, in part, to the modification of sulphide composition during cooling (see below). Despite this limitation, we conclude that it is possible to use the MRK equation of state to estimate fS₂ of charges lacking pyrrhotite, at least for H₂O-rich fluid compositions. An additional check on the accuracy of the calculated fS2 was also provided by comparing the H2O/S ratio of the fluid phase, as calculated from MRK, against that obtained through mass balance. In the latter, the amount of S and H₂O left over for the fluid phase can be determined. Thus, the H₂O/S ratio of the fluid can be obtained and compared with H₂O/S values calculated from the MRK-EOS approach. Pyrrhotite-free charges for which the calculated H₂O/S ratios from both methods failed to converge were not considered for deriving either the thermodynamic or the empirical models of sulphur solubility presented below. Sulphur fugacities calculated using an MRK approach have larger associated uncertainties than those calculated from the pyrrhotite composition (around \pm 0.5 log units), largely because of the propagation of the uncertainty associated with the determination of melt water contents. All values of fS2 are referenced to the FFS buffer, which corresponds to the equilibrium between iron and troilite :

$$Fe + \frac{1}{2}S_2 \Leftrightarrow FeS$$

$$\ln f S_2 = \frac{2}{RT} (-0.2655(P-1) - 35910 + 12.56T) \text{ (Froese & Gunter, 1976)}$$

with *T* in K, *P* in bar and *R* in cal/mol K. We extrapolated the data from Froese & Gunter (1976) to high temperature (above 900°C) and, at 2 kbar, the -log fS_2 (FFS) is 9.36 at 800°C, 7.75 at 930°C and 7.02 at 1000°C. Knowing fH_2 , fS_2 , and fO_2 , the equilibrium values of both fH_2S and fSO_2 were calculated using the following equilibria:

$$\frac{1}{2}S_2 + H_2 \Leftrightarrow H_2S$$

$$\frac{1}{2}S_2 + O_2 \Leftrightarrow SO_2$$

using the equilibrium constants of Ohmoto & Kerrick (1977).

Attainment of equilibrium

Kinetic studies performed by Turkdogan & Pearce (1963) on simultaneous oxidation and sulfidation reactions in anhydrous iron-bearing silicate liquids showed that sulfidation is faster than iron oxidation. The corresponding

	Po5	Po7
d(102) ¹	2.0815	2.0500
NFeS ²	0.975	0.920
% at Fe ³	48.77	45-97

¹Distance between inter-reticular 102 plane of hexagonal pyrrhotite determined by XRD. ²Mole fraction of FeS in pyrrhotite from Toulmin & Barton

(1964). ³Atomic proportion of Fe in pyrrhotite calculated after Yund & Hall (1969).

Table 3: Composition of synthetic pyrrhotites

two reactions are

 $\frac{1}{2}S_{2g} \Leftrightarrow S_m^{2-}$ $2FeO + \frac{1}{2}O_2 \Leftrightarrow Fe_2O_3.$

Both the sulfidation and oxidation reactions are related through the following equilibrium:

$$\frac{1}{2}\mathbf{S}_{2g} + 2\mathbf{F}\mathbf{e}_{\mathbf{m}}^{2+} \Leftrightarrow 2\mathbf{F}\mathbf{e}_{\mathbf{m}}^{3+} + \mathbf{S}_{\mathbf{m}}^{2-}.$$

Baker & Rutherford (1996b) and Gaillard et al. (2001) have shown that the Fe³⁺ /Fe²⁺ ratio is constant after 24 h run durations for hydrous rhyolitic compositions, equilibrated between 725 and 1150°C, 100 and 2000 bar, and fO_2 between NNO and MnO–Mn₂O₃. Given that our run durations are between 6 and 9 days, we can expect that the iron redox ratio is at equilibrium and, consequently, that sulphur solubility is also at equilibrium. The Fe content of the capsules was always found to be below detection (270 ppm), even under reduced conditions. At fO_2 higher than NNO, sulphur-free supraliquidus glasses have the same iron content as the starting composition. At lower fO_2 , Fe loss occurred but remained negligible. The maximum Fe loss occurred at 1000°C, where the glass has an FeO content of 1.5 wt % (instead of 2 wt %). However, in all cases, Fe

concentration profiles toward the glass-capsules contact were flat in the glass, which suggests that equilibrium between melt and capsule was attained with respect to Fe. To check the attainment of the fS_2 equilibrium in some experiments, we added two additional capsules, where 1 wt % sulphur was added as synthetic pyrrhotite (Table 3). Two different pyrrhotites (charges with Po5 and Po7 in Table 4) were synthesized in evacuated SiO2-glass tubes (Kullerud, 1971) using iron and sulphur powder (both from Aldrich, 99.99% purity). For the synthesis, the sample was heated rapidly to 400°C, kept at this temperature over 12 h and then held at 700°C for 48 h. The compositions of the two synthetic pyrrhotites are given in Table 3. In the first capsule, the synthetic starting pyrrhotite was iron-rich [NFeS = 0.975; NFeS is the mole fraction of FeS in the system FeS-S₂ (Toulmin & Barton, 1964)] and, in the second one, the pyrrhotite was sulphurrich (NFeS = 0.92). During the experiment, pyrrhotites in these two capsules reequilibrated to the prevailing conditions, yielding final pyrrhotite compositions identical within error and suggesting attainment of equilibrium fS_2 , as illustrated in Fig. 2 for the experiments MP10. In all pyrrhotite-bearing charges, the two sensor capsules yielded identical fS_2 (except when the prevailing fO_2 is outside the stability field of pyrrhotite, such as MP19 charges) and we conclude that f S2 is at equilibrium for all experiments presented here. Attainment of equilibrium conditions is corroborated by the compositional homogeneity of glasses, both for major (e.g. SiO₂) and minor element (S) concentrations.

Charges	wt% S ¹	aH202	logfO ₂ 3	^ANNO ⁴	d(102) ⁵	at % Fe ^a	log/S ₂ (po) ⁷	log/S ₂ (V) ⁰	AFFS (po) ²	AFFS (V) ¹⁰	ß	ы	۶×	75	Po	An \	
P = 2 162kbar	, T = 785°C, 142 ¹¹ = 2	274 bar, 143 h															
MP16 I	1-18 (S)	0-81 (0-09)	-15-30 (0-13)	-1-12 (0-10)	2-0008	47 67	-2.14 (0.42)	-0-78 (0-50)	745 (0-21)	8-81 (0-25)	94-41 (3.43)	3-62 (1-77)	0-87 (0-51)	I	1-17	I	1-39 (050)
MP16 II	2.29 (S)	62.0)080	-15-34 (0-32)	-1-16 (0-29)	2.0532	46.23	-0-16 (0.33)	-0-53 (0-57)	9-43 (0-19)	9-06 (0-26)	74-99 (2-69)	14:38 (1:59)	0.95 (0.43)	8-30 (158)	1-37	I	3-25 (084)
MP16 III	3-72 (S)	0-37 (0-08)	-16-01 (0-30)	-1-83 (0-22)	2.0481	15 62	0-36 (0:37)	0.03 (0.09)	9-95 (0-19)	9-62 (0-08)	57-64 (2:33)	25-04 (1-27)	0.55 (0.40)	15-41 (8-51)	1:38	I	6-18 (0:36)
MP15 IV	5-69 (S)	0.35 (0-15)	-16-11 (0-54)	-1-53 (0-39)	2.0449	45.58	0.66 (0.37)	0-05 (0-14)	10:25 (0:18)	9-63 (0-10)	47-82 (2:12)	32-69 (1-31)	0-73 (0-42)	17-90 (1-17)	1-37	I	9-15 (0-44)
MP15 V	10-62 (S)	0.01	-17-05	-3:47	2.0441	45 62	0-73 (0-37)	62:0	10:32 (0-19)	88 50	53-59 (2-84)	28-77 (1-77)	1-89 (0-58)	16-02 (1:35)	0.92	1	6-23 (0-20)
MP15 VI	1-36 (pd6po7)	1-00	-14-84	-0-53	2-0760	48 <u>2</u> 3	-3-21 (0-13)	-1-36 (0-30)	6-19 (0-13)	8-03 (0-30)	96-00 (1-21)	4-30 (0-91)	I	I	0-10 (0-16)	I	1-06 (0-78)
MP15 VII ¹³	3-70 (S)	1100	-14:84	-0.50	20754	48.18	-3-23 (0-11)	ı	636 (0-22)	ı	90.74 (0.56)	ı	ı	ı	97.6		
MP15 X	1-02 (S)	0-92 (0-09)	-15-19 (0-11)	-1-03 (0-08)	2.0690	47.58	-2.17 (0.42)	-1-12 (0-22)	742 (0.21)	8-46 (0-14)	S6-90 (1-21)	traces	ı	ı	1-10 (0-16)	I	3-21 (1-11)
MP15 XI	1-11 (S)	(20-0) / 6-0	- 15-14 (0-04)	(60-0) 95-0-	2-0706	47.75	-2:46 (0:43)	-1-00 (0-30)	7-13 (0-21)	7-99 (0-18)	86-89 (1-20)	1	I	I	111 (0-11)	I	6-06 (1-15)
MP15 SN	1-10 (S)	0.79 (0-18)	-15-34 (0-28)	-1-18 (0-20)	2-0702	47 69	-2:35 (0:42)	-0-59 (0-15)	724 (0.21)	9-00 (0-31)	96-42 (1:20)	1-73 (0-90)	0-56 (0-40)	I	1-27 (0-40)	I	2-67 (0.87)
PIN 15 VIII	342 (S)	0.78 (0.06)	-15-33 (0-09)	-1-16 (0-07)	2.0490	£ 83	0-27 (0-38)	-0-71 (0-23)	986 (0-19)	8-88 (0-15)	62-59 (1-88)	20-30 (1-17)	I	15-77 (1-03)	0.94	I	6-23 (0-27)
P = 7-973kbar	, T = 788° C, 142 ¹¹ =	1-8 bar, 139 h															
MP16 I	1-16 (S)	0-88 (0-13)	-12-59 (0-18)	1-30 (0-12)	2.0524	45-16	0-00 (0-15)	1-37 (0-31)	939 (0-07)	10-76 (0-19)	53-96 (1 - 61)	28-40 (0-97)	I	17-88 (1-14)	1-74	I	2.28 (048)
MP16 II	2-96 (S)	0-77 (0-12)	-12-71 (0-19)	1-18 (0-13)	2,0663	46.48	-0-42 (0-15)	1-61 (0-56)	897 (0-08)	10-99 (0-26)	41-67 (1-66)	34-02 (0-94)	ı	22-40 (104)	1-9	traces	6-33 (0.29)
MP16 III	4-40 (S)	0.75 (0-12)	-12-73 (0-18)	1-16 (0-19)	2:0667	46 51	-0-46 (0-19)	1-06 (0-46)	892 (0 10)	11-04 (0-24)	38-30 (151)	36·71 (0·88)	I	25-11 (0.97)	<u>18</u>	I	7-14 (0.29)
MP16 IV	6-10 (S)	0-61 (0-09)	-12-91 (0-18)	0.98 (0.13)	2:0562	46.47	-041 (016)	1-97 (0-17)	838 (0-08)	11-35 (0-11)	23-08 (1:30)	41-97 (0-87)	ı	26-46 (0-87)	1.9	I	9-30 (0:24)
MP16 V	10-74 (S)	0-67 (0-12)	-12.90 (0.12)	1-07 (0-16)	2.0570	48 54	-0.50 (0.20)	1-96 (0-12)	889 (0 10)	11-35 (0-08)	33-72 (150)	40-70 (0-96)	I	23-08 (0-94)	1-91	1	3.64 (0.30)
MP16 VII ¹³	4-00 (S)	086	-12.60	5 87	2.0674	46 58	-0.55 (0.15)	0-99 (0-92)	8.84 (0.80)	10-38 (0-46)	79-20 (1-17)	11-20 (0-84)	ı	ı	6-30 (0-20)	I	4-48 (0-46)
MP16 VIII	1-11 (S)	(20-0) 86-0	-12:49 (0:04)	1-41 (0-09)	2.0008	46.67	-1.00 (0:30)	0-67 (0-94)	843 (0.10)	10-06 (0-30)	38-30 (1 51)	38·71 (0·88)	I	25-11 (0.97)	8 <u>-</u>	I	7-14 (0.29)
MP16 IX	137 (S)	0-98 (0-02)	-12:48 (0:08)	1-41 (0-02)	2.0683	46.65	-0-70 (0:30)	0.68 10-63	8-73 (0-10)	10-08 (0-27)	57-46 (2-02)	21-04 (1-10)	I	20-21 (1-16)	1-29 (0-16)	I	6-64 (0.29)
PIN16 VI	4-39 (S)	0-68 (0-10)	-12-80 (0-18)	1-08 (0-13)	2-0516	46.10	0.06 (0.30)	1-81 (0-28)	946 (0:30)	11-20 (0-17)	42-30 (1-15)	30-31 (0-77)	I	26-44 (0-83)	96-0	I	7-22 (0:27)
P = 1-976kbar	, T = 811°C, 142 ¹² =	1 bar, 190 h															
MP17	1-21 (S)	1-00	-11-78	1-83 (0-20)	2.0546	48 (st	-0-13 (0-15)	-0-36	9-08 (0-07)	8-25	85-56 (3-31)	12-64 (1-05)	ı	traces	1:88	I	0-47 (0-45)
MP17	2.24 (S)	100	-11-78	1-83 (0-20)	2.0625	46-17	0.09 (0.20)	-0-36	9-30 (0-10)	8.25	78-96 (3-06)	16-96 (1-54)	I	3-19 (1-68)	1-9	I	1-36 (0-42)
MP17 III	443 (S)	1-00 (0-01)	-11-79 (0-01)	1-83 (0-20)	2.0549	46.37	-0 17 (0 16)	-1-10 (0-17)	3-04 (0-08)	8 11 (0 11)	78-62 (3 61)	15-64 (1-35)	I	3-82 (1-92)	1-87	traces	4-40 (036)
MP17 IV	6-03 (S)	0.97 (0-04)	-11-82 (0-06)	1-30 (0-09)	2.0672	46 56	-0-42 (0-15)	0-71 (0-38)	8-79 (0-08)	9-91 (0-30)	78-50 (3-62)	15·70 (1·89)	I	3-82 (1-91)	1-87	traces	6-47 (0-48)
MP17 V	10-17 (S)	(10-0) 66-0	(10-0) 01-11-	1-82 (0-01)	2.0683	46.05	-0-54 (0 16)	-0.39 (0.40)	867 (0.08)	8 82 (0 22)	76-25 (3-43)	17-30 (1-78)	ı	5-47 (183)	1-91	traces	9-78 (0-58)
MP17 VII ¹³	3-80 (S)	100	-11-78	1-83 (0-20)	2.0647	46.35	-0-14 (0-15)	I	9-06 (0-70)	I	89-98 (0 5 7)	I	I	I	10-14	traces .	
MP17 VIII	1-10 (pd6—pd7)	1100	-11-78	1-83 (0-20)	2.0052	47.05	-1-41 (0-13)	I	7-80 (0-13)	ı	88-70 (1.37)	10-00 (1-11)	ı	I	0-70 (0-16)		
PIN17 VI	340 (S)	0.95 (0-06)	-11:83	1-79 (0-06)	I	ı	I	1-06 (1-16)	ı	10-27	43-62 (1-14)	28:98 (0.75)	ı	26-46 (0.83)	96-0	I	6-87 (0:32)
P = 2-054kbar	., Т – 330°С, 14 ₂ ¹² – .	2-2 bar, 169 h															
MP2	1-00 (S)	086	66-6-	1-39 (0-08)	2.0458	45.65	1-46	I	9.22	ī	S6-34 (0 56)	ı	ı	I	1:68	Ì	
MP2 II	1-00 (pa)	0-77	-10.09	1-29 (0-15)	2-0088	45-13	1-97	I	9-72	I	S6-23 (0 56)	ı	I	I	1-77	I	1-39 (0-65)
MP2 III	1-00 (an)	081	-10-04	1-34 (0-15)	I	I	ı	I	I	I	96-07 (0-56)	I	I	I	150	243	
P = 2:257kbar	, T = 33° C, 14 ₂ ¹² = (0-41 bar, 175 h															
MP3 I	142 (S)	056	-8-90	2-42 (0-23)	I	I	I	I	I	I	S6-10 (0-56)	I	I	I	traces	1-7	5-61 (0-06)
MP3 II	1-00 (pa)	049	-9-02	2:30 (0:23)	I	I	I	I	I	I	99·13 (0.56)	ı	I	I	1	0.87	4-56 (0-07)
MP3 III	1-00 (an)	660	-8:41	2-91 (0-29)	I	I	I	I	I	I	89-08-06-06	I	I	I	1	231	3-39 (0-08)
P = 7-995kbar	, T = 332°C, fH ₂ ¹² = .	467 bar, 175 h															
MP4 I	1-03 (S)	062	-12:53	-1-58 (0-14)	2.0636	47-10	-0-21	I	761	I	86-33 (0 6 6)	ı	ı	I	1-67	I	1-96 (0-77)
MP4 II	1-00 (pa)	043	-13-24	-1-89 (0-14)	2-0790	49 4 3	-2.26	I	546	ı	97-12 (0.56)	ı	ı	ı	2.88	I	2-33 (0-69)
MP4 III	1-00 (an)	0-78	-12-73	-1-38 (0-14)	2,0084	47 53	0-81	I	652	ı	S6-64 (0 56)	I	ı	I	1:38	I	1-43 (0-58)

