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# The Solubility of Sulphur in Hydrous Rhyolitic Melts

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Experiments performed at 2 kbar, in the temperature range 800–1000°C, with  $fO_2$  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  $fS_2$  exerts a dominant control on the sulphur solubility in hydrous silicate melts and that, depending on  $fO_2$ , a rhyolitic melt can reach sulphur contents close to 1000 ppm at high  $fS_2$ . At  $fO_2$  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  $fO_2$ , the melt-sulphur-content increases with  $fS_2$ . For fixed  $fO_2$  and  $fS_2$ , temperature exerts a positive control on sulphur solubilities, at least for  $fO_2$  below  $NNO+1$ . The mole fraction of dissolved sulphur exhibits essentially linear dependence on  $fH_2S$  at low  $fO_2$  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  $fH_2S$  and  $fSO_2$  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  $H_2S$  and  $SO_2$  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  $fO_2$ . 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;  $fO_2$ ;  $fS_2$

## INTRODUCTION

Sulphur species are the most abundant magmatic volatiles, after  $H_2O$  and  $CO_2$ . 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  $fO_2$ ,  $fS_2$ , 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  $fO_2$  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  $\text{SO}_2$  input in 1 atm gas furnaces [or constant absolute value of  $f\text{S}_2$  for the study by Buchanan et al. (1983)], and a constant absolute value of  $f\text{O}_2$ , 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  $f\text{S}_2$  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  $f\text{S}_2$ . This hinders the understanding of the control that  $f\text{S}_2$  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  $f\text{O}_2$ ,  $f\text{S}_2$ ,  $T$  (temperature) and  $\text{XS}$  (dissolved melt sulphur content) for rhyolitic compositions. We have used rhyolitic compositions primarily because it makes it possible to work at relatively low temperatures ( $\leq 1000^\circ\text{C}$ ), where accurate control of critical parameters (namely  $T$ ,  $f\text{O}_2$ ,  $f\text{H}_2\text{O}$ , and  $f\text{S}_2$ ) 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 S-rich 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  $f\text{O}_2$  and  $f\text{S}_2$ . We emphasize how  $f\text{S}_2$ ,  $f\text{O}_2$  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–H<sub>2</sub> 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  $f\text{H}_2$  (Shaw, 1963; Scaillet et al., 1992), connected to a Protais gauge (accurate to 0.1 bar). For experiments performed at 1000°C, the experimental  $f\text{H}_2$  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 ZrO<sub>2</sub> 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  $f\text{O}_2$  (or  $f\text{H}_2$ ). Temperature was measured with three sheathed chromel–alumel thermocouples, calibrated at 1 atm against the melting point of NaCl and is accurate to within  $\pm 5^\circ\text{C}$ . 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 H<sub>2</sub>O was added, so as to reach conditions slightly below H<sub>2</sub>O 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<sub>tot</sub> 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 H<sub>2</sub>S 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

$$K_w = \frac{fH_2 \times fO_2^{1/2}}{fH_2O}.$$

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

	MP natural <sup>1</sup>	MP synthetic <sup>2</sup>	MP15VII <sup>3</sup>	MP16VII <sup>3</sup>	MP17VII <sup>3</sup>	MP18XII <sup>3</sup>	MP19XII <sup>3</sup>	Pinatubo <sup>4</sup>
SiO <sub>2</sub>	75.65	75.92	70.43	71.60	71.47	72.06	72.06	78.29
Al <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	4.34	4.14	3.84	3.90	3.93	3.93	3.93	3.29
K <sub>2</sub> 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.

<sup>1</sup>Natural interstitial glass composition of Mt Pelée andesite erupted in 1929 (Martel *et al.*, 1998). It also contains 0.26 wt % TiO<sub>2</sub> and 0.08 wt % MnO.

<sup>2</sup>Dry synthetic glass used in all non magnetite-doped charges.

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

<sup>4</sup>Dry synthetic glass similar to the Pinatubo 1991 dacite interstitial glass (Scaillet & Evans, 1999). It also contains 0.15 wt % TiO<sub>2</sub>.

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  $f_{H_2}$  of the experiment, the  $f_{H_2O}$  of the charge and the equilibrium constant of the reaction,  $K_w$  (Robie *et al.*, 1979). For experiments with solid sensors, the prevailing  $f_{H_2}$  was first computed from equation (2), using the sensor composition and the model of Pownceby & O'Neill (1994) and assuming that  $f_{H_2O}$  in the sensor was that of pure H<sub>2</sub>O. Then, the  $f_{O_2}$  of the charge was calculated with  $f_{H_2}$  and  $f_{H_2O}$  from the model of Burnham (1979). It should be noted that the above approach in controlling  $f_{O_2}$  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  $f_{O_2}$  calculation depends on the uncertainties in temperature,  $f_{H_2}$  and  $f_{H_2O}$ . Errors arising from uncertainties attached to either  $f_{H_2}$  ( $\pm 0.1$  bar) or temperature ( $\pm 5^\circ\text{C}$ ) measurements are minor, i.e. less than  $0.01 \log f_{O_2}$ . In contrast, the uncertainty attached to  $f_{H_2O}$  is the main source of error, as it depends both on the uncertainty of the determination of the melt H<sub>2</sub>O content, which is, here, estimated using the by-difference method (see below), and on the accuracy of the thermodynamic model used to calculate H<sub>2</sub>O fugacities from melt H<sub>2</sub>O contents. An error of  $\pm 0.5$  wt% in the melt H<sub>2</sub>O content, which corresponds to the analytical uncertainty of most charges, translates into an error of c. 10% in  $f_{H_2O}$  using the model of Burnham (1979), which, in turn, translates into an uncertainty of c. 0.2 log units in  $f_{O_2}$ , 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 SiO<sub>2</sub> 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 H<sub>2</sub>O 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  $f_{\text{H}_2\text{O}}$  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  $\text{H}_2\text{O}$  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  $f_{\text{H}_2\text{O}}$ . As explained below, the MRK-EOS of Holloway (1977) is used for the calculation of  $f_{\text{S}_2}$ . 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  $f_{\text{O}_2}$  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  $f_{\text{O}_2}$  are referenced to the NNO buffer (Holloway et al., 1992).

The  $f_{\text{S}_2}$  was determined from the composition of pyrrhotite, crystallized during the experiment (Froese & Gunter, 1976). The  $f_{\text{S}_2}$  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  $f_{\text{S}_2}$  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  $f_{\text{S}_2}$  and the fluid phase composition.

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

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

where  $C$  is the number of components,  $\phi$  is the number of phases and  $v$  is the degree of freedom (4 in this case). The pressure, the temperature and the  $f_{\text{H}_2}$  are fixed in our experiments and we know the  $f_{\text{H}_2\text{O}}$  of each charge. Therefore, the system is invariant and we can calculate the fluid phase composition and, thus, the  $f_{\text{S}_2}$ . 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):

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

$P$  is the pressure,  $T$  the temperature,

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 ( $P_c$ ) and temperature ( $T_c$ ) (Breedveld & Prausnitz, 1973; Ferry & Baumgartner, 1987). Calculation of the fluid phase compositions indicates that the major species under our experimental conditions are

H<sub>2</sub>O, H<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub> and S<sub>2</sub>. H<sub>2</sub>O is a polar molecule, the parameters *a* and *b* for water, taken from Holloway (1981). H<sub>2</sub>S and SO<sub>2</sub> 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 *P<sub>c</sub>* and *T<sub>c</sub>*, as given by Shi & Saxena (1992). For S<sub>2</sub>, *P<sub>c</sub>* and *T<sub>c</sub>* 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.

	<i>a</i> (atm × cm <sup>6</sup> K <sup>0.5</sup> /mole <sup>2</sup> )	<i>b</i> (cm <sup>3</sup> /mole)
H <sub>2</sub> <sup>1</sup>	3.56 × 10 <sup>6</sup>	15.15
H <sub>2</sub> S <sup>2</sup>	89.38 × 10 <sup>6</sup>	29.89
SO <sub>2</sub> <sup>2</sup>	142.92 × 10 <sup>6</sup>	39.46
S <sub>2</sub> <sup>2</sup>	25 × 10 <sup>6</sup>	20.57
	<i>a<sub>o</sub></i>	<i>b</i>
H <sub>2</sub> O <sup>1</sup>	35 × 10 <sup>6</sup>	14.6

<sup>1</sup>From Holloway (1981).

<sup>2</sup>From Shi & Saxena (1992).

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

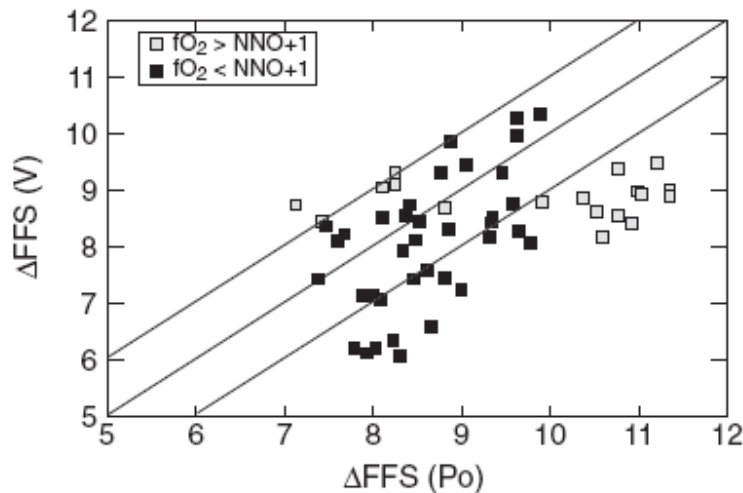
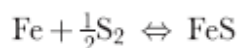


Fig. 1. Comparison between *f*S<sub>2</sub> measured by the pyrrhotite composition [ΔFFS(*p<sub>o</sub>*)] and *f*S<sub>2</sub> calculated from an MRK equation of state [ΔFFS(*V*)].