Table 4: Experimental conditions and run products

Charges	wt% S ¹	eH202	log/02 ³	^NNO4	d(102) ⁵	at % Fe ⁶	log'S ₂ (po) ⁷	log ^r S ₂ (V) ^a	AFFS (po) ²	ΔFFS (V) ¹⁰	GI	Ы	ž	20	Po	An	>
P = 2-116 ktva	r, Т = 336° С, fH	¹² = 0.9 bar, 16	94 h														
I 64W	1-07 (S)	960	-9-12	2-16 (0-13)	2,0606	46.65	0-16	I	7:86	I	99-22 (0-56)	I	ī	I	0-76	traces	1-16 (0-05)
III 6dW	1-00 (po)	<u>6</u>	-9-01	2-27 (0-16)	2:06:02	46-47	0.62	ı	831	I	Se-27 (0-56)	I	ī	I	1.72	traces	1
V 64W	1-00 (an)	100	-8:8	2-29 (0-16)	20667	47-10	-0-17	ı	743	ı	97-97 (0-56)	I	ī	ı	ı	2.03	I
P = 2-013 ktva	r, T = 333°C, fH	2 ¹¹ = 47-3 bar, 1	16611														
MP10 I	2 (S)	081	-12.71 (0.12)	-1-38 (0-09)	2.0645	47-19	-0.31 (0.14)	-0.34	742 (0-07)	7-38 (0-22)	97-84	I	ī	I	2.16	I	1-53 (0-45)
MP10 II	3 (S)	0.75	-12·78 (0·18)	-1-45 (0-13)	20685	46.67	0:35 (0:15)	- 1-211(1-96)	8-08 (0-07)	7-60 (0-22)	20-95	0-60 (0-74)	ī	I	1:88	I	3-15 (0-61)
MP10 III	4 (S)	0.72	-12:82 (0:16)	-1-48 (0-11)	20672	46 55	0.49 (0.14)	-0-23 (0-61)	8.21 (0-07)	7-68 (0-16)	8.96	189 (0-90)	ī	I	1:3	I	4-66 (0-53)
VI 01-9W	10 (S)	96	-13-18 (0-37)	-1-35 (0-27)	20640	46:30	0-79 (0-14)	0-27 (0-48)	8-51 (0-07)	8-11 (0-14)	92-53	536(1-04)	ī	I	1-71	I	10-73 (0-96)
V 01-1M	1 (po5)	-	-12:53 (0:14)	-1-18 (0-14)	2-07-61	稳定	-1-53 (0-18)	I	6.79 (0.09)	ı	96-16	I	ī	I	3.66	I	1
MP10 VI	1 (po7)	-	-12-53 (0-14)	-1-18 (0-14)	20700	48,23	-1-91 (0-15)	I	5-82 (0-09)	I	99-96	I	ī	I	3-45	I	I
P = 2:202 ktva	r, T = 335°C, fH	2 ¹¹ = 20 ⁻⁴ bot, 1	16411														
I LL I	2-12 (S)	0.74	-11-96 (0-20)	-0.05 (0.14)	2:0653	46:40	0-70 (0-13)	-0-45 (2-18)	8:43 (0.07)	8-52 (0-22)	96·18	ı	ī	I	1:83	I	2:20 (0:79)
MP11 II	4-83 (S)	0.78	-11-92 (0-18)	-0-61 (0-13)	20612	46-13	1-01 (0-14)	1-02	8-73 (0-07)	8-42 (0-24)	8. 8	I	ī	I	1-04	I	2.95 (0.64)
MP11 III	4-83 (S)	043	-12-11 (0-19)	-0.30 (0.14)	2.0570	4654	1-50 (0-14)	0.94 (0.42)	(20-0) 62-6	8-76 (0-13)	SG-15	250 (1-36)	I	2-30 (1-51)	1-05	I	5488 (0-05)
VI 114M	10-12 (S)	0-51	-12:31 (0:37)	-1-00 (0-26)	n.d.			1-09 (0-50)	ı	8-96 (0-15)	88-7	440 (1-33)	ī	4-20 (1-50)	1:65	I	11-39 (0-96)
P = 2-202 ktvs	r, T = 335°C, fH	2 ¹¹ = 20-4 bot, 1	16414														
VI11 V	1-20 (Po6)	0-67	-11-71 (0-06)	-0.41 (0.06)	2-07.48	48:12	-1.08 (0.15)	I	6.05 (0.07)	I	6.96	1	I	I	9.1 9.1	1	
IV 111M	1-10 (Po7)	0-87	-11-71 (0-05)	-0-41 (0-05)	20750	48-15	-1-72 (0-16)		6-00 (0-08)	1	8 0-//6	1	1		2.91	1	
0 - 2000 the	r T = 036C 4U	11 - 15 Aur 20	46														
MPR II	0.62 (S)	0.83	-11-66 (0.20)	-0.34 0.14	24739	70.02	-1.57 0.21)	1	6.15 (0.10)	1	99.13		I		0.87		
	101 001	000	10.00 (0.00)	101-04-00-0	00.00			100 00 12 00	101-01-01-0	0.00 00.00	21-00				1.00		110 10101
MP6	(S) 20-1	0.74 (0.11)	(21-0) 6/-11-	-0.46 0.13	50/02	21.18	(qL-0) \$L-L-	0.57 (0.32)	(20.0) 24.0	0.00 (0.70)	5	1	I	I	8	I	(19-0) 53-1
MP6 IV	1-33 (S)	0-76 (0-15)	-11-76 (0-24)	-0:43 (0:17)	2.0631	47-06	-0-14 (0-14)	1-25	7-67 (0-07)	8 62 (0 27)	86:31	1	I	1	1-08	ī	149 (0.03)
MP6VI	1-03 (Pb7)	0-93	-11-56 (0-08)	-0.24 (0.08)	2-0740	48-06	-1.59 (0.15)	ı	6-13 (0-07)	I	97-31	I	I	I	2.03	I	
MP6VII	1-04 (Po5)	-	-11-50 (0-08)	-0-17 (0-08)	2.07.40	48.05	-1-59 (0-15)	I	6-12 (0-08)	ı	97-52	I	ı.	I	2.48	I	I
P = 2:092 ktvs	r, T = 334°C, fH	2 ¹¹ - 6 bar, 147.	4.														
MP12 I	2-31 (S)	0-77 (0-13)	-10.92 (0.21)	0-40 (0-15)	20641	46:30	0.80 (0.14)	1-97	852 (0-07)	9-35 (0.28)	30-26	ı	ī	I	2-15	I	1-67 (0-05)
MP12	3-90 (S)	0.79 (0.14)	-10.90 (0.21)	0-41 (0-15)	2:06:62	66,97	0-70 (0-14)	1-96	8-42 (0-07)	9-33 (0-27)	88 ∙/6	ı	I	I	2-11	I	404 (0.85)
MP12 III	5-98 (S)	0.65 (0.17)	-11.09 (0.33)	0-22 (0-23)	2.06.09	46.53	0-53 (0-17)	2.23	8:25 (0.07)	9-65 (0:22)	91-85 (2-68)	3-60 (1-30)	ī	3-00 (1-51)	1:65	I	6:23 (0.78)
MP12 IV	10-31 (S)	0.57 (0.18)	-11-22 (0-40)	0-10 (0-29)	20688	46.70	0.33 (0.20)	1-71	8-06 (0-10)	9-78 (0-19)	88·20 (2·75)	9-10 (1-34)	ī	3-00 (1-56)	1-05	I	11-68 (0-88)
P = 7-960 ktvs	r, T = 338°C, fH	2 ¹¹ = 4 bat, 162.	4														
MP7 III	1-00 (S)	0-78 (0-13)	-10.50 (0.21)	0-75 (0-15)	2.0443	45 53	1-62 (0-12)	2.16	9-29 (0-06)	9-46 (0.27)	56·61	I	ī	I	1-88 1-	I	1-40 (0-63)
MP7 IV	1-25 (S)	0-72 (0-08)	-10.56 (0.14)	0.69 (0.10)	20509	46.04	7-10 (0-13)	1-74 (0-60)	8.76 (0.06)	9-58 (0-16)	96-98	I	ı	I	1:05	I	2.25 (0:43)
P = 2:001 kba	r, T = 330°C, fH	2 ¹¹ = 0.8 bar, R	489														
MP13 I	2-00 (S)	0.38 (0-03)	-9-92 (0-06)	1-47 (0-06)	2:06:30	46.21	0.98 (0.14)	2.75 (0.18)	8-62 (0-07)	10-52 (0:05)	96-21 (0-89)		ī	I	1-65	0-37	3-90 (0-18)
MP13 II	3-87 (S)	0-38 (0-05)	-9-97 (0-15)	1:42 (0:11)	2.0677	46-00	0-41 (0-14)	2-79 (0-27)	8-17 (0-07)	10-59 (0-09)	96-74 (0-88)	I	ī	2.13 (0.68)	1:00	0.43	6-00 (0-30)
MP13 III	6-04 (S)	(20-0) 62-0	-10-15 (0-13)	1:23 (0:09)	2.0538	46:28	0 73 (0 16)	3:00 (0:15)	8-55 (0-08)	10-77 (0-06)	97-41 (0-90)	I	I	traces	1-79 (0.65)	0.42	8-82 (0-63)
MP13 IV	10-11 (S)	0.22 (0.02)	-10:38 (0:13)	1-00 (0-09)	20654	46.41	0.64 (0.22)	3-16 (0-09)	839 (0 11)	10-92 (0-03)	80.0S	traces	ı	traces	1.73	0:24	13:37 (0:41)
P = 2-168 ktva	r, T = 394° C, fH	12 ¹² - 30 bar, 15.	24														
MP18	1-25 (S)	0-55 (0-09)	-11-64 (0-43)	-1:28 (0:43)	2.0737	48-02	-1-04 (0-16)	0.69 (1-12)	6-07 (0-08)	8-30 (0-20)	99·27	I	I	I	0.73	I	2:46 (0.13)
MP18 II	0-00 (S)	0.75 (0.06)	-11-29 (0-44)	-0.53 (0.44)	2.0734	47-99	-1:00 (0:22)	0-41 (0-98)	6-11 (0-11)	7-94 (0:20)	8-96	I	I	I	1:32	I	1-16 (0-20)
MP18 IV	2-04 (S)	0-02 (0-04)	-11-69 (0-52)	-1-34 (0-37)	2:0655	47-27	0-02 (0-14)	-0-10 (1-67)	7-13 (0-07)	7-89 (0.21)	98·42	ı	I	I	1-55	I	2.72 (0.18)
MP18 V	4-32 (S)	0.37 (0-03)	-12-11 (0-42)	-1.75 (0.42)	20680	46.63	0-81 (0-13)	0-94 (0-78)	7-92 (0-06)	8-34 (0-18)	36 -41	I	ī	I	1-59	I	601 (0:20)
MP18 VI	6-33 (S)	0-23 (0-02)	-12.52 (0.42)	-2.15 (0.30)	20533	46:23	1-24 (0-12)	1-09 (0-77)	8.35 (0-06)	7-48 (0-18)	96-27	I	ī	I	1-73	I	8-63 (0-15)

harges	wt% S ¹	aH202	logfO2 ²	^NNO4	d(102) ⁵	at % Fo ⁶	log/S ₂ (pol ⁷	log/S ₂ (V) ^B	ΔFFS (po) ⁹	ΔFFS (V) ¹⁰	ß	M	ž	5	Po	An	>
- 2 188 kthar,	T = 394°C, fH ₂ ¹² = 3	10 test, 152h															
IN 8 MI	10-84 (S)	(20-0) 22-0	-12:21 (0:42)	-1-85 (0-30)	2.0609	46.04	1-44 (0-13)	(77-0) 66-0	8-55 (0-06)	8:38 (0:18)	98·17	I	I		163	I	12-73 (0:31)
1P18 X	3-62 (S)	0-56 (0-11)	-11-77 (0-40)	-1-41 (0-48)	2-0061	47-33	-0.05 (0.14)	0-63 (0-88)	7-06 (0-07)	8-09 (0-19)	38-45	I	I	I	1-55	I	6-52 (0-56)
IP18 XI	3·77 (S)	0-72 (0-15)	-11-55 (0-40)	-1-19 (0-48)	2-0727	47 53	-0-90 (0-15)	0-52 (0-52)	6-21 (0-07)	7-79 10-28	8-95	ı	ı		134	ı	9-75 (0-62)
IP18 XII ¹³	3-30 (S)	0-83 (0-07)	-11-11 (0-07)	-0-75 (0-07)	2-1718	47.64	-0.78 (0.14)	-136(1·39)	6:33 (0:07)	8:23 (0:70)	97·24 (0·56)	I	I	I	2.76	I	2-64 (0-62)
IP18 SN	1-32 (po6-po7)	0-83	1-11-	-0.74	2.0741	48.06	(11-0) 11-1-	1	6-00 (0-12)	ı	96-47	I	I	I	3-53*	I	1
IN18 DK	3-26 (S)	0.24 (0.12)	-12-62 (0:64)	-2:26 (0:77)	2:0677	46-00	1-00 (0-13)	1-18 (0-62)	8-11 (0-06)	8:48 (0:27)	SC-13 (0-56)	I	I	I	1-87	I	5-74 (0-63)
- 2-068 kthar,	T = 396°C, fH ₂ ¹² = 2	2 bar, 162h															
IIV 9 MI	0-54 (S)	0-49 (0-11)	(22.0) 92.6-	1-06 (0-19)	I	I	I	2.22 (0.90)	I	9-59 (0-19)	100	I	I	I	I	I	2-09 (0-47)
11911	1-42 (S)	0.75 (0.10)	-8-36 (0-16)	1-46 (0-12)	I	ı	ı	0.97 (0.97)	I	8-67 (0-25)	100	I	I	I	1	I	2-33 (0-46)
II 61-0 III	2:34 (S)	0-61 (0-16)	(22:0) 30:6	1-25 (0-24)	I	ı	I	131 (1-31)	I	9-34 (0-27)	8.8	I	I	I	0.68	I	3-57 (0-74)
N 919 IV	3-09 (S)	0.38 (0.17)	-9-52 (0-57)	0-81 (0-41)	I	I	I	155 (1-55)	I	9-96 IV-22)	8 8	I	I	I	061	I	5-33 (0-82)
IP19 VI	5-03 (S)	0-01	-12-61	-2-29	I	ı	I	3.24	I	10-31	36·70	8	I	ន	140	I	4-47 (0-10)
NP19 DK	3-39 (S)	0.88 (0.13)	-8-74 (0-18)	1-59 (0-12)	I	I	I	0-75 (0-57)	I	8:20 (0:31)	39.95	I	I	I	0.36	I	6-97 (0-00)
1P19 X	3:30 (S)	0-87 (0-13)	-8-74 (0-18)	1-59 (0-19)	I	ı	I	0-78 (0-59)	I	8:25 (0:31)	100	I	I	I	traces	I	6-12 (1-12)
IN 919 XI	3-29 (S)	(60-0) 88-0	-8.74 (0.12)	1-59 (0-09)	I	ı	I	0-67 (0-50)	I	62.0 20.8	@ 8	I	I	I	0.20	I	8-90 (047)
IP19 XII ¹³	3-50 (S)	0-83 (0-17)	-8-80 (0-19)	1-53 (0-18)	I	ı	I	-0-81 (2-05)	I	6-25 (1-32)	99-10 (0-56)	I	I	I	060	I	3-79 (0:00)
IIIX 614	1-27 (pd6-pd7)	0-47	-9-27	1.05	I	I	I	248 (0.30)	I	9-55 (0:30)	R 8	I	I	I	1.71*	I	2-31 (0-78)
IIIA 61NI	3-15 (S)	0-41 (0-14)	-9:45 (0:45)	0-88 (0-32)	I	I	I	2-18 (1-21)	I	9-81 (0-21)	100	I	I	I	I	I	5-00 (0-06)
 1-992 kttmr, 	$T = 387^{\circ}C, 1H_2^{12} = 0$	P.6 ber, 167h															
141	1-99 (S)	0-47 (0-04)	-8-24 (0-12)	2-23 (0-09)	I	ı	I	0-61 (0-49)	ı	7-89 (0-14)	99-15 (0-92)	ı	ı	I	trace	0.95	3-99 (0:22)
IP14 II	3-96 (S)	0:43 (0:02)	(20-0) 62-8	2.18 (0.06)	I	I	I	080 (0:23)	I	(60·0) 00·8	9.86	I	I	I	trace	0.92	6-00 (0:21)
IP14 III	6-04 (S)	0-31 (0-05)	-8-62 (0-19)	1-85 (0-14)	2.0629	46:20	1-21 (0-17)	142 (0.78)	8-37 (0-08)	8-35 (0-18)	(68-0) 06-26	I	I	I	1-08	1:02	8-31 (0-53)
1P14 IV	10-11 (S)	0-23 (0-03)	-8-96 (0-19)	2-00 (0-31)	2:0662	80 SF	1-01 (0-14)	2.09 (0.37)	8 17 (0-07)	9-32 (0-12)	97 62	traces	I	I	138	-	12-09 (0:46)
IP14 VI	1-50 (pd6-pd7)	0.40 (0.05)	-8:38 (0:11)	2:03 (0:06)	2:0668	1 8 é	0.95 (0-12)	1-08 (0-30)	8 11 (0 12)	8:49 (0:30)	96-00 (1·25)	I	I	I	1:20 (0:22)	traces	3-45 (0.29)
IP14 VII ¹³	3-50 (S)	0-57 (0-04)	-8-12 (0-02)	2-36 (0-03)	I	I	I	0-22 (0-19)	I	7-37 (0-09)	96-70 (0-59)	I	I	I	3-10	06·0	5-08 (0:22)
IN 4 VIII	3-78 (S)	0-43 (0-03)	-8-32 (0.08)	2-14 (0-08)	ı	I	I	0.87 (0:32)	I	8-09 (0-10)	(16-08 (0-91)	ı	ı	I.	traces	traces	6-00 (0:21)
Mater &	t of sulphur a hotivity calcul houted from	added to t lated from equation (he charge (Burnham ((2).	either as el (1979).	ementa 10001	I (S) or a	s pyrrhotite	e (Po5—Po	o7; see Tal	ole 3).							

⁴/O₂ referenced to the NNO buffer (Holloway *et al.*, 1992).
⁴/O₂ referenced to the NNO buffer (Holloway *et al.*, 1992).
⁶ Distance between inter-reticular planes 102 of hexagonal pyrrhotite determined by XRD.
⁶ Distance between inter-reticular planes 102 of hexagonal pyrrhotite determined by XRD.
⁷ Log fS₂ given by the pyrrhotite cannoic) from Yund & Hall (1976) using *d*(102).
⁸ Log fS₂ given by the pyrrhotite cannoic) from Yund & Hall (1976) using *d*(102).
⁹ Log fS₂ given by the pyrrhotite cannoic from the subhur content calculated from mass balance.
¹⁰ Log fS₂ given by the MRK-EOS (see taxt). Numbers in italics are for charges whose total sulphur content computed from MRK-EOS calculated from mass balance.
¹⁰ Log fS₂ given by the MRK-EOS referenced to the iron--troilite (FFS) buffer (see taxt).
¹¹ Log fS₂ given by the MRK-EOS referenced to the iron--troilite (FFS) buffer (see text).
¹¹ from the suphur content calculated from mass balance.
¹¹ from NiPd sensor measurement.
¹² Magnetite-added charges.
¹³ Magnetite-added charges.
¹⁴ from NiPd sensor measurement.



Fig. 2. Attainment of equilibrium in fS_2 for the experiment MP10. d(102) is the inter-reticular distance of the 102 plane of hexagonal pyrrhotite determined by XRD. Error bars are smaller than symbols. The starting pyrrhotite compositions (Po5 and Po7) are shown as black dots. Open dots are the final pyrrhotite compositions. The arrows indicate the changes in pyrrhotite compositions. Each pyrrhotite was loaded in separate capsules run at the same $P-T-fH_2$ conditions and the compositional similarity [similar d(102)] observed after the experiment indicates that both pyrrhotites record the same fS_2 .

ANALYTICAL TECHNIQUES

Run products were examined by optical and scanning electron microscopy (SEM). We used X-ray diffractometry to confirm the phase assemblage determined by optical microscopy and SEM. Besides the characterization of the run products, X-ray diffractometry of powdered run products was also used to measure the composition of pyrrhotites (Arnold & Reicher, 1962; Toulmin & Barton, 1964; Boorman, 1967; Yund & Hall, 1969). Our measurements were made on an Inel CPS 120 diffractometer at ambient temperature using Co radiation ($\lambda = 1.78897$ A) with quartz as an external standard. The measured peak positions are accurate to within 0.01° (Roux & Volfinger, 1996).

Analyses of the major elements of the experimental charges were performed on both Camebax and SX50 electron microprobes. The operating analytical conditions were: accelerating voltage 15 kV, beam current 6 and 12 nA for glass and crystals, respectively, beam diameter 10 μ m for glass and focused beam (1–2 μ m) for crystals. A ZAF correction procedure was applied. Correction for electron beam induced alkalimigration and determination of H₂O concentration in glasses by the bydifference method (Devine et al., 1995) were performed by using calibration curves constructed from three hydrous standard glasses, analysed by wet chemistry for their Na and K content (Pichavant, 1987). These standards have the same composition as our starting material (without sulphur) and their water contents (up to 6.5wt%) are known from Karl Fisher titration. Major element calibration used wollastonite (Ca), hematite (Fe), albite (Na, Si), corundum (Al), olivine (Mg) and orthoclase (K) standards. The detection limit for major elements is about 1000 ppm. For the *f*H₂ sensor, the analytical conditions for Pt, Pd, Ni

were: accelerating voltage 20 kV and a focused beam current of 20 nA. Counting time was 10 s on the peak and 5 s on the background for all major element analyses. Anhydrite was analyzed (using a JEOL JXA-8600 electron microprobe) under analytical conditions of 15 kV, 6 nA and 5 μ m beam diameter, using anhydrite as a standard.

The concentration of total sulphur in glasses was determined by electron microprobe analysis (Camebax). In silicate melts, sulphur is assumed to be present as sulphide (S^{2-}) or sulfate (S⁶⁺) (Richardson & Withers, 1950; Ricke, 1960; Schneider, 1970). The position of the SKa X-ray has been shown to be a function of the sulphur valence state and of the complexation of sulphur (e.g. Carroll & Rutherford, 1988; Kucha et al., 1989). In our glasses, sulphur is present either as sulphide or sulfate, or as a mixture of the two. In this last case, the SKa X-ray peak is between the sulphide and sulfate positions. Therefore, at the beginning of each analytical session, we established two calibration curves—one for S as sulphide and one for S as sulfate. These curves were constructed with three synthetic hydrous dacitic standard glasses, containing 750, 1400, and 1900 ppm sulphur, determined by wet chemistry. The difference between the two calibration curves increases with the sulphur content, but remains below detection for S contents below 400 ppm. Consequently, the S-peak position was determined for all glasses with sulphur contents higher than 400 ppm, and the counting was performed on each specific peak. For S analyses, we used three PET crystal spectrometers, using the following analytical procedure: accelerating voltage 15 kV, sample current 50 nA, beam diameter 10 mm. Counting time was 60 s on each spectrometer, resulting in a total counting time of 180 s. The background was determined by analysing a glass of the same composition without sulphur, using the above analytical procedure. The detection limit under these analytical conditions is about 80 ppm, as calculated from Ancey et al. (1978). Single spot analyses of 1 h duration with these analytical conditions showed no migration of sulphur. Qualitative analyses of oxygen in sulphides by electron microprobe (SX50) have been performed to check whether the pyrrhotites are the products of back reactions of immiscible Fe–S–O liquids upon quenching. Specifically, under conditions of high fO_2 , pyrrhotite may partially break down to an Fe–O–S liquid. It appeared that, indeed, for fO_2 > NNO, most guench sulphides contained detectable amounts of oxygen. Therefore, the pyrrhotite in these charges may be because of the crystallization of Fe-S-O immiscible liquids during the quench, and we did not consider as reliable the fS_2 retrieved from pyrrhotite composition in those charges.

RESULTS

The experimental conditions, phase assemblages and proportions, and glass compositions are summarised in Tables 4 and 5.