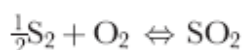
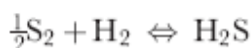
The MRK program was checked against the program of Connolly & Cesare (1993) and, for given *P*, *T*, *f*H<sub>2</sub> and *f*H<sub>2</sub>O conditions, both methods were found to agree within 0.2 log *f*S<sub>2</sub>.

As discussed previously, for reducing conditions ( $fO_2 < NNO$ ),  $fS_2$  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  $fS_2$  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  $fO_2$  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  $fS_2$  of charges lacking pyrrhotite, at least for H<sub>2</sub>O-rich fluid compositions. An additional check on the accuracy of the calculated  $fS_2$  was also provided by comparing the H<sub>2</sub>O/S ratio of the fluid phase, as calculated from MRK, against that obtained through mass balance. In the latter, the amount of S and H<sub>2</sub>O left over for the fluid phase can be determined. Thus, the H<sub>2</sub>O/S ratio of the fluid can be obtained and compared with H<sub>2</sub>O/S values calculated from the MRK-EOS approach. Pyrrhotite-free charges for which the calculated H<sub>2</sub>O/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  $fS_2$  are referenced to the FFS buffer, which corresponds to the equilibrium between iron and troilite :



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

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:



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
$N_{FeS}^2$	0.975	0.920
% at Fe <sup>3</sup>	48.77	45.97

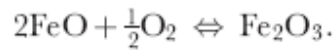
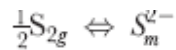
<sup>1</sup>Distance between inter-reticular 102 plane of hexagonal pyrrhotite determined by XRD.

<sup>2</sup>Mole fraction of FeS in pyrrhotite from Toulmin & Barton (1964).

<sup>3</sup>Atomic proportion of Fe in pyrrhotite calculated after Yund & Hall (1969).

Table 3: Composition of synthetic pyrrhotites

two reactions are



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



Baker & Rutherford (1996b) and Gaillard et al. (2001) have shown that the  $Fe^{3+}/Fe^{2+}$  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–Mn<sub>2</sub>O<sub>3</sub>. 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 supra-liquidus 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 SiO<sub>2</sub>-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 [ $N_{FeS} = 0.975$ ;  $N_{FeS}$  is the mole fraction of FeS in the system FeS–S<sub>2</sub> (Toulmin & Barton, 1964)] and, in the second one, the pyrrhotite was sulphur-rich ( $N_{FeS} = 0.92$ ). During the experiment, pyrrhotites in these two capsules re-equilibrated 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  $fS_2$  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. SiO<sub>2</sub>) and minor element (S) concentrations.



Charges	wt % S <sup>1</sup>	wt% CO <sub>2</sub>	log <sub>10</sub> CO <sub>2</sub>	Δ <sub>HNCO</sub> <sup>2</sup>	d[102] <sup>3</sup>	at % Fe <sup>4</sup>	log <sub>10</sub> (po) <sup>7</sup>	log <sub>10</sub> (V) <sup>8</sup>	ΔFFS (po) <sup>9</sup>	ΔFFS (V) <sup>10</sup>	GI	PI	Px	Qtz	Po	An	V
<i>P = 2.116 kbar, T = 805°C, f<sub>H<sub>2</sub>O</sub> = 0.9 bar, 164h</i>																	
MP9 I	1.07 (S)	0.96	-9.12	2.16 (0.13)	2.00.06	46.85	0.16	-	7.95	-	99.22 (0.56)	-	-	-	0.76	traces	116 (0.66)
MP9 II	1.00 (po)	1.00	-9.01	2.27 (0.16)	2.05.62	46.47	0.62	-	8.31	-	96.27 (0.56)	-	-	-	1.72	traces	-
MP9 V	1.00 (an)	1.00	-8.99	2.29 (0.16)	2.06.67	47.10	-0.17	-	7.63	-	97.97 (0.56)	-	-	-	-	2.03	-
<i>P = 2.013 kbar, T = 830°C, f<sub>H<sub>2</sub>O</sub> = 47.3 bar, 166h</i>																	
MP10 I	2 (S)	0.81	-12.71 (0.12)	-1.38 (0.09)	2.06.45	47.19	-0.31 (0.14)	-0.34	7.42 (0.07)	7.38 (0.22)	97.94	-	-	-	2.16	-	1.93 (0.46)
MP10 II	3 (S)	0.75	-12.78 (0.18)	-1.46 (0.13)	2.06.85	46.67	0.36 (0.15)	-F.27 (F.86)	8.08 (0.07)	7.60 (0.22)	98.02	0.60 (0.74)	-	-	1.38	-	3.15 (0.61)
MP10 III	4 (S)	0.72	-12.82 (0.16)	-1.48 (0.11)	2.06.72	46.95	0.49 (0.14)	-0.23 (0.61)	8.21 (0.07)	7.88 (0.16)	98.18	1.89 (0.90)	-	-	1.3	-	4.66 (0.63)
MP10 IV	10 (S)	0.65	-13.18 (0.37)	-1.86 (0.27)	2.06.40	46.30	0.79 (0.14)	0.27 (0.48)	8.61 (0.07)	8.11 (0.14)	92.93	5.33 (1.04)	-	-	1.71	-	10.73 (0.96)
MP10 V	1 (po6)	1	-12.83 (0.14)	-1.18 (0.14)	2.07.61	48.25	-1.93 (0.18)	-	5.79 (0.06)	-	96.16	-	-	-	3.95	-	-
MP10 VI	1 (po7)	1	-12.83 (0.14)	-1.18 (0.14)	2.07.60	48.23	-1.91 (0.15)	-	5.82 (0.06)	-	96.95	-	-	-	3.45	-	-
<i>P = 2.202 kbar, T = 835°C, f<sub>H<sub>2</sub>O</sub> = 20.4 bar, 164h</i>																	
MP11 I	2.12 (S)	0.74	-11.98 (0.20)	-0.65 (0.14)	2.08.53	46.40	0.70 (0.13)	-0.46 (2.18)	8.43 (0.07)	8.52 (0.22)	98.18	-	-	-	1.82	-	2.20 (0.79)
MP11 II	4.83 (S)	0.78	-11.92 (0.18)	-0.61 (0.13)	2.05.12	46.13	1.01 (0.14)	F.02	8.73 (0.07)	8.42 (0.24)	98.96	-	-	-	1.04	-	2.95 (0.64)
MP11 III	4.83 (S)	0.83	-12.11 (0.19)	-0.80 (0.14)	2.06.70	46.54	1.90 (0.14)	0.94 (0.42)	9.29 (0.07)	8.76 (0.13)	98.15	2.60 (1.30)	-	2.80 (1.61)	1.65	-	5.88 (0.66)
MP11 IV	10.12 (S)	0.91	-12.31 (0.37)	-1.00 (0.26)	n.d.		-	1.09 (0.90)	-	8.96 (0.16)	89.7	4.40 (1.33)	-	4.20 (1.90)	1.65	-	11.39 (0.96)
<i>P = 2.202 kbar, T = 835°C, f<sub>H<sub>2</sub>O</sub> = 20.4 bar, 164h</i>																	
MP11 V	1.20 (F65)	0.97	-11.71 (0.05)	-0.41 (0.05)	2.07.48	48.12	-1.08 (0.15)	-	6.05 (0.07)	-	96.9	-	-	-	3.1	-	-
MP11 VI	1.10 (F67)	0.97	-11.71 (0.05)	-0.41 (0.05)	2.07.50	48.15	-1.72 (0.16)	-	6.00 (0.08)	-	97.09	-	-	-	2.91	-	-
<i>P = 2.003 kbar, T = 834°C, f<sub>H<sub>2</sub>O</sub> = 15 bar, 218h</i>																	
MP6 II	0.62 (S)	0.83	-11.96 (0.20)	-0.34 (0.14)	2.07.39	48.04	-1.57 (0.21)	-	6.15 (0.10)	-	99.13	-	-	-	0.87	-	-
MP6 III	1.02 (S)	0.74 (0.11)	-11.79 (0.18)	-0.46 (0.13)	2.07.09	47.76	-1.14 (0.15)	0.57 (0.82)	6.68 (0.08)	6.66 (0.20)	98.34	-	-	-	1.66	-	1.43 (0.61)
MP6 IV	1.33 (S)	0.76 (0.19)	-11.76 (0.24)	-0.43 (0.17)	2.08.31	47.06	-0.14 (0.14)	F.25	7.67 (0.07)	8.62 (0.27)	98.31	-	-	-	1.69	-	1.49 (0.68)
MP6VI	1.03 (F67)	0.83	-11.66 (0.08)	-0.24 (0.08)	2.07.40	48.06	-1.59 (0.15)	-	6.13 (0.07)	-	97.31	-	-	-	2.69	-	-
MP6VII	1.04 (F65)	1	-11.90 (0.08)	-0.17 (0.08)	2.07.40	48.06	-1.59 (0.15)	-	6.12 (0.08)	-	97.62	-	-	-	2.48	-	-
<i>P = 2.002 kbar, T = 834°C, f<sub>H<sub>2</sub>O</sub> = 6 bar, 147h</i>																	
MP12 I	2.31 (S)	0.77 (0.13)	-10.92 (0.21)	0.40 (0.15)	2.06.41	46.30	0.60 (0.14)	1.97	8.52 (0.07)	9.35 (0.26)	97.95	-	-	-	2.15	-	1.87 (0.65)
MP12 II	3.90 (S)	0.79 (0.14)	-10.90 (0.21)	0.41 (0.15)	2.06.52	46.39	0.70 (0.14)	1.96	8.42 (0.07)	9.33 (0.27)	97.99	-	-	-	2.11	-	4.04 (0.65)
MP12 III	5.98 (S)	0.65 (0.17)	-11.09 (0.33)	0.22 (0.23)	2.06.69	46.53	0.53 (0.17)	2.23	8.26 (0.07)	8.26 (0.22)	91.86 (2.06)	3.60 (1.30)	-	3.00 (1.51)	1.65	-	6.23 (0.78)
MP12 IV	10.31 (S)	0.67 (0.18)	-11.22 (0.40)	0.10 (0.29)	2.06.88	46.70	0.33 (0.20)	1.71	8.65 (0.10)	9.78 (0.19)	89.20 (2.75)	9.10 (1.34)	-	3.00 (1.56)	1.65	-	11.86 (0.82)
<i>P = 1.980 kbar, T = 830°C, f<sub>H<sub>2</sub>O</sub> = 4 bar, 162h</i>																	
MP7 III	1.00 (S)	0.78 (0.13)	-10.90 (0.21)	0.76 (0.15)	2.04.43	46.53	F.62 (F.12)	2.16	9.29 (0.06)	9.46 (0.27)	98.01	-	-	-	1.39	-	1.40 (0.63)
MP7 IV	1.26 (S)	0.72 (0.08)	-10.66 (0.14)	0.89 (0.10)	2.06.09	46.04	F.10 (F.13)	1.74 (0.90)	8.76 (0.06)	9.68 (0.16)	98.95	-	-	-	1.05	-	2.25 (0.43)
<i>P = 2.407 kbar, T = 830°C, f<sub>H<sub>2</sub>O</sub> = 0.8 bar, 168h</i>																	
MP13 I	2.00 (S)	0.38 (0.03)	-9.92 (0.06)	1.47 (0.05)	2.06.30	46.21	0.86 (0.14)	2.75 (0.18)	8.62 (0.07)	10.52 (0.06)	96.21 (0.89)	-	-	-	1.63	0.37	3.80 (0.18)
MP13 II	3.87 (S)	0.36 (0.06)	-9.97 (0.15)	1.42 (0.11)	2.06.77	46.60	0.47 (0.14)	2.79 (0.27)	8.77 (0.07)	10.59 (0.09)	95.74 (0.88)	-	-	2.13 (0.88)	1.69	0.43	5.80 (0.30)
MP13 III	6.04 (S)	0.29 (0.03)	-10.15 (0.13)	1.23 (0.09)	2.06.38	46.29	0.79 (0.16)	3.00 (0.15)	8.95 (0.06)	10.77 (0.06)	97.41 (0.90)	-	-	traces	1.79 (0.85)	0.42	8.82 (0.62)
MP13 IV	10.11 (S)	0.22 (0.02)	-10.38 (0.13)	1.00 (0.09)	2.06.54	46.41	0.64 (0.22)	3.16 (0.09)	8.39 (0.11)	10.92 (0.03)	98.03	traces	-	traces	1.73	0.24	13.37 (0.41)
<i>P = 2.189 kbar, T = 844°C, f<sub>H<sub>2</sub>O</sub> = 30 bar, 162h</i>																	
MP18 I	1.26 (S)	0.95 (0.09)	-11.44 (0.43)	-1.28 (0.43)	2.07.37	48.02	-1.04 (0.16)	0.69 (1.12)	6.07 (0.08)	6.30 (0.20)	96.27	-	-	-	0.73	-	2.46 (0.13)
MP18 II	0.76 (S)	0.76 (0.06)	-11.29 (0.44)	-0.93 (0.44)	2.07.34	47.99	-1.00 (0.22)	0.41 (0.88)	6.11 (0.11)	7.84 (0.20)	96.68	-	-	-	1.32	-	1.16 (0.20)
MP18 IV	2.04 (S)	0.65 (0.04)	-11.69 (0.52)	-1.34 (0.37)	2.06.95	47.27	0.02 (0.14)	-0.10 (1.67)	7.13 (0.07)	7.89 (0.21)	96.42	-	-	-	1.68	-	2.72 (0.18)
MP18 V	4.32 (S)	0.67 (0.03)	-12.11 (0.42)	-1.76 (0.42)	2.06.90	46.63	0.81 (0.13)	0.94 (0.78)	7.82 (0.06)	8.34 (0.18)	98.41	-	-	-	1.69	-	6.01 (0.20)
MP18 VI	6.33 (S)	0.23 (0.02)	-12.82 (0.42)	-2.16 (0.30)	2.06.33	46.23	1.24 (0.12)	1.09 (0.77)	8.36 (0.06)	7.48 (0.18)	96.27	-	-	-	1.73	-	8.63 (0.15)