Phase assemblages

The phase assemblages are portrayed in Fig. 3. Besides direct evidence of fluid in excess upon opening of the capsules, such as drops of water and hissing, fluid-saturated conditions were also assumed when bubble sizes in quenched glasses exceeded 10 mm. However, virtually all charges contain micrometric to sub-micrometric bubbles, which most probably represent remnants of air trapped in the capsules. No magnetite crystallized, except at high fO_2 (> NNO+1.3), where a trace amount of this oxide was detected (charges MP16 VII, MP17 VII and MP14 VII, Table 4). Previous experimental work, performed on various rhyolitic compositions, has shown that the

quench rates used in the present study are high enough to prevent quench crystallization of oxides (Gaillard et al., 2001). The comparison between magnetitedoped and undoped charges shows that below NNO+1, addition of magnetite to a sulphur-bearing charge merely results in extensive sulphide crystallization (Table 4). At all temperatures with fO_2 < NNO, the sulphide is pyrrhotite, whereas above NNO, the sulphide is an Fe–S–O immiscible liquid ± pyrrhotite, as indicated by detection of O by EMPA (Fig. 3). For charges in which the amount of added sulphur exceeds the sulphur solubility of the melt, an S-O-H fluid phase forms, and water becomes partitioned between melt and fluid. Further addition of sulphur to the system decreases the activity of water through a simple dilution effect (i.e. the H_2O/S ratio in the fluid decreases) and because of interaction with sulphur species (i.e. production of H₂S). A significant decrease in aH₂O may lead to the partial crystallization of other, S-free phases, such as plagioclase, pyroxene or quartz. For instance, at 800°C, plagioclase is stable for aH₂O slightly below 1, pyroxene is stable under reducing conditions for aH2O slightly below 1, and guartz crystallizes for $aH_2O \leq 0.85$. Similarly, at 930°C, plagioclase is stable for $aH_2O \leq 0.75$ and quartz is stable for $aH_2O \leq 0.65$ above NNO-1. At 1000°C, apart from one charge which crystallized plagioclase, only S-bearing phases were present in charges loaded with elemental sulphur. Charges doped with magnetite resulted in extensive sulphide crystallization (up to 10 wt %), depending on the amount of sulphur added (Table 4), except at high fO₂ at 800 and 930°C, where iron oxides crystallized (MP16 VII, MP17 VII and MP14 VI charges, Table 4). Anhydrite is stable under oxidizing conditions only, confirming other experimental studies (Carroll & Rutherford, 1987; Luhr, 1990; Scaillet & Evans, 1999). At 800 and 930°C, anhydrite is stable at fO₂ > NNO+1. At 1000°C, anhydrite appears at $fO_2 > NNO+1.8$, which indicates that the fO_2 needed to crystallize anhydrite in rhyolitic melts increases with T (Fig. 3). Anhydrite stability in rhyolitic magmas appears to be in the same fO₂ range as that for trachyandesite magmas at $T < 950^{\circ}$ C (Carroll & Rutherford, 1987; Luhr, 1990).

Fluid phase composition

The composition of the coexisting fluid-phase was calculated using the MRK equation of state, as explained above. The mole fraction of H_2O in the fluid (XH_2O_{fl}) ranges between near 1 and 0.1, yet, for the vast majority of charges, it is within the range 0.75–0.30. The few charges having XH_2O_{fl} significantly lower than 0.2 are those for which the bydifference method yields H₂O melt content close to zero (e.g. charge MP15V, Table 4). At all temperatures, as long as the fO₂ is below NNO+1, H₂S is the dominant sulphurbearing species, and its mole fraction in the fluid (XH_2S_{fl} I) ranges from 0.1 up to 0.85. Thus, at 2 kbar and at an fO_2 below NNO+1, the fluid phase can be considered as a binary mixture of H₂O and H₂S, other fluid species (H₂, SO₂, S₂) amounting to no more than 0.01 mole fraction. SO₂ becomes abundant at higher fO_2 and its mole fraction (XSO_{fl}) may even exceed that of H₂S at 930 and 1000°C. At 930°C, an fO_2 of NNO+1.4 is required to have $XSO_{fl} > XH_2S_{fl}$. At 1000°C, the same happens at slightly lower fO_2 , that is around NNO+1. At 800°C, however, H_2S dominates over SO₂, even with an fO_2 as high as NNO+1.8. At fO_2 > NNO+1, and in charges loaded with massive amounts of sulphur (5–10 wt %, Table 4), S₂ makes up a significant proportion of sulphur-bearing species in the fluid—up to 0.3 of XS_{2fl} .

Charges	ΔNN0 ¹	ΔFFS^2	SiO ₂	Al ₂ O ₃	FeO ³	MgO	CaO	Na ₂ 0	K ₂ 0	H ₂ 0 ⁴	S (ppm) ⁵	log S
P = 2·152 kbar, T = 785° C												
MP15 I	-1.12 (0.10)	7-45 (0-21)	78-35 (0-91)	13-25 (0-37)	0-28 (0-10)	0-29 (0-10)	1-62 (0-13)	4-17 (0-21)	2-02 (0-14)	4-69 (0-43)	Q	I
MP15 II	-1-16 (0-29)	9-43 (0-19)	78-52 (0-99)	13-08 (0-41)	0-14 (0-10)	0-27 (0-10)	1-01 (0-11)	4-44 (0-24)	2.52 (0.18)	4-70 (1-00)	440 (11)	2.64
MP15 III	-1-83 (0-22)	9-95 (0-19)	78-63 (0-90)	12-54 (0-36)	0-14 (0-10)	0-26 (0-10)	0.94 (0.10)	4-18 (0-21)	3-30 (0-18	2·65 (0·44)	612 (19)	2-79
MP15 IV	-1-93 (0-39)	10.25 (0.18)	78-59 (0-65)	12-57 (0-26)	0-18 (0-10)	0-18 (0-10)	0.67 (0.10)	3-92 (0-15)	3-88 (0-14)	2.56 (0.70)	753 (40)	2·88
MP15 VI ⁶	-0-33	6-19 (0-13)	78-03 (0- 65)	13-02 (0-26)	1-51 (0-10)	0-17 (0-10)	1-65 (0-10)	3-71 (0-14)	1-89 (0-10)	5-54 (0-75)	₽	I
MP15 VII7	-0-33	6.36 (0.22)	76-57 (1-27)	12-98 (0-52)	1-59 (0-18)	0-28 (0-10)	2.08 (0.21)	4-44 (0-32)	2-07 (0-23)	6-78 (0-65)	₽	I
MP15 X	-1-03 (0-08)	7-42 (0-21)	77-53 (0-65)	13-71 (0-27)	0-17 (0-10)	0-32 (0-10)	1-98 (0-10)	4-34 (0-15)	1-94 (0-10)	5-93 (1-06)	126 (34)	2.10
MP15 XI	-0.98 (0.09)	7.13 (0.21)	77-46 (1-01)	13.75 (0.42)	0-63 (0-11)	0.35 (0.10)	2.00 (0.16)	3-87 (0-23)	1.93 (0.16)	6-37 (1-10)	Q	I
MP15 SN	-1.18 (0.20)	7.24 (0.21)	77-96 (0-58)	13-51 (0-24)	0-23 (0-10)	0.34 (0.10)	1.77 (0.10)	4-27 (0-14)	1.92 (0.10)	4-60 (0-60)	96 (61)	1.98
PIN15/III	-1.16 (0.07)	9.86 (0.19)	77-84 (1-17)	12.79 (0.47)	0.09 (0.10)	0.29 (0.10)	0.57 (0.10)	4-03 (0.28)	4-38 (0-29)	4.70 (0.30)	787 (21)	2.90
P = 1-973 kbar, T = 798°C												
MP16 I	1-30 (0-12)	10.76 (0.19)	78-78 (0-83)	12-31 (0.33)	0.16 (0.10)	0-33 (0-10)	1.45 (0.11)	2-87 (0-17)	4-10 (0-19)	5-01 (0-75)	108 (64)	2.03
MP16 II	1-18 (0-13)	10.99 (0.26)	78-83 (1-06)	12-20 (0-42)	0-08 (0-10)	0-33 (0-10)	1.04 (0.12)	2-79 (0-21)	4-71 (0-26)	4-32 (0-52)	294 (9)	2-47
MP16 III	1-16 (0-19)	11-04 (0-24)	78-10 (0-49)	12-16 (0-19)	0-10 (0-10)	0-36 (0-10)	0.99 (0.10)	3-02 (0-10)	5-27 (0-13)	4-31 (0-52)	240 (72)	2.38
MP16 IV	0-98 (0-13)	11.35 (0.11)	77-28 (0-74)	12-50 (0-30)	0-10 (0-10)	0-34 (0-10)	0.65 (0.10)	3-02 (0-15)	6-16 (0-21)	3-71 (0-41)	356 (22)	2-55
MP16 V	1-07 (0-16)	11.35 (0.08)	78-09 (0-57)	12-28 (0-22)	0-10 (0-10)	0-37 (0-10)	0.85 (0.10)	2.98 (0.11)	5-39 (0-15)	3-97 (0-54)	274 (16)	2.44
MP16 VII7	1.29	10.38 (0.46)	74-36 (0-49)	12-67 (0-20)	0-26 (0-10)	0-28 (0-10)	1-88 (0-10)	6-93 (0-15)	3-60 (0-11)	4-84 (0-41)	₽	I
MP16VIII	1-41 (0-09)	10.06 (0.30)	78-04 (0-50)	12-47 (0-20)	0-58 (0-10)	0-29 (0-10)	1-67 (0-10)	2-96 (0-10)	3-97 (0-11)	5-71 (0-52)	Q∣	I
MP16 IX	1-41 (0-02)	10.08 (0.27)	77-27 (0-39)	13-62 (0-16)	0-33 (0-10)	0-33 (0-10)	2.01 (0.10)	3-12 (0-10)	3-76 (0-10)	5-58 (0-34)	₽	I
PIN16 VI	1-08 (0-13)	11-20 (0-17)	77-01 (0-52)	12-53 (0-21)	0-10 (0-10)	0.23 (0-10)	0-73 (0-10)	2-51 (0-10)	6-89 (0-15)	4-04 (0-47)	373 (14)	2-57
$P = 1.9\%$ kbar, $T = 811^{\circ}C$												
MP17 I	1.83 (0.20)	I	80-01 (0-73)	12.06 (0.30)	0.10 (0.10)	0.37 (0.10)	1.41 (0.12)	3-89 (0-10)	2.15 (0.12)	5-88 (0.39)	125 (16)	2.1
MP17 II	1-83 (0-20)	I	79-93 (0-83)	12-13 (0-14)	0.08 (0.10)	0-40 (0-10)	1.21 (0.11)	3-93 (0-19)	2-32 (0-10)	5-86 (0.39)	263 (11)	2.42
MP17 III	1-83 (0-20)	I	79-90 (0-39)	12-17 (0-12)	0.11 (0.12)	0-40 (0-10)	1.12 (0.10)	3-98 (0-10)	2.32 (0.10)	5-49 (0-20)	304 (19)	2.48
MP17 IV	1-80 (0-09)	I	79-91 (0-70)	12.23 (0.26)	0.12 (0.10)	0-40 (0-10)	1.06 (0.10)	3-94 (0-15)	2.33 (0.18)	5-46 (0-43)	279 (18)	2.45
MP17 V	1-82 (0-01)	I	79-96 (0-70)	12-21 (0-22)	0-06 (0-10)	0-42 (0-10)	1-04 (0-16)	3-87 (0-21)	2-44 (0-17)	5-62 (0-38)	307 (11)	2.49
MP17 VII7	1-83 (0-20)	I	77-84 (0-81)	13-42 (0-41)	0-40 (0-43)	0-31 (0-10)	1-99 (0-15)	4-19 (0-18)	1-95 (0-10)	6-21 (0-47)	83 (24)	1-92
MP17 VIII ⁶	1-83 (0-20)	I	78-62 (1-33)	12-48 (0-24)	1-39 (0-27)	0-21 (0-10)	1-51 (0-10)	3-67 (0-41)	2-12 (0-23)	6-74 (1-25)	Q	I
PIN 17 VI	1-79 (0-05)	I	79-05 (0-70)	13-04 (0-20)	0-11 (0-14)	0-22 (0-10)	1-05 (0-10)	3-30 (0-13)	3-22 (0-11)	5-43 (0-56)	281 (11)	2.45
$P=2.054kbar,T=330^\circ C$												
MP2 I	1-39 (0-08)	9-22	76-92 (0-10)	13-62 (0-10)	0-48 (0-10)	0-35 (0-10)	2.07 (0.10)	4-57 (0-10)	1-99 (0-10)	4-97 (0-37)	158 (12)	2.20
MP2 II	1-29 (0-15)	9-72	75-83 (0-23)	13-34 (0-10)	2-41 (0-10)	0-33 (0-1à)	1-95 (0-10)	4-22 (0-10)	1-92 (0-10)	4-44 (0-59)	112 (13)	2.05
MP2 III	1-34 (0-15)	I	77-25 (0-33)	13-55 (0-14)	0-45 (0-10)	0-35 (0-10)	2.01 (0-10)	4-43 (0-10)	1-94 (0-10)	4-71 (0-79)	285 (15)	2.46

Table 5: Compositions of experimental glasses (normalized to 100 wt % anhydrous)

Charges	^NNO ¹	ΔFFS^2	SiO ₂	AI ₂ 0 ₃	FeO ³	MgO	CaO	Na ₂ O	K ₂ 0	H ₂ 0 ⁴	S (ppm) ⁵	log S
$P=2.257 kbar, T=933^{\circ}C$												
MP3 I	2-42 (0-29)	I	77-30 (0-23)	13-73 (0-10)	1-85 (0-10)	0-32 (0-10)	0-39 (0-10)	4-40 (0-10)	2-01 (0-10)	3-04 (0-47)	989 (19)	2-99
MP3 II	2-30 (0-29)	I	76-90 (0-32)	13-50 (0-13)	1-81 (0-10)	0-33 (0-10)	1-18 (0-10)	4-37 (0-10)	1-90 (0-10)	2-83 (0-70)	307 (14)	2.49
MP3 III	2-91 (0-29)	I	76-22 (0-30)	13-40 (0-13)	1-93 (0-10)	0-33 (0-10)	2-10 (0-10)	4-05 (0-10)	1-96 (0-10)	4-89 (0-60	186 (13)	2.27
P = 1-986 kbar, T = 932° C												
MP4 I	-1-58 (0-14)	7-51	77-19 (0-10)	13-66 (0-23)	0-19 (0-10)	0-32 (0-10)	2.04 (0.10)	4-60 (0-13)	1-99 (0-10)	3-72 (0-72)	313 (13)	2-50
MP4 II	-1-89 (0-14)	5-46	76-31 (0-26)	13-59 (0-11)	1-43 (0-10)	0-34 (0-10)	2.02 (0.10)	4-38 (0-10)	1-93 (0-10)	2-81 (0-65)	Q	I
MP4 III	-1.38 (0.14)	6-92	75-55 (0-22)	13-38 (0-10)	0-43 (0-10)	0-20 (0-10)	4-23 (0-10)	4-28 (0-10)	1-93 (0-10)	4-37 (0-53)	148 (11)	2·17
P = 2 116 kbar, T = 936° C												
I 64M	2.16 (0.13)	7.86	76-85 (0-66)	13-54 (0.31)	1-16 (0-16)	0-32 (0-10)	2.02 (0.10)	3-99 (0-12)	2.12 (0.10)	4.74 (0.58)	77 (61)	1-89
III 64W	2.27 (0.16)	8.31	76-08 (0-77)	13-53 (0-28)	2.40 (0.27)	0-34 (0-10)	1-91 (0-10)	3.70 (0.59)	2.03 (0.10)	5-13 (0-56)	Q	I
V 64M	2.29 (0.16)	7.53	75-81 (0-63)	13-24 (0-34)	1-87 (0-17)	0-35 (0-10)	2-64 (0-10)	3-98 (0-17)	2-11 (0-10)	5-76 (0.49)	154 (6)	2.19
P = 2.013 kbar, T = 933°C												
MP101	-1.38 (0.09)	7.42 (0.07)	77.34 (0.67)	13-52 (0-22)	0-31 (0-17)	0-30 (0-10)	2.04 (0.10)	4.38 (0.12)	2.10 (0.10)	4-51 (0.36)	189 (36)	2.28
MP10 II	-1-45 (0-13)	8-08 (0-07)	77-42 (0-61)	13-60 (0-25)	0-13 (0-25)	0-32 (0-10)	1-39 (0-10)	1-39 (0-14)	2.15 (0.10)	4-25 (0-48)	544 (20)	2-74
MP10 III	-1-48 (0-11)	8-21 (0-07)	77-71 (0-38)	13-35 (0-16)	0-20 (0-16)	0-32 (0-10)	1-95 (0-10)	4-38 (0-10)	2.08 (0.10)	4-09 (0-40)	691 (76)	2.84
MP10 IV	-1-85 (0-27)	8-51 (0-07)	77-08 (1-72)	12-94 (0-73)	0-12 (0-16)	0-33 (0-10)	1-70 (0-18)	5-55 (1-39)	2.26 (0.10)	3-14 (0-67)	883 (33)	2.95
MP10 V ⁶	-1-18 (0-14)	5-79 (0-09)	76-76 (0-76)	13·37 (0·23)	1-35 (0-22)	0-31 (0-10)	1-39 (0-10)	4-15 (0-15)	2-07 (0-10)	5-90 (0-55)	₽ı	I
MP10 VI ⁶	-1-18 (0-14)	5-82 (0-09)	76-81 (0-77)	13-35 (0-25)	1-22 (0-25)	0-32 (0-10)	1-99 (0-10)	4-26 (0-15)	2-04 (0-10)	5-54 (0-52)	Q	I
P = 2:202 kbar, T = 935° C												
MP111	-0-65 (0-14)	8-43 (0-07)	77-31 (0-67)	13-40 (0-29)	0-34 (0-25)	0-32 (0-10)	2.04 (0.10)	4-48 (0-14)	2-11 (0-10)	4-39 (0-55)	211 (52)	2:32
MP11 II	-0-61 (0-13)	8-73 (0-07)	77-44 (0-70)	13-55 (0-20)	0-05 (0-10)	0-33 (0-10)	2·08 (0·10)	4-48 (0-12)	2-07 (0-11)	4-56 (0-54)	644 (31)	2.81
MP11 III	-0-80 (0-14)	9-29 (0-07)	77-27 (0-66)	13-60 (0-22)	0-11 (0-14)	0-32 (0-10)	2·05 (0·10)	4-52 (0-10)	2-12 (0-10)	3-86 (0-46)	718 (44)	2-86
MP11 IV	-1-00 (0.26)	8-95 (0-15)	77.39 (0.80)	13-54 (0-28)	0.09 (0.10)	0.35 (0.10)	1.92 (0.10)	4-50 (0-22)	2.21 (0.10)	3-31 (0-71)	901 (22)	2.95
MP11 V ⁶	-0.41 (0.05)	6-05 (0-07)	76-38 (0-68)	13-16 (0-24)	1-86 (0-21)	0-33 (0-10)	2-01 (0-14)	4-17 (0-26)	2.08 (0.10)	5-36 (0-37)	Q	I
MP11VI ⁶	-0.41 (0.05)	6-00 (0-08)	76:40 (0.50)	13-38 (0-27)	1-54 (0-17)	0-31 (0-10)	2-01 (0-10)	4.24 (0.19)	2-11 (0-11)	5-38 (0.30)	Q	I
$P = 2.003 kbar$, $T = 934^{\circ} C$												
MP6 II	-0-34 (0-14)	6-15 (0-10)	76-79 (1-10)	13-67 (0-27)	1-06 (0-56)	0-35 (0-10)	1-97 (0-10)	3-99 (0-15)	2.16 (0.10)	4-50 (0-57)	72 (62)	1-86
MP6 III	-0-46 (0-13)	6-58 (0-08)	77-34 (0-51)	13-77 (0-25)	0-44 (0-22)	0-35 (0-10)	2-00 (0-10)	4-02 (0-18)	2.08 (0.10)	4-07 (0-46)	74 (62)	1-87
MP6 IV	-0-43 (0-13)	7-57 (0-07)	77-33 (0-68)	13-67 (0-22)	0-43 (0-27)	0-34 (0-10)	1-98 (0-11)	4-13 (0-15)	2.11 (0.13)	4-21 (0-29)	Q∣	I
MP6 VI ⁶	-0-24 (0-08)	6-13 (0-07)	76-49 (0-83)	13-55 (0-16)	1-62 (0-21)	0-31 (0-10)	2-06 (0-11)	3-88 (0-18)	2-08 (0-10)	4-86 (0-79)	Q∣	I
MP6 VII ⁶	-0-17 (0-08)	6-12 (0-08)	76-03 (0-59)	13-51 (0-24)	2·11 (0·23)	0-33 (0-10)	1-97 (0-10)	3-94 (0-10)	2-10 (0-10)	5-38 (0-45)	Q∣	I

Charges	∆NNO ¹	ΔFFS^2	SiO ₂	Al ₂ 0 ₃	Fe0 ³	MgO	CaO	Na ₂ O	K₂O	H ₂ 0 ⁴	S (ppm) ⁵	log S
$P = 2.092 kbar$, $T = 934^{\circ} C$												
MP121	0.40 (0.15)	9.36 (0.26)	77-43 (0-65)	13-53 (0-24)	0.09 (0.10)	0.34 (0.10)	2-01 (0-10)	4.45 (0.11)	2.13 (0.10)	4-43 (0-59)	273 (38)	1: 83
MP12 II	0-41 (0-15)	9-33 (0-27)	77-33 (0-83)	13.62 (0.20)	0-12 (0-12)	0.33 (0.10)	2.05 (0.12)	4.39 (0.16)	2.15 (0.10)	4.48 (0.62)	334 (77)	2.52
MP12 III	0.22 (0.23)	9.65 (0.22)	77-60 (1-17)	13.48 (0.31)	0-11 (0-10)	0.33 (0.10)	1-94 (0-10)	4.35 (0.23)	2.18 (0.13)	3-83 (0-77)	535 (47)	2.73
MP12 IV	0.10 (0.29)	9.78 (0.19)	78-77 (1-03)	12.75 (0.43)	0.07 (0.12)	0.32 (0.10)	1-47 (0-14)	4.36 (0.23)	2.25 (0.10)	3.47 (0.82)	554 (43)	2.74
P = 1-980kbar, T = 938°C												
MP7 III	0-75 (0-15)	9-46 (0-27)	76-98 (0-54)	13-79 (0-19)	0-69 (0-14)	0.32 (0.10)	2-04 (0-10)	4-08 (0-11)	2-08 (0-10)	4-27 (0-57)	Q	I
MP7 IV	0-69 (0-10)	9-58 (0-16)	76-90 (0-74)	13-60 (0-20)	0.94 (0.59)	0.36 (0.10)	2-03 (0-10)	4-06 (0-15)	2-11 (0-10)	4-02 (0-36)	Q	I
$P=2.001 \text{kbar}, T=930^\circ\text{C}$												
MP13 I	1-47 (0-05)	10-52 (0-05)	77-31 (0-44)	13-94 (0-19)	0.38 (0.10)	0.31 (0.10)	1-79 (0-10)	4-39 (0-11)	1-88 (0-10)	2.51 (0.11)	371 (51)	2-57
MP13 II	1-42 (0-11)	10-59 (0-09)	77-21 (0-76)	13.97 (0.32)	0-31 (0-10)	0.30 (0.10)	1-72 (0-11)	4-63 (0-19)	1-86 (0-12)	2.45 (0.19)	422 (25)	2.83
MP13 III	1-23 (0-09)	10-77 (0-05)	77-75 (0-54)	13-75 (0-23)	0-21 (0-10)	0.33 (0.10)	1-70 (0-10)	4-38 (0-13)	1-87 (0-10)	2.10 (0.13)	494 (86)	2.69
MP13 IV	1-00 (0-09)	10-92 (0-03)	77-19 (0-44)	13-87 (0-19)	0-29 (0-10)	0.38 (0.10)	1-89 (0-10)	4-53 (0-11)	1-85 (0-10)	1-83 (0-10)	429 (31)	2.63
$P=2.188kbar, T=994^{\circ}C$												
MP18 I	-1.28 (0.43)	6-07 (0-08)	77-32 (0-40)	13.73 (0.17)	0.46 (0.10)	0.34 (0.10)	2.02 (0.10)	4-23 (0-10)	1-89 (0-10)	3.37 (0.12)	284 (47)	2.45
MP18 II	-0.93 (0.44)	6-11 (0-11)	77-08 (0-59)	13.68 (0.25)	0.92 (0.10)	0.32 (0.10)	2.07 (0.10)	4.12 (0.14)	1-80 (0-10)	4.24 (0.19)	147 (29)	2.17
MP18 IV	-1.34 (0.37)	7.13 (0.07)	77-51 (0-49)	13-69 (0-21)	0.26 (0.10)	0.33 (0.10)	2.07 (0.10)	4-26 (0-12)	1-87 (0-10)	3.82 (0.15)	453 (98)	2.66
MP18 V	-1-75 (0-42)	7.92 (0.06)	77-22 (0-59)	13-80 (0-25)	0-16 (0-10)	0-31 (0-10)	2-10 (0-10)	4-53 (0-14)	1-88 (0-0)	2.62 (0.15)	660 (38)	2.82
MP18 VI	-2.15 (0.30)	8-35 (0-06)	77-31 (0-46)	13·78 (0·20)	0.09 (0.10)	0.34 (0.10)	2.12 (0.10)	4-52 (0-11)	1-83 (0-10)	1-92 (0-10)	907 (41)	2.96
MP18 VII	-1-85 (0-30)	8-55 (0-06)	77-52 (0-58)	13·64 (0·24)	0-12 (0-10)	0.31 (0.10)	2-09 (0-10)	4-46 (0-14)	1-85 (0-10)	2·34 (0·14)	1154 (21)	3.06
MP18 XII	-0-75 (0-07)	6-33 (0-07)	76-70 (0-51)	13-67 (0-22)	1-09 (0-10)	0.33 (0.10)	2-07 (0-10)	4-24 (0-12)	1-90 (0-10)	4-82 (0-49)	178 (57)	2.25
MP18 SN ⁶	-0-74	6-00 (0-12)	76-33 (0-44)	13·72 (0·19)	1-50 (0-10)	0.32 (0.10)	2-03 (0-10)	4-20 (0-10)	1-90 (0-10)	4-47 (0-61)	116 (23)	2·06
PIN18 IX	-2.26 (0.77)	8-11 (0-06)	77-00 (0-77)	13-51 (0-32)	0-27 (0-10)	0.33 (0.10)	2-09 (0-13)	4-89 (0-19)	1-90 (0-12)	1-80 (0-54)	698 (64)	2.84
$P=2.068 \textit{kbar}, T=996^\circ\textit{C}$												
MP19 VII	1-06 (0-19)	9-59 (0-19)	75-98 (0-48)	13-43 (0-20)	1-94 (0-10)	0.33 (0.10)	2-07 (0-10)	4-36 (0-12)	1-89 (0-10)	3-01 (0-46)	₽	I
MP19 II	1-46 (0-12)	8-67 (0-25)	76-06 (0-49)	13-41 (0-20)	2-11 (0-10)	0.33 (0.10)	2-11 (0-10)	4-13 (0-11)	1-85 (0-10)	4-17 (0-43)	₽	I
MP19 III	1-25 (0-24)	9-34 (0-27)	76-36 (0-51)	13-54 (0-22)	1-46 (0-10)	0.35 (0-10)	2-08 (0-10)	4-28 (0-12)	1-91 (0-10)	3-57 (0-71)	132 (70)	2.12
MP19 IV	0-81 (0-41)	9-86 (0-23)	76-23 (0-68)	13-54 (0-29)	1-50 (0-10)	0.32 (0.10)	2.15 (0.11)	4-33 (0-16)	1-93 (0-11)	2.61 (0.77)	₽	I
MP19 VI	-2.29	10-31	77-44 (0-88)	11-79 (0-34)	1-13 (0-11)	0.39 (0.10)	0-91 (0-10)	3-17 (0-18)	5-17 (0-23)	0.25 (0.25)	Q∣	I
MP19 IX	1-59 (0-12)	8-20 (0-31)	76-91 (0-53)	13-83 (0-22)	1-71 (0-10)	0.33 (0.10)	2-08 (0-10)	3-28 (0-11)	1-85 (0-10)	4-53 (0-52)	Q	I
MP19 X	1-59 (0-19)	8-25 (0-31)	76-28 (0-80)	13.47 (0.33)	2.09 (0.13)	0.35 (0.10)	2.14 (0.13)	3-74 (0-18)	1-92 (0-13)	5-15 (1-08)	122 (70)	2.09
MP19 XI	1-59 (0-09)	8-03 (0-29)	76-40 (0-50)	13-57 (0-21)	1-84 (0-10)	0.33 (0.10)	2-06 (0-10)	3-90 (0-11)	1-89 (0-10)	4-65 (0-37)	145 (21)	2.16
MP19 XII	1-53 (0-18)	6-25 (1-23)	75-36 (0-48)	13-44 (0-20)	3-06 (0-10)	0.32 (0.10)	2-03 (0-10)	3-85 (0-11)	1-93 (0-10)	4-44 (0-73)	167 (23)	$2\cdot 23$
MP19 XIII ⁶	1-05	9-55 (0-30)	74-93 (0-48)	13-49 (0-21)	3-40 (0-11)	0.32 (0.10)	1-97 (0-10)	4·04 (0·11)	1-85 (0-10)	2-84 (0-79)	Q∣	I
PIN 19 VIII	0-88 (0-32)	9-81 (0-21)	78-32 (0-62)	12.99 (0.25)	0-80 (0-10)	0.25 (0.10)	1-29 (0-10)	3-49 (0-13)	2·85 (0·12)	2-60 (0-61)	Q	I