Charges	wt % S <sup>1</sup>	aH <sub>2</sub> O <sup>2</sup>	logfO <sub>2</sub> <sup>3</sup>	ΔNNO <sup>4</sup>	d(102) <sup>5</sup>	wt % Fe <sup>6</sup>	logfS <sub>2</sub> (po) <sup>7</sup>	logfS <sub>2</sub> (V) <sup>8</sup>	ΔFFS (V) <sup>9</sup>	ΔFFS (po) <sup>8</sup>	GI	PI	Px	Oz	Po	An	V
P = 2.089 kbar, T = 594°C, fH <sub>2</sub> <sup>15</sup> = 30 bar, fS <sub>2</sub> <sup>h</sup>																	
MP18 VII	10.84 (S)	0.33 (0.03)	-12.21 (0.42)	-1.95 (0.30)	2.0609	46.04	1.44 (0.13)	0.99 (0.77)	8.38 (0.18)	8.95 (0.06)	98.17	-	-	-	1.63	-	12.73 (0.31)
MP18 X	3.62 (S)	0.56 (0.11)	-11.77 (0.40)	-1.41 (0.48)	2.0681	47.33	-0.05 (0.14)	0.63 (0.88)	8.09 (0.19)	7.06 (0.07)	98.45	-	-	-	1.65	-	6.52 (0.66)
MP18 XI	3.77 (S)	0.72 (0.16)	-11.55 (0.40)	-1.19 (0.48)	2.0727	47.93	-0.90 (0.15)	0.52 (0.52)	8.21 (0.07)	6.21 (0.07)	98.68	-	-	-	1.94	-	9.75 (0.52)
MP18 XII <sup>a</sup>	3.30 (S)	0.83 (0.07)	-11.11 (0.07)	-0.75 (0.07)	2.1718	47.94	-0.78 (0.14)	-1.98 (1.59)	8.23 (0.70)	6.33 (0.07)	97.24 (0.56)	-	-	-	2.76	-	2.54 (0.62)
MP18 SN	1.32 (po+po?)	0.83	-11.11	-0.74	2.0741	48.08	-1.11 (0.11)	-	6.00 (0.12)	6.00 (0.12)	96.47	-	-	-	3.63*	-	-
PI18 IX	3.26 (S)	0.24 (0.12)	-12.62 (0.64)	-2.26 (0.77)	2.0677	46.90	1.00 (0.13)	1.18 (0.62)	8.11 (0.06)	8.48 (0.27)	98.13 (0.56)	-	-	-	1.87	-	5.74 (0.63)
P = 2.089 kbar, T = 596°C, fH <sub>2</sub> <sup>15</sup> = 2 bar, fS <sub>2</sub> <sup>h</sup>																	
MP19 VII	0.64 (S)	0.49 (0.11)	-9.26 (0.23)	1.06 (0.19)	-	-	-	2.22 (0.90)	-	9.59 (0.19)	100	-	-	-	-	-	2.09 (0.47)
MP19 II	1.42 (S)	0.75 (0.10)	-8.96 (0.16)	1.46 (0.12)	-	-	-	0.97 (0.97)	-	8.67 (0.25)	100	-	-	-	-	-	2.33 (0.46)
MP19 III	2.34 (S)	0.61 (0.16)	-9.08 (0.33)	1.25 (0.24)	-	-	-	1.31 (1.31)	-	9.34 (0.27)	99.34	-	-	-	-	-	3.57 (0.74)
MP19 IV	3.09 (S)	0.39 (0.17)	-9.62 (0.67)	0.81 (0.41)	-	-	-	1.95 (1.95)	-	9.86 (0.22)	99.39	-	-	-	-	-	5.33 (0.62)
MP19 V	5.03 (S)	0.01	-12.61	-2.29	-	-	-	3.24	-	10.31	36.70	39	23	1.40	-	-	4.47 (0.10)
MP19 IX	3.29 (S)	0.88 (0.13)	-8.74 (0.18)	1.59 (0.12)	-	-	-	0.75 (0.57)	-	8.20 (0.31)	99.64	-	-	-	0.98	-	5.97 (0.60)
MP19 X	3.30 (S)	0.87 (0.13)	-8.74 (0.18)	1.59 (0.19)	-	-	-	0.78 (0.59)	-	8.25 (0.31)	100	-	-	-	0.98	-	6.12 (1.12)
MP19 XI	3.29 (S)	0.88 (0.08)	-8.74 (0.12)	1.69 (0.08)	-	-	-	0.67 (0.50)	-	8.03 (0.29)	99.80	-	-	-	0.20	-	8.90 (0.47)
MP19 XII <sup>a</sup>	3.90 (S)	0.83 (0.17)	-8.90 (0.19)	1.53 (0.18)	-	-	-	-0.61 (2.65)	-	6.25 (1.52)	99.10 (0.56)	-	-	-	0.90	-	3.79 (0.90)
MP19 XIII	1.27 (po+po?)	0.47	-9.27	1.06	-	-	-	2.48 (0.30)	-	9.55 (0.30)	98.29	-	-	-	1.71*	-	2.31 (0.78)
PI19 VIII	3.15 (S)	0.41 (0.14)	-9.45 (0.46)	0.88 (0.32)	-	-	-	2.18 (1.21)	-	9.81 (0.21)	100	-	-	-	-	-	5.60 (0.98)
P = 1.882 kbar, T = 597°C, fH <sub>2</sub> <sup>15</sup> = 0.5 bar, fS <sub>2</sub> <sup>h</sup>																	
MP14 I	1.59 (S)	0.47 (0.04)	-8.24 (0.12)	2.23 (0.09)	-	-	-	0.61 (0.49)	-	7.89 (0.14)	99.15 (0.52)	-	-	-	trace	0.85	3.59 (0.22)
MP14 II	3.98 (S)	0.43 (0.02)	-8.29 (0.07)	2.18 (0.06)	-	-	-	0.60 (0.29)	-	8.00 (0.09)	99.08	-	-	-	trace	0.92	6.00 (0.21)
MP14 III	6.04 (S)	0.31 (0.05)	-8.62 (0.19)	1.95 (0.14)	2.0629	46.20	1.27 (0.17)	1.42 (0.78)	8.37 (0.68)	8.85 (0.18)	97.90 (0.89)	-	-	-	1.08	1.02	8.31 (0.63)
MP14 IV	10.11 (S)	0.23 (0.03)	-8.98 (0.19)	2.00 (0.31)	2.0662	46.38	1.07 (0.14)	2.09 (0.37)	8.17 (0.07)	9.32 (0.12)	97.62	traces	-	-	1.38	1	12.09 (0.46)
MP14 V	1.90 (po+po?)	0.40 (0.05)	-8.38 (0.11)	2.03 (0.06)	2.0668	46.44	0.56 (0.12)	1.08 (0.30)	8.11 (0.12)	8.49 (0.30)	98.00 (1.25)	-	-	-	1.20 (0.22)	traces	3.45 (0.29)
MP14 VI <sup>13</sup>	3.60 (S)	0.57 (0.04)	-8.12 (0.02)	2.38 (0.03)	-	-	-	0.22 (0.19)	-	7.37 (0.09)	96.70 (0.59)	-	-	-	3.10	0.90	5.08 (0.22)
PI14 VIII	3.78 (S)	0.43 (0.03)	-8.32 (0.08)	2.14 (0.06)	-	-	-	0.67 (0.32)	-	8.09 (0.10)	99.08 (0.51)	-	-	-	traces	traces	6.00 (0.21)

<sup>1</sup> Amount of sulphur added to the charge either as elemental (S) or as pyrrhotite (Po5—Po7; see Table 3).

<sup>2</sup> Water activity calculated from Burnham (1979).

<sup>3</sup> fO<sub>2</sub> computed from equation (2).

<sup>4</sup> fO<sub>2</sub> referenced to the NNO buffer (Holloway *et al.*, 1992).

<sup>5</sup> Distance between inter-reticular planes 102 of hexagonal pyrrhotite determined by XRD.

<sup>6</sup> Iron-content of pyrrhotite (atomic) from Yund & Hall (1976) using d(102).

<sup>7</sup> Log fS<sub>2</sub> given by the pyrrhotite composition, using the calibration of Froese & Gunter (1976). Numbers in italics are for fO<sub>2</sub> > NNO (quenched Fe—S—O liquid).

<sup>8</sup> Log fS<sub>2</sub> calculated using MRK-EOS (see text). Numbers in italics are for charges whose total sulphur content computed from MRK-EOS calculation is significantly different from the sulphur content calculated from mass balance.

<sup>9</sup> Log fS<sub>2</sub> calculated from pyrrhotite composition referenced to the iron-troilite (FFS) buffer (see text).

<sup>10</sup> Log fS<sub>2</sub> given by the MRK-EOS calculation.

<sup>11</sup> fH<sub>2</sub> from membrane reading.

<sup>12</sup> fH<sub>2</sub> from NIPD sensor measurement.

<sup>13</sup> Magnetite-added charges.

Modal composition determined by mass balance. Phase abbreviations: GI, glass; PI, plagioclase; Px, pyroxene; Oz, quartz; Po, pyrrhotite; An, anhydrite; V, fluid phase.

1σ for GI, Po, An, which are not given in parentheses, are 0.56, 0.16 and 0.13, respectively.

Table 4: continued



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  $\mu\text{m}$  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 ( $\text{S}^{2-}$ ) or sulfate ( $\text{S}^{6+}$ ) (Richardson & Withers, 1950; Ricke, 1960; Schneider, 1970). The position of the SK $\alpha$  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 SK $\alpha$  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 Ancy 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  $f\text{O}_2$ , pyrrhotite may partially break down to an Fe–O–S liquid. It appeared that, indeed, for  $f\text{O}_2 > \text{NNO}$ , most quench 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  $f\text{S}_2$  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  $\mu\text{m}$ . 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  $f\text{O}_2 (> \text{NNO}+1.3)$ , 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 magnetite-doped 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  $\pm$  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  $H_2S$ ). A significant decrease in  $a_{H_2O}$  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  $a_{H_2O}$  slightly below 1, pyroxene is stable under reducing conditions for  $a_{H_2O}$  slightly below 1, and quartz crystallizes for  $a_{H_2O} \leq 0.85$ . Similarly, at 930°C, plagioclase is stable for  $a_{H_2O} \leq 0.75$  and quartz is stable for  $a_{H_2O} \leq 0.65$  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  $fO_2$  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  $fO_2 > NNO+1$ . 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  $fO_2$  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 ( $X_{H_2O_{fl}}$ ) 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  $X_{H_2O_{fl}}$  significantly lower than 0.2 are those for which the by-difference method yields  $H_2O$  melt content close to zero (e.g. charge MP15V, Table 4). At all temperatures, as long as the  $fO_2$  is below NNO+1,  $H_2S$  is the dominant sulphur-bearing species, and its mole fraction in the fluid ( $X_{H_2S_{fl}}$ ) 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  $H_2O$  and  $H_2S$ , other fluid species ( $H_2$ ,  $SO_2$ ,  $S_2$ ) amounting to no more than 0.01 mole fraction.  $SO_2$  becomes abundant at higher  $fO_2$  and its mole fraction ( $X_{SO_{fl}}$ ) may even exceed that of  $H_2S$  at 930 and 1000°C. At 930°C, an  $fO_2$  of NNO+1.4 is required to have  $X_{SO_{fl}} > X_{H_2S_{fl}}$ . At 1000°C, the same happens at slightly lower  $fO_2$ , that is around NNO+1. At 800°C, however,  $H_2S$  dominates over  $SO_2$ , 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),  $S_2$  makes up a significant proportion of sulphur-bearing species in the fluid—up to 0.3 of  $X_{S_{2fl}}$ .



Charges	$\Delta$ NNO <sup>1</sup>	$\Delta$ FFS <sup>2</sup>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sup>3</sup>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O <sup>4</sup>	S (ppm) <sup>5</sup>	log S
<i>P = 2.152 kbar, T = 785°C</i>												
MP15 I	-1.12 (0.10)	7.45 (0.21)	78.35 (0.91)	13.25 (0.37)	0.28 (0.10)	0.23 (0.10)	1.62 (0.13)	4.17 (0.21)	2.02 (0.14)	4.69 (0.43)	≤D	—
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)	0.25 (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 V <sup>6</sup>	-0.83	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)	1.88 (0.10)	5.54 (0.75)	≤D	—
MP15 VII <sup>7</sup>	-0.93	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)	≤D	—
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)	4.94 (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)	≤D	—
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
<i>P = 1.973 kbar, T = 788°C</i>												
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 (84)	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)	366 (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 VII <sup>7</sup>	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)	≤D	—
MP16 VIII	1.41 (0.09)	10.06 (0.30)	78.04 (0.50)	12.47 (0.20)	0.58 (0.10)	0.23 (0.10)	1.67 (0.10)	2.96 (0.10)	3.97 (0.11)	5.71 (0.52)	≤D	—
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)	≤D	—
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
<i>P = 1.976 kbar, T = 811°C</i>												
MP17 I	1.83 (0.20)	—	80.01 (0.73)	12.06 (0.30)	0.10 (0.10)	0.37 (0.10)	1.41 (0.12)	3.88 (0.10)	2.15 (0.12)	5.88 (0.39)	125 (16)	2.1
MP17 II	1.83 (0.20)	—	79.93 (0.83)	12.13 (0.14)	0.08 (0.10)	0.40 (0.10)	1.21 (0.11)	3.83 (0.19)	2.32 (0.10)	5.86 (0.39)	263 (11)	2.42
MP17 III	1.83 (0.20)	—	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)	—	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)	—	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 VII <sup>7</sup>	1.83 (0.20)	—	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 <sup>8</sup>	1.83 (0.20)	—	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)	≤D	—
PIN 17 VI	1.79 (0.05)	—	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
<i>P = 2.054 kbar, T = 890°C</i>												
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 (0.10)	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)	—	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	$\Delta\text{NNO}^1$	$\Delta\text{FFS}^2$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{FeO}^3$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}^4$	S (ppm) <sup>5</sup>	log S
<i>P = 2.257 kbar, T = 933°C</i>												
MP3 I	2.42 (0.29)	—	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)	969 (19)	2.99
MP3 II	2.30 (0.29)	—	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)	—	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
<i>P = 1.966 kbar, T = 932°C</i>												
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)	≤D	—
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
<i>P = 2.116 kbar, T = 936°C</i>												
MP9 I	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
MP9 III	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)	≤D	—
MP9 V	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
<i>P = 2.013 kbar, T = 933°C</i>												
MP10 I	-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)	1.99 (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 <sup>6</sup>	-1.18 (0.14)	5.79 (0.09)	76.76 (0.76)	13.37 (0.23)	1.35 (0.22)	0.31 (0.10)	1.99 (0.10)	4.15 (0.15)	2.07 (0.10)	5.90 (0.55)	≤D	—
MP10 VI <sup>6</sup>	-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)	≤D	—
<i>P = 2.202 kbar, T = 935°C</i>												
MP11 I	-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 <sup>6</sup>	-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)	≤D	—
MP11 VI <sup>6</sup>	-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)	≤D	—
<i>P = 2.003 kbar, T = 934°C</i>												
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)	6.88 (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)	≤D	—
MP6 V <sup>6</sup>	-0.24 (0.08)	6.13 (0.07)	76.49 (0.63)	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)	≤D	—
MP6 VI <sup>6</sup>	-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)	≤D	—