Charges	∆NNO ¹	ΔFFS^2	Si0 ₂	AI ₂ 0 ₃	FeO ³	MgO	CaO	Na ₂ O	K ₂ 0	H ₂ 0 ⁴	S (ppm) ⁵	log S
P = 1-992 kbar, T = 987° C	-											
MP14 I	2-23 (0-09)	7.89 (0.14)	76-71 (0-66)	13-67 (0-28)	2.20 (0.12)	0-34 (0-10)	1-30 (0-10)	3-93 (0-15)	1-84 (0-10)	2-80 (0-18)	674 (104)	2.83
MP14 II	2.18 (0.06)	8.00 (0.09)	76-88 (0.44)	13-73 (0-18)	2.13 (0.10)	0-32 (0-10)	1-24 (0-10)	3-90 (0-10)	1.79 (0.10)	2-67 (0-11)	563 (77)	2.75
MP14 III	1-85 (0-14)	8.85 (0.18)	77-60 (0-83)	13-90 (0.35)	0.92 (0.11)	0-35 (0-10)	1.15 (0.10)	4-16 (0-19)	1.92 (0.13)	2.11 (0.20)	734 (49)	2.87
MP14 IV	2.00 (0.31)	9.32 (0.12)	77-60 (0-45)	14-02 (0-19)	0.63 (0.10)	0-33 (0-10)	1-18 (0-10)	4-34 (0-11)	1-89 (0-10)	1.78 (0.10)	771 (31)	2.89
MP14 VI ⁶	2.03 (0.06)	8.49 (0.30)	75-88 (0-77)	13.35 (0.32)	3-17 (0-16)	0-30 (0-10)	1-62 (0-11)	3-88 (0-18)	1.79 (0.12)	2.53 (0.20)	339 (88)	2.60
MP14 VII	2-36 (0-03)	10.88 (0.09)	76-08 (0-58)	13-48 (0-24)	3·26 (0·12)	0-31 (0-10)	1-15 (0-10)	3-90 (0-13)	1-81 (0-10)	3-19 (0-16)	645 (75)	2.64
PIN14 VIII	2-14 (0-06)	I	78-66 (0-48)	12-99 (0-19)	0-89 (0-10)	0-23 (0-10)	1-19 (0-10)	3·28 (0-10)	2-76 (0-10)	2-64 (0-12)	186 (14)	2.27
Numbers in parenthe ¹ /O ₂ normalized to th ² /S ₂ normalized to th ³ Total Fe, given as F ⁴ /Vater content deter ⁵ Pyrrhotite-added ch, ⁷ Magnetite-added ch,	ses indicate (e NNO buffe e FFS buffer e0. mined using rt. D is the de arges.	I standard de r (see Table 4) (see Table 4) (see Table 4) the by-differe etection limit	viation of repl .). . nce method. (80 ppm).	icate analyse	ŵ							

Table 5: continued



Fig. 3. Stability domains of sulphur-bearing phases as a function of *f*O₂ and temperature. Phase abbreviations: anh, anhydrite; po, pyrrhotite; S, immiscible Fe–S–O liquid; mt, magnetite.



Fig. 4. Fugacities of H_2S and SO_2 fluid species versus the corresponding fO_2 for all charges for which fS_2 could be determined, calculated using equations (7) and (8) (see Table 4 and text). The increase in fO_2 favours SO_2 relative to H_2S species in the fluid phase. At any given fO_2 , the spread in either fH_2S or fSO_2 reflects the variations in fS_2 that are a result of the varying amounts of sulphur loaded to the charge.

Figure 4 shows the calculated fugacities of both H_2S and SO_2 species in the fluid for all charges for which fS_2 is available, plotted against the corresponding fO_2 . The fugacity of H_2S (fH_2S) ranges from 10 to 4.977 kbar, whereas that of SO_2 (fSO_2) covers a wider range, from 10⁻⁴ to 7.804 kbar. The crossover between f H_2S and fSO_2 occurs at around

NNO+1. In fact, it is only at $fO_2 > NNO+2$ and at 930 and 1000°C that fSO_2 is several orders of magnitude larger than f H₂S.

Major element glass composition

Glasses obtained using the Pinatubo composition, which is richer in alkalis than that from Mt Pelee (Table 1), display similar sulphur concentrations when held under similar fO_2 and fS_2 , except at high fO_2 , where Pinatubo charges are slightly richer in sulphur than the Mt Pelee ones. Overall, however, because Pinatubo charges do not depart significantly from the trends defined by the Mt Pelee ones, in the following, both groups are considered together. The glasses are rhyolitic, with SiO2 contents

predominantly in the range 76–78 wt % and $Al_2O_3 = 13 \pm 1$ wt %. Variations in the concentrations of other elements affect primarily Fe and Ca, as both elements are removed by either sulphide or sulfate crystallization. In addition, at 930 and 800°C, the crystallization of plagioclase, quartz and pyroxene also affects the melt chemistry, most notably its CaO and K₂O concentrations (Tables 4 and 5). In particular, at 800°C, a continuous increase in K₂O arises as a result of the dominantly incompatible behaviour of this element (see MP16 series, Table 5). At all values of fS2, fO2 and T, a broad negative correlation can be established between FeO and melt sulphur content in sulphide-bearing charges (Fig. 5). All glasses to which elemental sulphur was added and which were held at $fO_2 < NNO+1$ are depleted to various extents in iron compared with the starting composition (2 wt % FeO), because of crystallization of sulphide (Fig. 5). In contrast, most charges with sulphur added as pyrrhotite have glasses richer in iron than other charges run under the same T, fO₂ but loaded with elemental sulphur (see Table 5). Charges doped with magnetite also display higher iron contents than undoped ones held at the same T and fO_2 . It is important to note that most glasses with low to very low iron contents display the highest sulphur contents, whereas those with the highest iron content have the lowest sulphur content, often below the detection limit (Fig. 5). Glasses of charges held at an fO_2 > NNO+1 display consistently higher iron contents than all other charges having similar amounts of dissolved sulphur (Fig. 5)-an effect of the crystallization of anhydrite in lieu of pyrrhotite at high fO_2 .



Fig. 5. FeO_{tot} vs melt-sulphur content of experimental glasses at all investigated temperatures for reduced and oxidized conditions. The latter correspond in general to anhydrite-bearing charges. Note the general leftward displacement relative to the starting composition (dashed line at 2 wt %) of most charges. The arrow indicates that, below NNO+1, the general increase in melt-sulphur content is a result of the increase in *f*H₂S (and temperature).



Fig. 6. Sulphur concentration in glass as a function of fO_2 and fS_2 at 930°C. Dotted lines are contours of iso- fS_2 , labelled with Δ FFS in bold and corresponding fS_2 in parentheses.

Solubility of sulphur as a function of intensive parameters

The interrelationships between melt sulphur content, fS_2 and fO_2 at 930°C, where most of the data were obtained, are shown in Fig. 6. The solubility of sulphur is clearly a function of both fO_2 and fS_2 . Below NNO+1, for a fixed fO_2 , the solubility of sulphur

increases with fS₂. Above NNO+1, the data are scarce but suggest the same trend of increasing sulphur content with increasing fS_2 . For any given fS_2 , the sulphur solubility decreases when fO₂ increases, so as to reach a minimum between NNO and NNO+1. The data suggest that this minimum in sulphur solubility moves towards more oxidizing conditions when fS_2 increases. The relationships between melt sulphur concentration (Smelt), fS₂, fH₂S, fSO₂ for various fO₂ and at the three investigated temperatures are shown in Fig. 7. There is a general systematic increase in Smelt with fS_2 , most clearly seen at low fO₂ (< NNO + 1). As a rule, an increase in fO₂ leads to a decrease in Smelt at fixed fS₂. This effect is most apparent at 800 and 930°C. Exceptions to this behaviour concern experiments performed at 930 and 1000°C in the fO₂ range NNO+0.7 to NNO+1, where the Smelt content displays few variations, being close to the detection limit (Fig. 7). No clear trend appears when using fSO_2 in place of f S₂ (Fig. 7), even under high fO₂, where SO₂ is the dominant sulphur-bearing species in the fluid. In contrast, Smelt correlates strongly with *f*H₂S. At 800°C, the two data groups at NNO-1.4 and NNO+1.2 merge into a single, well-defined trend, whereas using fS_2 leads to two distinct series. Similarly, at 930°C, a general single positive correlation emerges, with much less dispersion than when fS_2 is used as a variable. At 1000°C, a strong positive correlation is clearly defined only for an fO2 of NNO-1.4. At all temperatures, Smelt exceeds 200 ppm once f H₂S is above a few hundred bars. At NNO-1.4, when the mole fraction of S (X_{s} , calculated using common rock-forming oxides such as SiO₂, Al₂O₃, etc.) is used in place of concentration (Smelt), the correlations defined with f H₂S appear to be linear at all temperatures (Fig. 8). Under high fO₂, a broad positive correlation exists between X_S and fSO_2 , but with significant scatter and no apparent temperature effect can be resolved, unlike at low fO2. The scatter is because of the difficulties in precisely determining fS_2 under high fO_2 conditions.

Sulphur speciation in hydrous rhyolite melt

Since the pioneering work of Fincham & Richardson (1954), it is common to envision sulphur dissolution in anhydrous silicate melts either as sulphide ($low-fO_2$) or as sulphate (high- fO_2) species, depending on prevailing redox state, through the following two reactions (see Carroll & Webster, 1994):

$$\frac{1}{2}S_2 + O^{2-} \Leftrightarrow \frac{1}{2}O_2 + S^{2-}$$

$$\frac{1}{2}S_2 + \frac{3}{2}O_2 + O^{2-} \Leftrightarrow SO_4^{2-}$$

where S²⁻ and SO^{2 4-} refer respectively to sulphide and sulphate species dissolved in the melt and O²⁻ represents oxygen anions in the silicate melt. A quantitative assessment of reactions (12) and (13) has been so far limited by our inhability to rigorously evaluate the proportion, as well as the activity–composition relationships, of O²⁻ in complex hydrous alumino-silicate melts such as magmatic liquids. The strong correlation existing between Fe and Smelt in both natural and experimental anhydrous glasses suggests that S²⁻ exchanges preferentially with O²⁻ bound to ferrous iron in melts under low fO2, whereas at high fO_2 , anhydrite precipitation suggests that the exchange primarily takes place with

oxygens associated to Ca. In hydrous melts, the same reactions are supposed to operate (Carroll & Webster, 1994). In particular, under low fO_2 , sulphur dissolution might happen through a reaction such as (Carroll & Webster, 1994)

$$H_2S_{gas} + FeO_{melt} \Leftrightarrow FeS_{melt} + H_2O_{gas}$$
.

This reaction predicts that sulphur solubility in ironbearing hydrous melt should increase with the activity of FeO, which is contrary to what our experimental data show (Fig. 5). However, based on experimental as well as on energetic and volumetric considerations, in particular the similarity of H_2O and H_2S molecules, Burnham (1979) proposed that sulphur dissolution into iron-poor hydrous rhyolitic melts is analogous to the H_2O solution reaction, and can be described by the following reaction :

$$H_2O_{gas} + SH_{melt}^- \Leftrightarrow H_2S_{gas} + OH_{melt}^-$$
.



Fig. 7. Relationships between melt-sulphur concentration (Smelt), and f S₂, *f*H₂S, *f*SO₂ for various *f*O₂, at the three investigated temperatures. For clarity at 930°C, the data have been grouped into three *f*O₂ intervals, each broadly corresponding to a different type of S-bearing phase (as *f*O₂ increases: pyrrhotite, occurrence of an immiscible Fe–S– O liquid, and anhydrite).