Charges	$\Delta\text{NNO}^1$	$\Delta\text{FFS}^2$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{FeO}^3$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}^4$	S (ppm) <sup>5</sup>	log S
<i>P = 2.082 kbar, T = 834°C</i>												
MP12 I	0.40 (0.15)	9.35 (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)	1.58
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 (0.28)	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
<i>P = 1.960 kbar, T = 838°C</i>												
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)	≤D	—
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)	≤D	—
<i>P = 2.007 kbar, T = 830°C</i>												
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)	2.63
MP13 III	1.23 (0.08)	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 (0.08)	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
<i>P = 2.188 kbar, T = 894°C</i>												
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)	2.46
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 <sup>6</sup>	-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
<i>P = 2.058 kbar, T = 898°C</i>												
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)	≤D	—
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)	≤D	—
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)	≤D	—
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)	≤D	—
MP19 X	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)	≤D	—
MP19 XI	1.59 (0.19)	8.25 (0.31)	76.28 (0.80)	13.47 (0.38)	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 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)	1.89 (0.10)	4.65 (0.37)	145 (21)	2.16
MP19 XIII <sup>6</sup>	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)	≤D	—
PIN19 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)	≤D	—

Charges	$\Delta\text{NNO}^1$	$\Delta\text{FFS}^2$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{FeO}^3$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}^4$	$\text{S (ppm)}^5$	$\log \text{S}$
<i>P = 1.952 kbar, T = 987°C</i>												
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	1.86 (0.14)	8.85 (0.18)	77.60 (0.83)	13.90 (0.36)	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 (0.46)	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 <sup>6</sup>	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)	399 (88)	2.60
MP14 VII	2.36 (0.03)	10.88 (0.09)	76.08 (0.88)	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)	646 (76)	2.64
PIN14 VIII	2.14 (0.06)	—	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 parentheses indicate 1 standard deviation of replicate analyses.

<sup>1</sup> $\text{fO}_2$  normalized to the NNO buffer (see Table 4).

<sup>2</sup> $\text{fS}_2$  normalized to the FFS buffer (see Table 4).

<sup>3</sup>Total Fe, given as FeO.

<sup>4</sup>Water content determined using the by-difference method.

<sup>5</sup>Total sulphur content. D is the detection limit (80 ppm).

<sup>6</sup>Pyrrhotite-added charges.

<sup>7</sup>Magnetite-added charges.

Table 5: continued

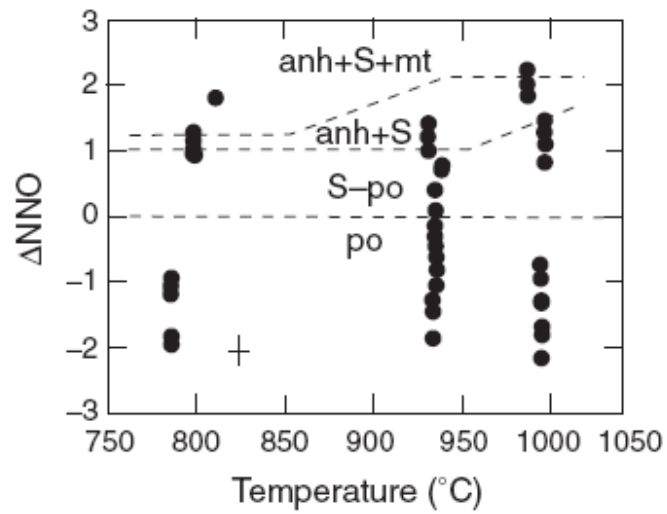


Fig. 3. Stability domains of sulphur-bearing phases as a function of  $fO_2$  and temperature. Phase abbreviations: anh, anhydrite; po, pyrrhotite; S, immiscible Fe–S–O liquid; mt, magnetite.

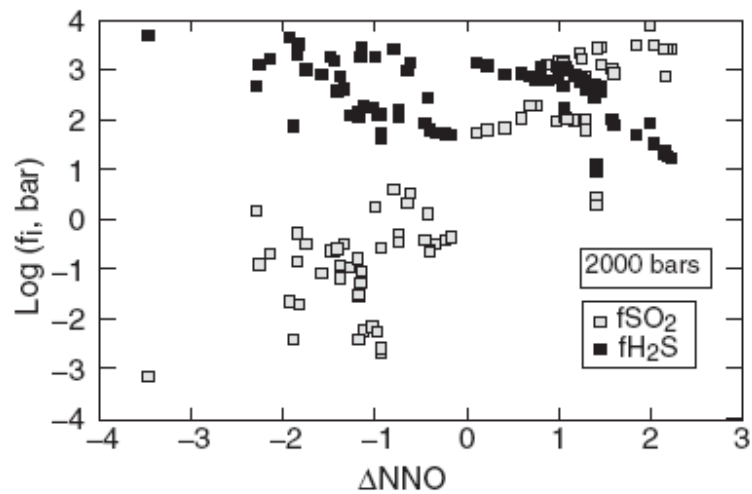


Fig. 4. Fugacities of  $H_2S$  and  $SO_2$  fluid species versus the corresponding  $fO_2$  for all charges for which  $fS_2$  could be determined, calculated using equations (7) and (8) (see Table 4 and text). The increase in  $fO_2$  favours  $SO_2$  relative to  $H_2S$  species in the fluid phase. 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  $fH_2S$  and  $fSO_2$  occurs at around

NNO+1. In fact, it is only at  $fO_2 > \text{NNO}+2$  and at 930 and 1000°C that  $fSO_2$  is several orders of magnitude larger than  $fH_2S$ .

### **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 SiO<sub>2</sub> contents predominantly in the range 76–78 wt % and Al<sub>2</sub>O<sub>3</sub> = 13 ± 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 K<sub>2</sub>O concentrations (Tables 4 and 5). In particular, at 800°C, a continuous increase in K<sub>2</sub>O arises as a result of the dominantly incompatible behaviour of this element (see MP16 series, Table 5). At all values of  $fS_2$ ,  $fO_2$  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  $fO_2 < \text{NNO}+1$  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  $T$ ,  $fO_2$  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  $fO_2 > \text{NNO}+1$  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  $fO_2$ .

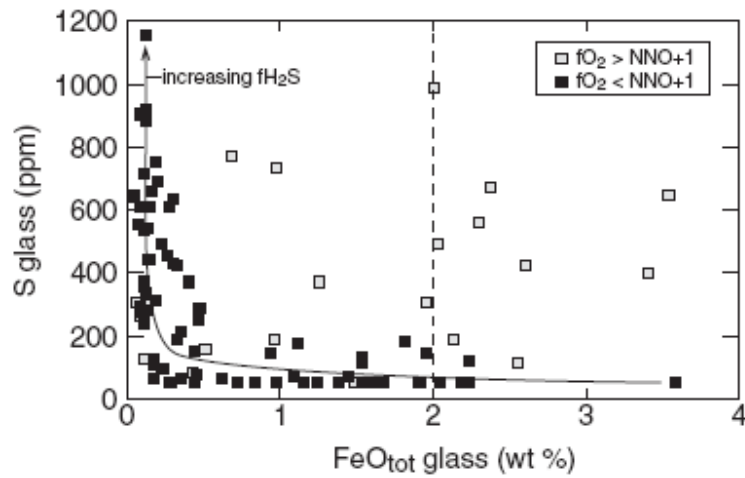


Fig. 5.  $\text{FeO}_{\text{tot}}$  vs melt-sulphur content of experimental glasses at all investigated temperatures for reduced and oxidized conditions. The latter correspond in general to anhydrite-bearing charges. Note the general leftward displacement relative to the starting composition (dashed 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  $f_{\text{H}_2\text{S}}$  (and temperature).

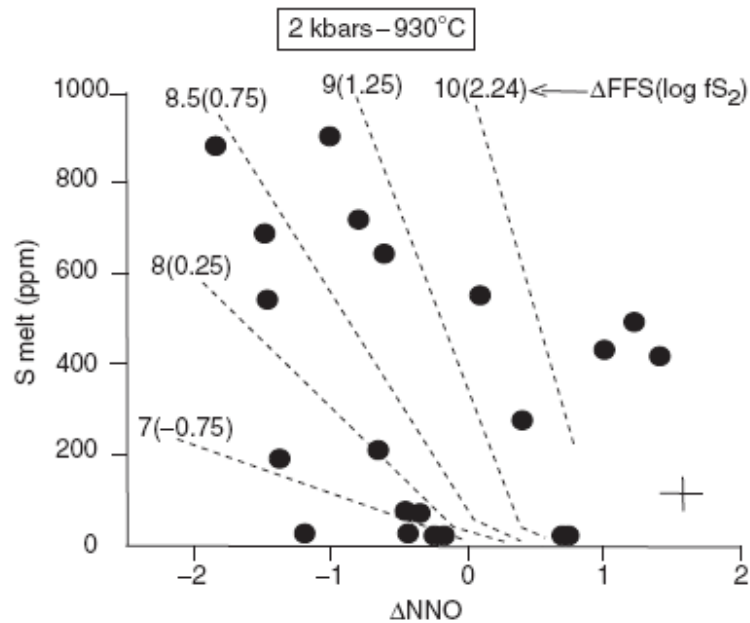


Fig. 6. Sulphur concentration in glass as a function of  $f_{\text{O}_2}$  and  $f_{\text{S}_2}$  at  $930^\circ\text{C}$ . Dotted lines are contours of iso- $f_{\text{S}_2}$ , labelled with  $\Delta\text{FFS}$  in bold and corresponding  $f_{\text{S}_2}$  in parentheses.

### Solubility of sulphur as a function of intensive parameters

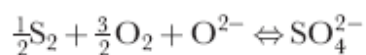
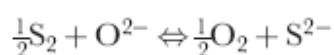
The interrelationships between melt sulphur content,  $f_{\text{S}_2}$  and  $f_{\text{O}_2}$  at  $930^\circ\text{C}$ , where most of the data were obtained, are shown in Fig. 6. The solubility of sulphur is clearly a function of both  $f_{\text{O}_2}$  and  $f_{\text{S}_2}$ . Below NNO+1, for a fixed  $f_{\text{O}_2}$ , the solubility of sulphur



increases with  $fS_2$ . 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  $fO_2$  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),  $fS_2$ ,  $fH_2S$ ,  $fSO_2$  for various  $fO_2$  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  $fO_2$  ( $< NNO + 1$ ). As a rule, an increase in  $fO_2$  leads to a decrease in Smelt at fixed  $fS_2$ . This effect is most apparent at 800 and 930°C. Exceptions to this behaviour concern experiments performed at 930 and 1000°C in the  $fO_2$  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  $fS_2$  (Fig. 7), even under high  $fO_2$ , where  $SO_2$  is the dominant sulphur-bearing species in the fluid. In contrast, Smelt correlates strongly with  $fH_2S$ . 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  $fO_2$  of NNO-1.4. At all temperatures, Smelt exceeds 200 ppm once  $fH_2S$  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  $SiO_2$ ,  $Al_2O_3$ , etc.) is used in place of concentration (Smelt), the correlations defined with  $fH_2S$  appear to be linear at all temperatures (Fig. 8). Under high  $fO_2$ , 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  $fO_2$ . The scatter is because of the difficulties in precisely determining  $fS_2$  under high  $fO_2$  conditions.

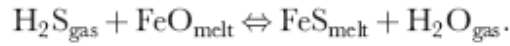
### Sulphur speciation in hydrous rhyolite melt

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) :



where  $S^{2-}$  and  $SO_4^{2-}$  refer respectively to sulphide and sulphate species dissolved in the melt and  $O^{2-}$  represents oxygen anions in the silicate melt. A quantitative assessment of reactions (12) and (13) has been so far limited by our inability to rigorously evaluate the proportion, as well as the activity–composition relationships, of  $O^{2-}$  in complex hydrous aluminosilicate melts such as magmatic liquids. The strong correlation existing between Fe and Smelt in both natural and experimental anhydrous glasses suggests that  $S^{2-}$  exchanges preferentially with  $O^{2-}$  bound to ferrous iron in melts under low  $fO_2$ , 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)



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 :

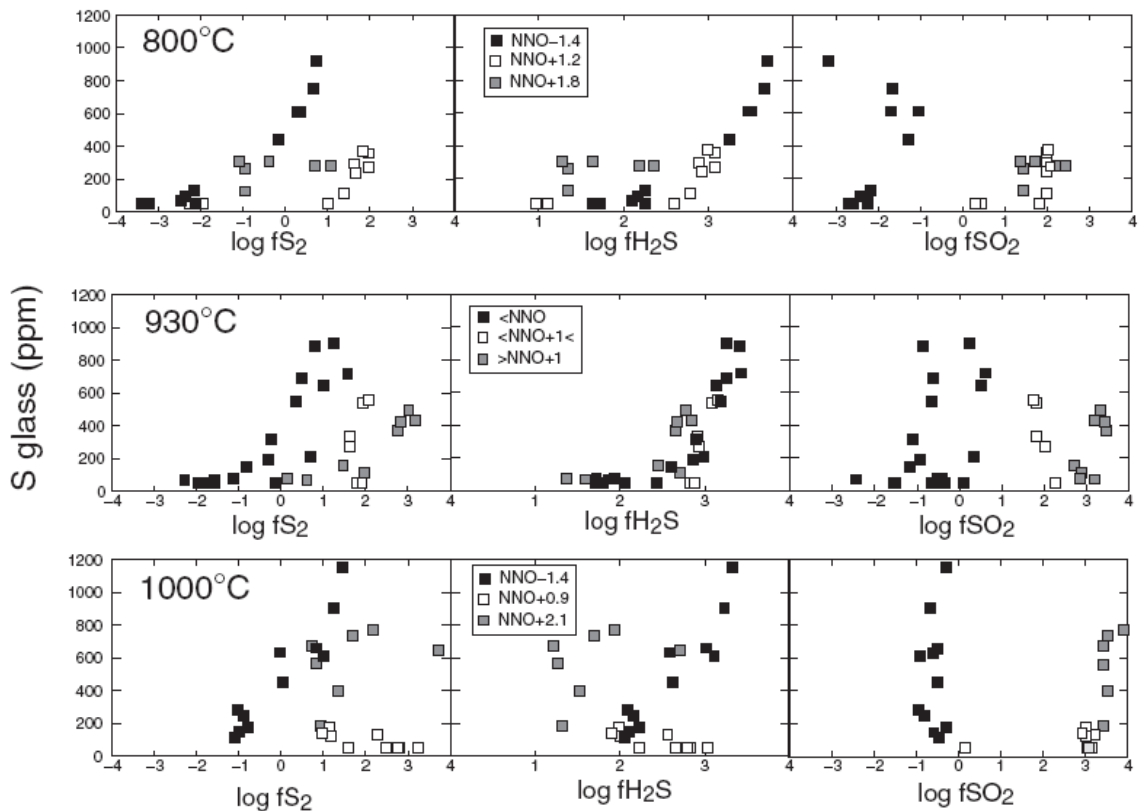
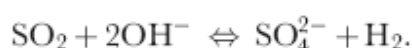


Fig. 7. Relationships between melt-sulphur concentration ( $S_{melt}$ ), and  $fS_2$ ,  $fH_2S$ ,  $fSO_2$  for various  $fO_2$ , at the three investigated temperatures. For clarity at 930°C, the data have been grouped into three  $fO_2$  intervals, each broadly corresponding to a different type of S-bearing phase (as  $fO_2$  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  $f_{O_2}$ . The very fact that similar, or even higher, sulphur concentrations compared with those achieved in the present work have been reported in either H<sub>2</sub>O bearing (Keppler, 1999) or H<sub>2</sub>O-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  $f_{H_2S}$  and  $S_{melt}$  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 :



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<sub>2</sub>S and SO<sub>2</sub> 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<sub>2</sub>S and SO<sub>2</sub> dissolution reactions. The extent of each dissolution reaction is controlled by the magnitude of both H<sub>2</sub>S and SO<sub>2</sub> fugacities in the system. We thus have

$$X_S = X_{reduced} + X_{oxidized}$$

where  $X_{reduced}$  and  $X_{oxidized}$  represent the mole fractions of sulphur species dissolved under the reduced and oxidized forms, hereafter referred to as  $X_{H_2S_{melt}}$  and  $X_{SO_2_{melt}}$ , 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) :