Burnham (1979) reported a sulphur solubility of 1700 ppm at 2 kbar, 850°C in a hydrous, pyrrhotite saturated, rhyolitic melt (initial iron content of 0.3 wt %). This sulphur concentration is higher than the maxima attained in our study, and, upon completion of the run, it was found that, essentially, all the iron initially present in the system is fixed in pyrrhotite (Burnham, 1979)—an observation that corroborates our findings at low fO₂. The very fact that similar, or even higher, sulphur concentrations compared with those achieved in the present work have been reported in either H_2O bearing (Keppler, 1999) or H2O-free (Mysen & Popp, 1980) haplogranite or albite melts (i.e. melts without iron) shows that iron is not instrumental in achieving high sulphur concentration in silicate melts. That, first, a negative correlation exists between dissolved iron and sulphur (Fig. 5), secondly, the glasses having the highest sulphur concentration are also those having the lowest iron content, close to the detection limit and, thirdly, a strong positive correlation exists between f H₂S and Smelt all suggest that reactions such as (15) may better account for our experimental observations, at least those below NNO+1, rather than reactions in which iron-bearing species are involved. Under oxidizing conditions, the situation is less clear but sulphur dissolution in hydrous melts may occur via the following reaction :

$$SO_2 + 2OH^- \Leftrightarrow SO_4^{2-} + H_2.$$

Unfortunately, a rigorous evaluation of reactions (14)–(16) is hampered primarily by the lack of knowledge about the nature of sulphur species dissolved in silicate melts, as well as of the activity–composition relationships of melt components, and these are clearly two main avenues for future research on the behaviour of sulphur in silicate melts.

Thermodynamic model of sulphur solubility in hydrous and iron-poor rhyolite melts

In this section, in the absence of specific speciation data and on the basis that H_2S and SO_2 are the major sulphurbearing species in the coexisting fluid phase, we assume that the total dissolved sulphur in the melt results from the addition of sulphur dissolved from H_2S and SO_2 dissolution reactions. The extent of each dissolution reaction is controlled by the magnitude of both H_2S and SO_2 fugacities in the system. We thus have

$$X_{\rm S} = X_{\rm reduced} + X_{\rm oxidized}$$

where $X_{reduced}$ and $X_{oxidized}$ represent the mole fractions of sulphur species dissolved under the reduced and oxidized forms, hereafter referred to as $X_{H2Smelt}$ and $X_{SO2melt}$, respectively. Regardless of the actual sulphur species in the melt, the data allow us to evaluate the standard thermodynamic parameters of the following heterogeneous reactions between fluid and melt (e.g. Spera & Bergman, 1980):



Fig. 8. Xi–fi relationships. (a) Under reduced conditions ($\Delta NNO \le 0$), where the dominant S-bearing species in the fluid is H₂S. (b) Under oxidizing conditions ($\Delta NNO \ge 1.0$), where the dominant S-bearing species in the fluid is SO₂. Dashed curves are sulphur solubilities calculated using the thermodynamic model developed in the text.

$$H_2S_{melt} \Leftrightarrow H_2S_{fluid}$$

and

$$SO_{2melt} \Leftrightarrow SO_{2fluid}$$

whose equilibrium constants are

$$K_{18} = f H_2 S_{\text{fluid}} / a_{\text{H2Smelt}}$$

And

$$K_{19} = f SO_{2 fluid} / a_{SO2 melt}$$
.

Assuming that $a_i = X_{i_j}$ then

$$K_{18} = f H_2 S_{\text{fluid}} / X_{\text{H2Smelt}}$$

And

$$K_{19} = f SO_{2 \text{fluid}} / X_{SO2 \text{melt}}.$$

To evaluate the above reactions, we proceed by considering separately charges at $fO_2 < NNO$, in which H₂S is the dominant sulphur-bearing species in the fluid, and then charges at $fO_2 > NNO+1.5$, in which SO₂ is the dominant sulphur-bearing species. Under those conditions, the right-hand side of equation (17) simplifies to either $X_{H2Smelt}$ ($fO_2 < NNO$) or $X_{SO2melt}$ ($fO_2 > NNO+1.5$).

H₂S dissolution

At all temperatures and $fO_2 \le NNO$, the relationships between X_s and f H₂S is within error linear (Fig. 8) and, thus, the solubility of H₂S in rhyolite melt obeys Henry's Law, i.e. at fixed *P* and *T*,

$$f H_2 S = X_{H2Smelt} k_H$$

where $k_{\rm H}$ is the Henry's Law constant and is obviously equivalent to K_{18} . As shown in Fig. 8, the f H₂S– $X_{H2Smelt}$ relationships display well organized trends with temperature. Departure from the simple Henrian behaviour, because of both temperature and pressure variations, can be accounted for by using the following classical equation (e.g. Fogel & Rutherford, 1990) :

$$\ln(f H_2 S / X_{H2Smelt}) = \ln k_{H(Pr,Tr)} + (\Delta H / R) (1/T - 1/T_r) + (V_{H2S}(P - P_r)) / RT$$
(21)

which, upon rearrangement, gives

$$X_{\text{H2Smelt}} = f H_2 S / k_{\text{H}(\text{Pr},\text{Tr})} \exp[-(\Delta H/R)(1/T - 1/T_{\text{r}}) - (V_{\text{H2S}}(P - P_{\text{r}}))/RT]$$
(22)

in which T_r and P_r are the reference temperature and pressure, respectively, ΔH is the heat of H₂S dissolution into the melt, R is the gas constant and V_{H2S} the partial molar volume of H₂S melt species. T_r and P_r were, respectively, chosen to be 930°C, as most of the data were gathered along or close to this isotherm, and 0 bar. Equation (22) has been extensively used in the thermodynamic modelling of H₂O and CO₂ solubilities in various silicate-melt compositions (e.g. Stolper et al., 1987; Fogel & Rutherford, 1990; Blank et al., 1993). Non-linear least-squares regression using charges with an $fO_2 \leq$ NNO-1.4 gives the following values: $k_{\rm H,930^{\circ}C} = 0.801 \ 10^{6}$ bar, $\Delta H = 54.85$ kJ/mol and $V_{\rm H2S} = 26.03 \text{ cm}^{3}/\text{mol}$. The Henry constant is similar to that found for CO₂ dissolution in rhyolite melt (1.106 10⁶ bar, Fogel & Rutherford, 1990). However, contrary to both H₂O and CO₂ species, the enthalpy of H₂S solution is positive in sign, which simply means that, at a given fH₂S, temperature increases the solubility of sulphur. Although the partial molar volume of H₂S in rhyolite melt appears to be similar to that of H₂O, we stress that our data cover a range in f H₂S too small to allow extraction of volume properties with great accuracy. In fact, the investigated pressure domain falls in the range where sulphur exhibits essentially linear dependence on fH_2S , i.e. where V_{H2S} plays a negligible role in equation (22).

SO₂ dissolution

At $fO_2 > NNO+1.5$, because of the difficulties in retrieving fluid species fugacities in the oxidized range, the dispersion in the X_S-fSO_2 (Fig. 8) plot is much more severe than for H₂S, and it can only be assumed that sulphur dissolution at high fO_2 also follows Henry's Law. Linear regression of the data obtained at an $fO_2 > NNO+1.5$ gives the following value for the Henry constant: $K_{SO2} = K_{19} = 4.13 \times 10^6$ bar.

Sources of error

The calculated versus measured sulphur mole fractions for various fH_2S are shown in Fig. 9 for charges held at an fO_2 of NNO–1·4 or lower.



Fig. 9. Experimental versus calculated mole fractions of sulphur for charges at an fO_2 of below NNO-1.4, using the thermodynamic model developed in the text.

Although the model correctly reproduces the measured values, there is a substantial scatter around the 1:1 correlation line. Besides the obvious fact that not all dissolved sulphur needs to be in the H₂S form, one major source of error that affects the derivation of thermodynamic parameters comes from the calculated values of fH₂S. In experimental studies designed to calibrate H₂O or CO₂ solubility models, the fluid species fugacities are calculated from equations of state in which uncertainties in fugacities essentially come from uncertainties in P and T measurements. Here, the H₂S fugacities are also affected by this source of uncertainty, but also by (1) the analytical uncertainty attached to the determination of pyrrhotite composition and (2) the lack of well-calibrated EOS for sulphur-bearing volatile species. The analytical uncertainty in measured fS_2 is typically 0.2 log units (Table 3). Taking charge MP15V as an example, its measured fS_2 is 5.46 bar (log $fS_2 = 0.74$), to which corresponds an fH_2S of 4.977 kbar, given the fH_2 of 27 bar. If, instead, fS_2 is 8.66 bar (log $fS_2 = 0.94$), then the calculated fH_2S would be 6.265 kbar or c. 25% higher absolute. There is thus no doubt that the thermodynamic quantities derived above need to be confirmed, in particular by designing specific experimental procedures to achieve equilibration of rhyolite melts with pure H₂S fluid (or SO₂) and by exploring the behaviour at higher fH_2S and fSO_2 than those attained in the present study to constrain more rigorously the partial molar volumes of H₂S and SO₂-related species (see below also). The data suggest, however, that, under low fO_2 and in iron-poor silicate melts, H₂S dissolution may occur through formation of HS-like complexes, and that at high fO_2 , SO₂ reacts with OH⁻ groups to yield SO_4^{2-} . Clearly, however, there is a need for more direct information (spectroscopic) about potential S complexes present in silicate melts (e.g. Winther et al., 1998), as the common peak-shift method is unable to distinguish between S²-associated with Fe^{2+} from those linked to H⁺ cations.

Solubility minimum and speciation Despite these caveats, the thermodynamic properties derived above for H₂S and SO₂ dissolution in hydrous rhyolite melt can be combined to compute the behaviour of total dissolved sulphur, X_S (= $X_{H2Smelt}$ + $X_{SO2melt}$, as defined above in equations (18)-(22)) under various T and fO_2 conditions. An Excel spreadsheet, which calculates the fugacities of S₂, H₂S, SO₂ and H₂O, species at fixed P, T, S_{melt} and fO₂, using the thermodynamic approach detailed above, is available upon request from the second author. The results of such calculations are shown in Fig. 10a for 930°C, 2 kbar, several fS_2 within the fO_2 range NNO-2 to NNO+3. As shown in Fig. 10a, the model reproduces the classical inverted bell-shaped pattern of sulphur solubility with varying fO_2 . At all fS_2 , the minimum calculated centers at NNO+1, in good agreement with experimental observations in the present (Fig. 6) as well as in other studies (see Carroll & Webster, 1994).



Fig. 10. Application of the thermodynamic model. (a) Calculated total dissolved sulphur (S_{ppm}) against fO_2 (Δ NNO) at 930°C and for an fS_2 of Δ FFS+7 (log $fS_2 = -0.75$), Δ FFS+8 (log $fS_2 = 0.24$), and Δ FFS+9 (log $fS_2 = 1.24$). All calculations have been performed with $fH_2O = 1$ kbar, which corresponds to a melt-water content of *c*. 4.5 wt %. (b) Comparison between observed and calculated melt sulphur contents for all charges in which fS_2 could be estimated. (c) Calculated proportions of S⁶⁺ at 1100 and 800°C, as a function of Δ NNO. The gray squares represent the experimental data of Carroll & Rutherford (1988).

It shows also that as fS_2 decreases, this bell-shaped pattern opens wide to the extent of becoming almost flat at very low values of fS_2 . Specifically, at 930°C, any fS_2 lower than 0·17 bar (FFS+7) results in no apparent variations in sulphur concentrations with varying fO_2 (note that the curve still has a bell-shaped pattern, even at very low sulphur concentrations, but the concentration scale over which it occurs is well below the detection limit of EPMA). Conversely, an fS_2 of 18 bar (FFS+9) leads to a strongly asymmetrical and steep-sided shape of the sulphur concentration curve with varying fO_2 . The calculated melt-sulphur concentrations for all charges for which fS_2 and fH_2 are available are plotted against those measured in Fig. 10b. The model reproduces well the experiments in the high concentration range, above 200 ppm, which reflects, in part, that the analytical accuracy is better at high concentration.

Given the above model assumptions, we can also calculate the proportions of S^{2-} and S^{6+} melt species, assuming that S^{2-} and S^{6+} abundances are fixed by H₂S and SO₂ dissolution reactions (18) and (19), respectively. Figure 10c shows the proportion of S^{6+} calculated for 1100 and 800°C isotherms. At a given *P*, *T* and *f*O₂, the *f*S₂ has no effect on species proportions. In contrast, temperature does affect the calculated proportions so that lower temperature increases the proportion of sulphide species at any fixed *f*O₂. As shown in Fig. 10c, the calculated pattern of species proportion broadly conforms with that obtained by Carroll & Rutherford (1988) from peak-shift measurements carried out on a series of synthetic sulphur-bearing glasses, annealed under various redox conditions in the temperature range 920–1150°C. The difference between model and observations may be a result of the fact that melt compositions synthesized by Carroll & Rutherford (1988)+ are less silicic than those of the present work.

Empirical model of sulphur solubility in rhyolite melts application of the thermodynamic model presented above requires the The determination of both fH₂S and fSO₂. These two guantities are not usually measured on magmatic rocks, in contrast to both fO_2 and fS_2 , which are more easily estimated from Fe–Ti oxides or sulfide barometry (Whitney, 1984). Although derivation of fSO_2 from fO_2 and fS_2 is straightforward, calculation of fH_2S requires fH_2 to be known in addition to fS_2 or, alternatively, the determination of fH_2O if fO_2 is known. This supplementary step introduces an additional source of uncertainty, that is, the determination of melt water content from which fH_2O is calculated. To overcome this potential problem and given the restricted compositional range displayed by the experimental glasses, we have derived an empirical model in which T, fO_2 and fS_2 are the only required input parameters: such a model is simpler in its application and, therefore, of more direct petrological use. Given that many arc magmas have fO2 below NNO+1.5, we have restricted the fitting procedure to charges lying below this fO₂ threshold: this has the advantage that only the charges for which fS₂ is best known are taken into account. Considering the different effects of fO₂, fS₂ and T on the melt–sulphur content illustrated above, the experimental data were fitted by least-squares regression to the following equation, taking into account sulphur-content only glasses with higher than the detection limit:

log S (ppm) =
$$0.001T (^{\circ}C) - 0.2567 \Delta$$
NNO
+ 0.1713Δ FFS + 0.0034Δ NNO × Δ FFS

or

$$\frac{\log S - 0.001T + 0.2567 \Delta NNO}{0.1713 + 0.0034 \Delta NNO} = \Delta FFS.$$

As with fO_2 , referencing fS_2 to a standard solid buffer such as FFS removes the temperature dependence and improves the quality of the fit. Knowing the sulphur content of a glass, the temperature and fO_2 of the system, equation (24) allows calculation of fS_2 .