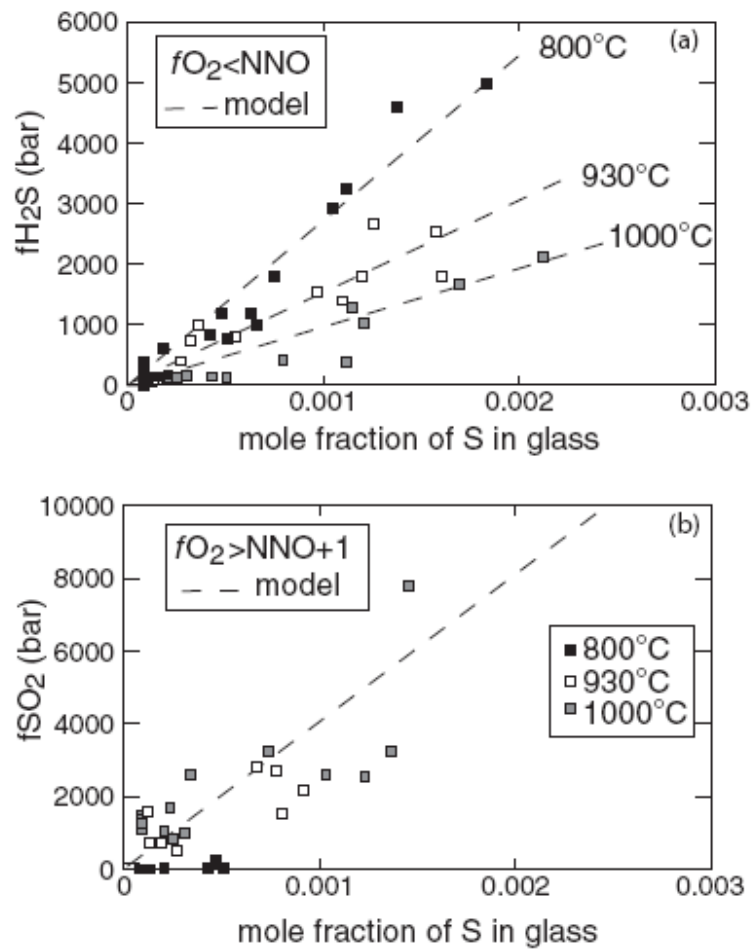


Fig. 8. Xi–fi relationships. (a) Under reduced conditions ( $\Delta\text{NNO} \leq 0$ ), where the dominant S-bearing species in the fluid is  $\text{H}_2\text{S}$ . (b) Under oxidizing conditions ( $\Delta\text{NNO} \geq 1.0$ ), where the dominant S-bearing species in the fluid is  $\text{SO}_2$ . Dashed curves are sulphur solubilities calculated using the thermodynamic model developed in the text.



and



whose equilibrium constants are

$$K_{18} = f\text{H}_2\text{S}_{\text{fluid}} / a_{\text{H}_2\text{S}_{\text{melt}}}$$

And

$$K_{19} = f\text{SO}_2_{\text{fluid}} / a_{\text{SO}_2_{\text{melt}}}$$

Assuming that  $a_i = X_i$ , then

$$K_{18} = f\text{H}_2\text{S}_{\text{fluid}} / X_{\text{H}_2\text{S}_{\text{melt}}}$$

And

$$K_{19} = f\text{SO}_2_{\text{fluid}} / X_{\text{SO}_2_{\text{melt}}}$$

To evaluate the above reactions, we proceed by considering separately charges at  $f\text{O}_2 < \text{NNO}$ , in which  $\text{H}_2\text{S}$  is the dominant sulphur-bearing species in the fluid, and then charges at  $f\text{O}_2 > \text{NNO}+1.5$ , in which  $\text{SO}_2$  is the dominant sulphur-bearing species. Under those conditions, the right-hand side of equation (17) simplifies to either  $X_{\text{H}_2\text{S}_{\text{melt}}}$  ( $f\text{O}_2 < \text{NNO}$ ) or  $X_{\text{SO}_2_{\text{melt}}}$  ( $f\text{O}_2 > \text{NNO}+1.5$ ).

#### *H<sub>2</sub>S dissolution*

At all temperatures and  $f\text{O}_2 \leq \text{NNO}$ , the relationships between  $X_S$  and  $f\text{H}_2\text{S}$  is within error linear (Fig. 8) and, thus, the solubility of  $\text{H}_2\text{S}$  in rhyolite melt obeys Henry's Law, i.e. at fixed  $P$  and  $T$ ,

$$f\text{H}_2\text{S} = X_{\text{H}_2\text{S}_{\text{melt}}} k_{\text{H}}$$

where  $k_{\text{H}}$  is the Henry's Law constant and is obviously equivalent to  $K_{18}$ . As shown in Fig. 8, the  $f\text{H}_2\text{S}-X_{\text{H}_2\text{S}_{\text{melt}}}$  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) :

$$\ln(f\text{H}_2\text{S}/X_{\text{H}_2\text{S}_{\text{melt}}}) = \ln k_{\text{H}(\text{Pr},\text{Tr})} + (\Delta H/R)(1/T - 1/T_r) + (V_{\text{H}_2\text{S}}(P - P_r))/RT \quad (21)$$

which, upon rearrangement, gives

$$X_{\text{H}_2\text{S melt}} = f_{\text{H}_2\text{S}} / k_{\text{H}(\text{Pr}, T_r)} \exp[-(\Delta H/R)(1/T - 1/T_r) - (V_{\text{H}_2\text{S}}(P - P_r))/RT] \quad (22)$$

in which  $T_r$  and  $P_r$  are the reference temperature and pressure, respectively,  $\Delta H$  is the heat of  $\text{H}_2\text{S}$  dissolution into the melt,  $R$  is the gas constant and  $V_{\text{H}_2\text{S}}$  the partial molar volume of  $\text{H}_2\text{S}$  melt species.  $T_r$  and  $P_r$  were, respectively, chosen to be  $930^\circ\text{C}$ , 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  $\text{H}_2\text{O}$  and  $\text{CO}_2$  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  $f\text{O}_2 \leq \text{NNO}-1.4$  gives the following values:  $k_{\text{H},930^\circ\text{C}} = 0.801 \cdot 10^6$  bar,  $\Delta H = 54.85$  kJ/mol and  $V_{\text{H}_2\text{S}} = 26.03$  cm<sup>3</sup>/mol. The Henry constant is similar to that found for  $\text{CO}_2$  dissolution in rhyolite melt ( $1.106 \cdot 10^6$  bar, Fogel & Rutherford, 1990). However, contrary to both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  species, the enthalpy of  $\text{H}_2\text{S}$  solution is positive in sign, which simply means that, at a given  $f_{\text{H}_2\text{S}}$ , temperature increases the solubility of sulphur. Although the partial molar volume of  $\text{H}_2\text{S}$  in rhyolite melt appears to be similar to that of  $\text{H}_2\text{O}$ , we stress that our data cover a range in  $f_{\text{H}_2\text{S}}$  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  $f_{\text{H}_2\text{S}}$ , i.e. where  $V_{\text{H}_2\text{S}}$  plays a negligible role in equation (22).

#### *SO<sub>2</sub> dissolution*

At  $f\text{O}_2 > \text{NNO}+1.5$ , because of the difficulties in retrieving fluid species fugacities in the oxidized range, the dispersion in the  $X_{\text{S}}-f\text{SO}_2$  (Fig. 8) plot is much more severe than for  $\text{H}_2\text{S}$ , and it can only be assumed that sulphur dissolution at high  $f\text{O}_2$  also follows Henry's Law. Linear regression of the data obtained at an  $f\text{O}_2 > \text{NNO}+1.5$  gives the following value for the Henry constant:  $K_{\text{SO}_2} = K_{19} = 4.13 \times 10^6$  bar.

#### *Sources of error*

The calculated versus measured sulphur mole fractions for various  $f_{\text{H}_2\text{S}}$  are shown in Fig. 9 for charges held at an  $f\text{O}_2$  of  $\text{NNO}-1.4$  or lower.

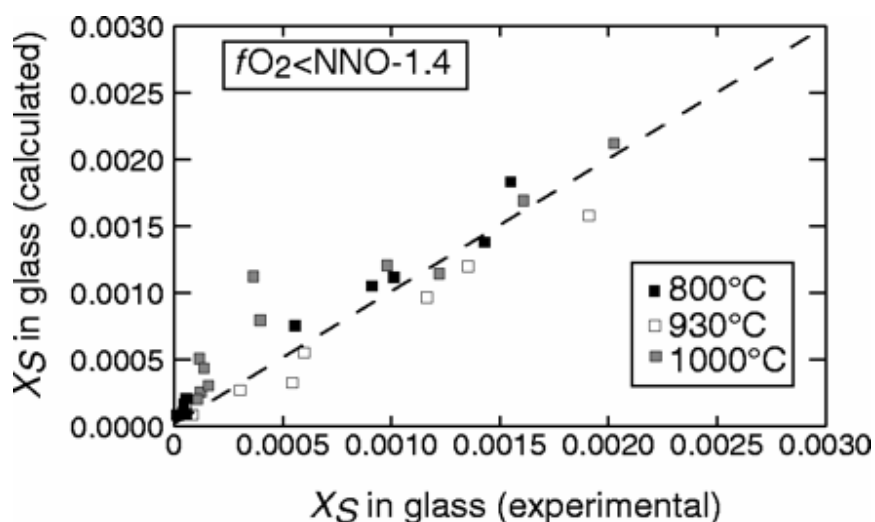


Fig. 9. Experimental versus calculated mole fractions of sulphur for charges at an  $fO_2$  of below NNO–1.4, using the thermodynamic model developed in the text.

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  $H_2S$  form, one major source of error that affects the derivation of thermodynamic parameters comes from the calculated values of  $fH_2S$ . In experimental studies designed to calibrate  $H_2O$  or  $CO_2$  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  $H_2S$  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  $H_2S$  fluid (or  $SO_2$ ) 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  $H_2S$  and  $SO_2$ -related species (see below also). The data suggest, however, that, under low  $fO_2$  and in iron-poor silicate melts,  $H_2S$  dissolution may occur through formation of HS-like complexes, and that at high  $fO_2$ ,  $SO_2$  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  $S^{2-}$ -associated with  $Fe^{2+}$  from those linked to  $H^+$  cations.

*Solubility minimum and speciation*

Despite these caveats, the thermodynamic properties derived above for H<sub>2</sub>S and SO<sub>2</sub> dissolution in hydrous rhyolite melt can be combined to compute the behaviour of total dissolved sulphur, X<sub>S</sub> (= X<sub>H<sub>2</sub>S</sub>melt + X<sub>SO<sub>2</sub></sub>melt, as defined above in equations (18)–(22)) under various T and fO<sub>2</sub> conditions. An Excel spreadsheet, which calculates the fugacities of S<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub> and H<sub>2</sub>O, species at fixed P, T, S<sub>melt</sub> and fO<sub>2</sub>, 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<sub>2</sub> within the fO<sub>2</sub> 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<sub>2</sub>. At all fS<sub>2</sub>, 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).

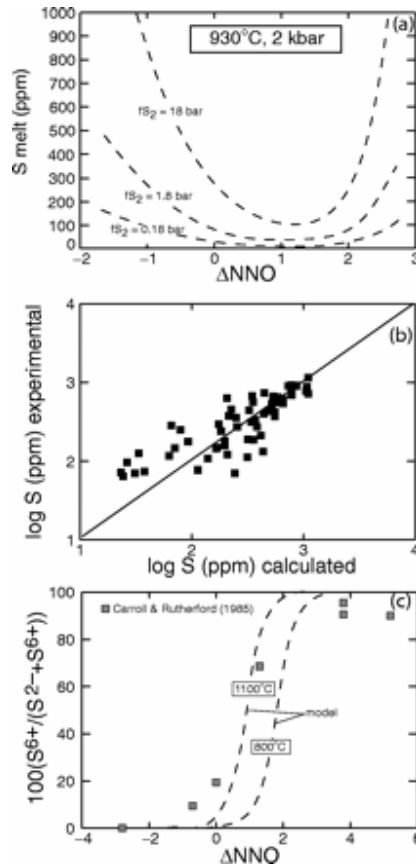


Fig. 10. Application of the thermodynamic model. (a) Calculated total dissolved sulphur (S<sub>ppm</sub>) against fO<sub>2</sub> (ΔNNO) at 930°C and for an fS<sub>2</sub> of ΔFFS+7 (log fS<sub>2</sub> = –0.75), ΔFFS+8 (log fS<sub>2</sub> = 0.24), and ΔFFS+9 (log fS<sub>2</sub> = 1.24). All calculations have been performed with fH<sub>2</sub>O = 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<sub>2</sub> could be estimated. (c) Calculated proportions of S<sup>6+</sup> at 1100 and 800°C, as a function of ΔNNO. 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  $H_2S$  and  $SO_2$  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  $fO_2$ , the  $fS_2$  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  $fO_2$ . 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**

The application of the thermodynamic model presented above requires the determination of both  $fH_2S$  and  $fSO_2$ . These two quantities 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  $fO_2$  below NNO+1.5, we have restricted the fitting procedure to charges lying below this  $fO_2$  threshold: this has the advantage that only the charges for which  $fS_2$  is best known are taken into account. Considering the different effects of  $fO_2$ ,  $fS_2$  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 only glasses with sulphur-content higher than the detection limit:

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

or

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

As with  $f\text{O}_2$ , referencing  $f\text{S}_2$  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  $f\text{O}_2$  of the system, equation (24) allows calculation of  $f\text{S}_2$ .

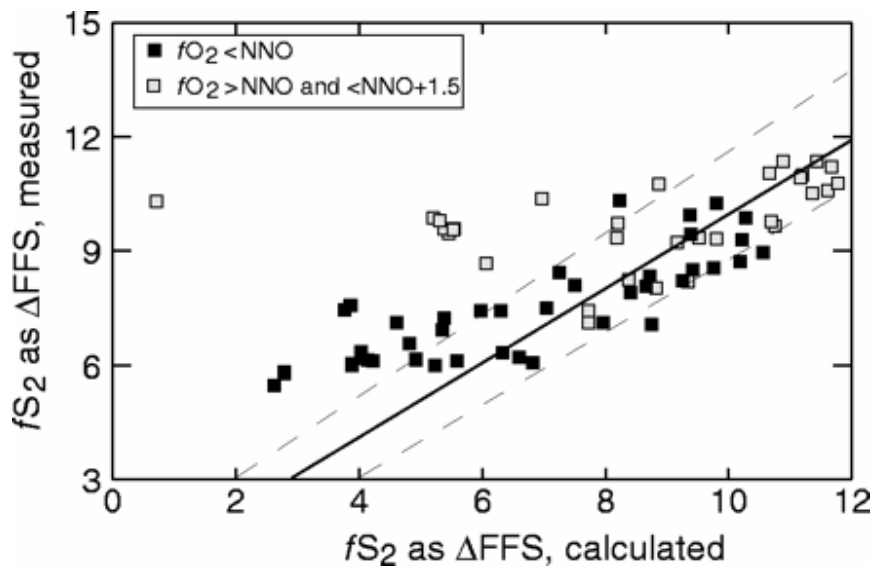


Fig. 11. Comparison between measured and calculated sulphur fugacities using the empirical model [equation (24)]. See text for explanation.

Figure 11 shows model performances for all charges held at an  $fO_2 < NNO+1.5$ . Equation (24) reproduces observed values to within 1 log units at  $\Delta FFS > 6$ , apart from a few charges in the  $fO_2$  range NNO to NNO+1.5. At lower  $\Delta FFS$ , 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 equation (24) 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

### Fluid and melt-sulphur 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  $fO_2$  profoundly affects the sulphur solubility. The more soluble sulphur species appear to be  $H_2S$  and  $SO_2$ . 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  $H_2O$  and  $CO_2$  volatiles in silicate melts, considering the additive effects of two basic dissolution reactions involving either  $H_2S$  or  $SO_2$  fluid species. At fixed  $P$  and  $T$ , Henry's Law is obeyed for  $H_2S$  and possibly  $SO_2$  species, up to fugacities of 5 and 8 kbar, respectively. At equal fugacities,  $H_2S$  appears to be more soluble than  $SO_2$ , 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  $H_2S$  and  $SO_2$  fluid species. The MRK model predicts that  $SO_2$  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  $SO_2$  or  $H_2S$  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  $H_2S$  and  $SO_2$  were to have identical Henry's Law constants, because the fugacities of pure  $H_2S$  or  $SO_2$  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  $H_2S$  and  $SO_2$  by performing experiments with pure  $H_2S$  and  $SO_2$  fluids. The minimum in solubility appears to lie in the redox range where  $H_2S$  and  $SO_2$  fugacities in the fluid are approximately equal (Fig. 4), and MRK calculations show that  $S_2$  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.

### The effect of iron

The 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 not been 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 quasi-constant  $fS_2$  and  $fO_2$ , 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 H<sub>2</sub>O and CO<sub>2</sub> 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<sup>2-</sup> 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  $\Delta H$  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<sub>2</sub>S—a behaviour at variance with that of both CO<sub>2</sub> and H<sub>2</sub>O, at least in the low-pressure range, whereas SO<sub>2</sub> 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. H<sub>2</sub>S, SO<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>) and anion groups' solubility (e.g. HS<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>). 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<sup>2-</sup> or HS<sup>-</sup> species over molecular H<sub>2</sub>S in rhyolite melts, i.e. that, essentially, all dissolved H<sub>2</sub>S reacts with the aluminosilicate melt framework to yield HS<sup>-</sup> units. Our data favor a reaction such as (15), in which exchange between gaseous H<sub>2</sub>S and hydroxyl groups is the dominant mechanism of sulphur incorporation into hydrous and iron-poor silicate melts. At high *f*O<sub>2</sub>, it is not yet possible to decipher the details of the solution reaction but if all SO<sub>2</sub> reacts with hydroxyl groups to form SO<sub>4</sub><sup>2-</sup> units, then it might be expected that there is a positive effect of temperature on solubility under oxidizing conditions as well. Thus, compared with H<sub>2</sub>O and CO<sub>2</sub>, 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<sub>2</sub>O and CO<sub>2</sub> 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 *f*O<sub>2</sub> and *f*S<sub>2</sub>. 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 *f*O<sub>2</sub> buffered by the quartz–fayalite–magnetite solid buffer (NNO–0.7). In contrast, at high *f*O<sub>2</sub>, 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 *a*SiO<sub>2</sub> or *f*S<sub>2</sub>, 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 *f*S<sub>2</sub>.

**The effect of pressure**  
The last parameter of interest is pressure. Recent experimental studies have confirmed the earlier findings of Wendlant (1982) that pressure decreases the sulphur solubility in dry 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  $S_{\text{melt}}$  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  $f_{\text{H}_2\text{S}}$ . By analogy with what happens with water, as total pressure decreases,  $f_{\text{H}_2\text{S}}$  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 %  $\text{SiO}_2$ ) equilibrated at 1 bar and 1250°C, with an H–C–S–O gas mixture over an  $f_{\text{O}_2}$  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  $\text{O}^{2-}$  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 ( $P$ ,  $T$ ,  $f_{\text{O}_2}$ ) in addition to  $f_{\text{S}_2}$  and the melt-sulphur concentration. These include the Bishop Tuff (0.76 Ma), Krakatau (1885), Katmai (1912), Mt St Helens (1980) and El Chichón (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 melt-sulphur content of 100 ppm is assumed, then the calculated  $\Delta\text{FFS}$  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  $f_{\text{O}_2}$  and  $f_{\text{S}_2}$  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  $f_{\text{S}_2}$  was measured either by the pyrrhotite ( $f_{\text{O}_2} < \text{NNO}+1$ ) or by the fluid phase ( $f_{\text{O}_2} > \text{NNO}+1.5$ ) compositions, using for the latter an MRK equation of state.

(2) At  $fO_2 < NNO+1$  and temperatures of  $<1000^\circ\text{C}$ , the addition of iron to a sulphur-bearing 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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