Fig. 11. Comparison between measured and calculated sulphur fugacities using the empirical model [equation (24)]. See text for explanation.

<u>Figure 11</u> shows model performances for all charges held at an $fO_2 < NNO+1.5$. <u>Equation (24)</u> reproduces observed values to within 1 log units at Δ FFS > 6, apart from a few charges in the fO_2 range NNO to NNO+1.5. At lower Δ FFS, the model tends to underestimate fS_2 —a reflection of the difficulty in measuring sulphur content in glasses in the low concentration range (<100 ppm). We stress that <u>equation (24)</u> is merely a convenient mathematical way to describe the interdependence between the various parameters that control the sulphur solubility in rhyolite melts at 2 kbar and it has no thermodynamic meaning.

DISCUSSION

melt-sulphur Fluid and relationships The general coherency of the experimental trends obtained between intensive (fO_2 , fS_2) and extensive (S in melt) parameters shows that the adopted experimental procedure has been successful in either accurately controlling fO_2 or measuring fS_2 . The observed solubility trends can be interpreted in terms of different solubility behaviour of the different S-species present in the coexisting fluid. Because the fluid phase composition is sensitive to redox conditions, any change in fO₂ profoundly affects the sulphur solubility. The more soluble sulphur species appear to be H₂S and SO₂. The sulphur behaviour in hydrous silicate melts can thus be modelled using a simple thermodynamic approach, similar to that employed for characterizing the solubilities of both H₂O and CO₂ volatiles in silicate melts, considering the additive effects of two basic dissolution reactions involving either H₂S or SO₂ fluid species. At fixed P and T, Henry's Law is obeyed for H₂S and possibly SO₂ species, up to fugacities of 5 and 8 kbar, respectively. At equal fugacities, H₂S appears to be more soluble than SO₂, and, hence, the asymmetrical behaviour of sulphur on both sides of the solubility minimum. This asymmetry is also a result of the differing *PVT* properties of H₂S and SO₂ fluid species. The MRK model predicts that SO₂ exhibits a more pronounced non-ideal behaviour than H_2S (that is higher fugacity coefficients), and thus the fugacities of either end-member (i.e. pure SO₂ or H₂S fluids at any fixed P and T) and their mixing behaviour will also control the shape of the solubility curve. In other words, even if both H₂S and SO₂ were to have identical Henry's Law constants, because the fugacities of pure H₂S or SO₂ differ at fixed P and T, this will ultimately impart an asymmetrical shape on the solubility curve with changing redox conditions. In this regard, it would be of interest to constrain the solubility of silicate melts with respect to H₂S and SO₂ by performing experiments with pure H₂S and SO₂ fluids. The minimum in solubility appears to lie in the redox range where H₂S and SO₂ fugacities in the fluid are approximately equal (Fig. 4), and MRK calculations show that S₂ is comparatively more abundant in this domain. This latter species is thus apparently weakly soluble in silicate melts and plays a minor role in the melt-sulphur budget.

TheeffectofironThe experimental procedure adopted here does not allow independent variation of fS_2 and the melt-FeO content (Fig. 5). In particular, at any given temperature, it has notbeen possible to produce charges displaying the same fS_2 and fO_2 but with widely

different iron-melt contents. Only charges belonging to the MP12 and MP7 series (Table 5) are suitable to test the effect of varying iron content on sulphur solubility under quasiconstant fS₂ and fO₂, albeit for iron content below 1 wt % only. These charges also display a negative trend between iron and sulphur in melt. Such a negative correlation is corroborated by the iron-rich but sulphur-poor melt in all magnetite-doped charges (Table 5). Altogether, the above lines of evidence demonstrate unequivocally that an iron-rich rhyolite will not dissolve more sulphur than a iron-poor one under the experimental conditions explored here—a result that is at variance with what has been found in mafic melts (e.g. Haughton et al., 1974). Clearly, addition of sulphur to a silicic magma in the stability field of sulphide has the main effect of crystallizing sulphide, which removes both iron and sulphur from the melt (and fluid). This scavenging of sulphur results in low fS_2 , as long as there is enough iron to produce pyrrhotite. One reason for the fundamental difference between mafic and felsic melts is that the liquidus temperature of S-free hydrous silicic melts is much lower than that of dry mafic melts. Experiments performed in mafic systems were performed at about 1200°C, where much of the iron remains in solution in the melt and where it may complex with sulphur, preventing extensive crystallization of either sulphide or oxides. In contrast, the experiments of the present study are performed at temperatures well below the liquidi of sulphides, as indicated by their occurrence in nearly all run products. It is mostly when $fO_2 > NNO+1.5$, or in the anhydrite stability field, that the negative trend observed between FeO and sulphur solubility becomes weaker, indicating conditions less appropriate for sulphide crystallization (Fig. 5). We note, in addition, that most of the 1 bar experiments investigated the sulphur behaviour without the involvement of H-bearing species (e.g. O'Neill & Mavrogenes, 2002), and, thus, the solubility mechanisms of sulphur in those studies are probably different from those proposed here.

The foregoing considerations show that the application of the present thermodynamic model to melt compositions other than metaluminous rhyolite, in particular to more mafic compositions, is not warranted. Studies carried out on the H₂O and CO₂ solubilities in various silicate-melt compositions have shown that the thermodynamic parameters, i.e. enthalpy of species dissolution and its partial molar volume, are strongly dependent on melt composition (see Holloway & Blank, 1994). This stems from the fact that dissolution mechanisms, and, thus, the energetics of solution, may widely vary with melt composition. An obvious difference is that sulphur may complex with iron in melts with higher FeO contents than those of the present study, which may lead to significantly different solution parameters. Another example concerns the alkalis over alumina balance (i.e. peralkaline, peraluminous) which evidently affects the proportion of O^{2-} and, thus, the sulphur behaviour. Therefore, although the thermodynamic model appears to reproduce successfully first-order observations bearing on the sulphur behaviour in silicate melts, its quantitative use on melt compositions other than metaluminous rhyolite requires prior experimental investigation of ΔH and V_i values associated with any given melt composition.

The effect of temperature on the solubility of sulphur and its speciation Temperature appears to exert a positive effect on the solubility of H_2S —a behaviour at variance with that of both CO_2 and H_2O , at least in the low-pressure range, whereas SO_2 appears to be less sensitive to this parameter. As Stolper *et al.* (1987) have emphasized, the bulk effect of temperature on volatile solubility in silicate melts is controlled by the energetic balance between the reactions controlling molecular (e.g. H₂S, SO₂, H₂O, CO₂) and anion groups' solubility (e.g. HS^{-} , SO_4^{2-} , OH^{-} , CO_3^{2-}). In general, the solubility of molecular species decreases with T (Stolper et al., 1987; Fogel & Rutherford, 1990), whereas the abundance of species formed by reaction with the melt is enhanced by temperature (see Zhang, 1999). Thus, the fact that under reduced conditions, the bulk sulphur solubility has a strong and positive temperature dependence might be interpreted as the dominant presence of S^{2-} or HS⁻ species over molecular H₂S in rhyolite melts, i.e. that, essentially, all dissolved H₂S reacts with the aluminosilicate melt framework to yield HS⁻ units. Our data favor a reaction such as (15), in which exchange between gaseous H₂S and hydroxyl groups is the dominant mechanism of sulphur incorporation into hydrous and iron-poor silicate melts. At high fO₂, it is not yet possible to decipher the details of the solution reaction but if all SO₂ reacts with hydroxyl groups to form SO_4^2 units, then it might be expected that there is a positive effect of temperature on solubility under oxidizing conditions as well. Thus, compared with H₂O and CO₂, which dissolve both physically and chemically, the case for sulphur is different, as its dissolution seems to proceed dominantly chemically, by reaction of gaseous species with the melt framework, keeping the abundance of molecular species at a marginal level. Another major difference is that, as far as we know, for fixed melt chemistry, both H_2O and CO_2 speciations are insensitive to redox conditions, whereas, clearly, this parameter is the major controlling factor of sulphur speciation in silicate melts.

Although significant, the dependence on temperature appears to be low compared with the effects exerted by fO_2 and fS_2 . Below NNO, the temperature dependence established in other studies performed on hydrous silicic melts (Carroll & Rutherford, 1987; Luhr, 1990) is lower than that reported here. For instance, the experiments of Luhr (1990) on the El Chichòn trachyandesite show almost no effect of temperature on the melt S content between 800 and 1000°C at an fO2 buffered by the guartz-favalitemagnetite solid buffer (NNO-0.7). In contrast, at high fO_2 , a strong positive temperature dependence has been evidenced by both Carroll & Rutherford (1987) and Luhr (1990). In these experiments, however, low-temperature runs are largely below the liquidus of the bulk composition used as starting material, which means that the residual melt composition changes significantly with rising temperature, unlike in the present study. In such experiments, the temperature effect on sulphur solubility may thus be hindered by the interplay of additional variables such as $aSiO_2$ or fS_2 , even when performed at fixed redox conditions. Thus, it remains to be demonstrated whether the strong positive temperature dependence of sulphur solubility observed under oxidizing conditions in hydrous silicic melts by Carroll & Rutherford (1987) and Luhr (1990) is, indeed, solely because of temperature, or the combined effects of varying melt composition with temperature in addition to varying fS_2 .

TheeffectofpressureThe last parameter of interest is pressure. Recent experimental studies have confirmedthe earlier findings of Wendlant (1982) that pressure decreases the sulphur solubility indry mafic systems (Mavrogenes & O'Neill, 1999; Holzheid & Grove, 2002). By contrast,in hydrous systems, Luhr (1990) concluded that pressure has an opposite effect.

Nevertheless, as for temperature, the experiments of Luhr (1990) in which pressure was varied involved also varying other parameters, in particular the melt composition, and it cannot be ruled out that the observed increase in Smelt also reflects a change in melt chemistry and not only an intrinsic and positive effect of pressure. Our experiments suggest that one of the controlling parameters of sulphur solubility in H-bearing systems is fH_2S . By analogy with what happens with water, as total pressure decreases, fH_2S will decrease too, so that the melt sulphur solubility should decrease eventually, in keeping with the Henrian behaviour shown above. In support of this are the experiments of Katsura & Nagashima (1974), which show that a rhyodacite melt (66.7 wt % SiO₂) equilibrated at 1 bar and 1250°C, with an H–C–S–O gas mixture over an fO₂ range of NNO-5 to NNO+5, displays sulphur concentration always below 50 ppm. Thus, given that natural silicic magmas have eruption temperatures that are 300-400°C lower, and that they have higher silica contents than the rhyodacite experimental melts, it can be anticipated that their equilibrium sulphur concentration at near atmospheric conditions is close to the ppm level. That, at 1 bar, silicic compositions have much lower sulphur solubility than mafic ones is related to the fact that, under anhydrous conditions, the proportion of O^{2-} is significantly higher in the latter than in the former.

Application of the empirical model The empirical model can be tested by applying it to eruption products for which common pre-eruptive parameters are well known (P, T, fO_2) in addition to fS_2 and the melt-sulphur concentration. These include the Bishop Tuff (0.76 Ma), Krakatau (1885), Katmai (1912), Mt St Helens (1980) and El Chichòn (1982) eruptions. Pre-eruptive parameters, as well as calculated melt-sulphur fugacities, are listed in Table 6. Equation (25) reproduces observed sulphur fugacities to within 1 log unit, except for Mt St Helens. The origin of the disagreement for Mt St Helens might be because of the relatively low sulphur content measured, close to the detection limit of EMPA: if, for instance, a pre-eruptive meltsulphur content of 100 ppm is assumed, then the calculated Δ FFS is 7.78, or within 0.2 log units of the measured one by the pyrrhotite composition (Whitney, 1984). As the experimental melt compositions are metaluminous and because of the empirical nature of equation (25), the model should not be applied to either peraluminous or peralkaline rhyolites.

SUMMARY

(1) Experiments with controlled fO_2 and fS_2 have been performed in the temperature range 800–1000°C on rhyolite-melt compositions, to establish the effect of those variables on the solubility of sulphur. The fS_2 was measured either by the pyrrhotite (fO_2 < NNO+1) or by the fluid phase (fO_2 > NNO+1·5) compositions, using for the latter an MRK equation of state.

(2) At fO_2 < NNO+1 and temperatures of <1000°C, the addition of iron to a sulphurbearing rhyolite melt promotes massive crystallization of pyrrhotite, which consequently removes most of the sulphur from the melt.

(3) At constant fO_2 , the sulphur solubility increases with fS_2 . Below NNO+1, there is a linear relationship between the melt-sulphur concentration and fH_2S , whereas above NNO+1, fSO_2 seems the dominant controlling factor.

(4) The sulphur solubility in rhyolite melts is a result of the dissolution of both H_2S and SO_2 fluid species. The strong positive dependence of solubility on temperature observed at $fO_2 < NNO+1$ suggests that the abundance of dissolved molecular H_2S is low and that most of the sulphur dissolves by chemical reaction with the aluminosilicate framework. SO_2 possibly behaves similarly but this needs to be checked by additional experimental work, with a more precise control of fS_2 under oxidizing conditions than that achieved in the present work.

(5) A simple thermodynamic model can be developed, adopting an approach similar to that used for modelling the solubilities of both H_2O and CO_2 in silicate melts. This model reproduces first-order observations concerning the sulphur solubility and speciation in silicate melts. Yet, there is an urgent need for rigorously determining the nature and abundance of different sulphur species dissolved in melts and their dependence on melt composition.

(6) An empirical model for metaluminous rhyolites that is easier to handle has been developed also. It may be used primarily to determine the fS_2 of common metaluminous silicic arc magmas.

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