

# Experimental and Thermodynamic Constraints on the Sulphur Yield of Peralkaline and Metaluminous Silicic Flood Eruptions

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Many basaltic flood provinces are characterized by the existence of voluminous amounts of silicic magmas, yet the role of the silicic component in sulphur emissions associated with trap activity remains poorly known. We have performed experiments and theoretical calculations to address this issue. The melt sulphur content and fluid/melt partitioning at saturation with either sulphide or sulphate or both have been experimentally determined in three peralkaline rhyolites, which are a major component of some flood provinces. Experiments were performed at 150 MPa, 800–900°C,  $fO_2$  in the range  $NNO - 2$  to  $NNO + 3$  and under water-rich conditions. The sulphur content is strongly dependent on the peralkalinity of the melt, in addition to  $fO_2$ , and reaches 1000 ppm at  $NNO + 1$  in the most strongly peralkaline composition at 800°C. At all values of  $fO_2$ , peralkaline melts can carry 5–20 times more sulphur than their metaluminous equivalents. Mildly peralkaline compositions show little variation in fluid/melt sulphur partitioning with changing  $fO_2$  ( $D_S \approx 270$ ). In the most peralkaline melt,  $D_S$  rises sharply at  $fO_2 > NNO + 1$  to values of  $>500$ . The partition coefficient increases steadily for  $S_{bulk}$  between 1 and 6 wt % but remains about constant for  $S_{bulk}$  between 0.5 and 1 wt %. At bulk sulphur contents lower than 4 wt %, a temperature increase from 800 to 900°C decreases  $D_S$  by  $\sim 10\%$ . These results, along with (1) thermodynamic calculations on the behaviour of sulphur during the crystallization of basalt and partial melting of the crust and (2) recent experimental constraints on sulphur solubility in metaluminous rhyolites, show that basalt fractionation can produce rhyolitic magmas having much more sulphur than rhyolites derived from crustal anatexis. In particular, hot and dry metaluminous silicic magmas produced by melting of dehydrated lower crust are virtually devoid of

sulphur. In contrast, peralkaline rhyolites formed by crystal fractionation of alkali basalt can concentrate up to 90% of the original sulphur content of the parental magmas, especially when the basalt is  $CO_2$ -rich. On this basis, we estimate the amounts of sulphur potentially released to the atmosphere by the silicic component of flood eruptive sequences. The peralkaline Ethiopian and Deccan rhyolites could have produced  $\sim 10^{17}$  and  $\sim 10^{18}$  g of S, respectively, which are comparable amounts to published estimates for the basaltic activity of each province. In contrast, despite similar erupted volumes, the metaluminous Paraná–Etendeka silicic eruptives could have injected only  $4.6 \times 10^{15}$  g of S in the atmosphere. Peralkaline flood sequences may thus have greater environmental effects than those of metaluminous affinity, in agreement with evidence available from mass extinctions and oceanic anoxic events.

KEY WORDS: silicic flood eruptions; sulphur; experiment; Ethiopia; Deccan

## INTRODUCTION

A detailed understanding of the solubility of sulphur in silicate melts is important for many geological processes (O'Neill & Mavrogenes, 2002): the origin of magmatic sulphide ores, the geochemical behaviour of the chalcophile trace elements, including the platinum group elements and the Re–Os isotopic system and their use as tracers of core–mantle and crust–mantle differentiation in the Earth and other planets or asteroids (e.g. Kracher &

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Wasson, 1982; Jana & Walker, 1997; Chabot, 2004). Sulphur solubility along with melt–vapour partitioning also determines sulphur degassing during volcanic activity and the potential effects on climate variability.

Most studies of sulphur solubility, cited by Carroll & Webster (1994), O'Neill & Mavrogenes (2002) and Jugo *et al.* (2005), have focused on mafic and intermediate melt compositions. Our understanding of S behaviour in silicic magmas is more restricted and comes mainly from work on Fe-poor, metaluminous compositions [mol.  $(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}) > \text{Al}_2\text{O}_3 > (\text{Na}_2\text{O} + \text{K}_2\text{O})$ ], of the type commonly associated with volcanic arcs (Carroll & Rutherford, 1985; Luhr, 1990; Scaillet *et al.*, 1998; Keppler, 1999; Scaillet & Evans, 1999; Clemente *et al.*, 2004; Costa *et al.*, 2004). Such compositions are not directly applicable to the magmatism of continental extensional zones, where the rhyolites tend to be alkali- and Fe-rich and either metaluminous or peralkaline [mol.  $(\text{Na}_2\text{O} + \text{K}_2\text{O}) > \text{Al}_2\text{O}_3$ ] (Macdonald *et al.*, 1992; King *et al.*, 1997). The alkali/alumina balance of silicate melts is known to profoundly affect their geochemical and physical behaviour (Mysen, 1988). Most notable among those effects are the increase in  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox ratio (Gwinn & Hess, 1989; Moore *et al.*, 1995; Gaillard *et al.*, 2001) and water solubility (Dingwell *et al.*, 1997), and the decrease of viscosity (Scarfe, 1977; Baker & Vaillancourt, 1995; Dingwell *et al.*, 1998) and liquidus temperatures (Bailey & Schairer, 1966) as peralkalinity increases. These important differences imply that insight gained from the study of sulphur in metaluminous silicate melts is of little help in anticipating its behaviour in peralkaline rhyolites.

Although many flood basalt provinces seem to be dominated by basaltic lavas, several recent studies have emphasized that some have significant volumes of associated silicic rocks (Bellieni *et al.*, 1986; Harris & Erlank, 1992; Ewart *et al.*, 1998, 2004; Ayalew *et al.*, 2002; Bryan *et al.*, 2002; Peccerillo *et al.*, 2003). The objective of the present study is to evaluate the sulphur yield potentially delivered to the atmosphere by silicic flood eruptions. Given that peralkaline rhyolites can largely dominate over metaluminous types in some silicic provinces (Ayalew *et al.*, 2002), we currently lack the fundamental information on which to base any such evaluation. We have, therefore, performed melt solubility and fluid/melt partitioning experiments for sulphur in peralkaline rhyolites from the Kenya Rift Valley, which broadly typify the felsic end-member of bimodal associations in rift-related settings (Bellieni *et al.*, 1986; Harris & Erlank, 1992; Ewart *et al.*, 1998, 2004; Ayalew *et al.*, 2002; Bryan *et al.*, 2002; Peccerillo *et al.*, 2003). We combine these data with thermodynamic and mass-balance calculations to evaluate the sulphur contents of potential sources of felsic magmas associated with flood basalts, considering two end-member cases for the origin of the silicic

end-member: fractional crystallization of flood basalt and partial melting of dehydrated lower crust. We show that the attainment of peralkaline conditions dramatically increases the sulphur-carrying capacity of rhyolite magmas. We then estimate the sulphur yields of some silicic flood sequences. The results appear to be significant for the current debate on the volcanic origin of some of the main mass extinctions (e.g. Wignall, 2001; Morgan *et al.*, 2004).

## EXPERIMENTAL AND ANALYTICAL TECHNIQUES

We have performed sulphur solubility and fluid/melt partitioning experiments on three well-characterized, peralkaline rhyolitic obsidians from the Naivasha area of the Kenya Rift Valley (Table 1). Two (ND, SMN) are mildly peralkaline comendites [ $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3 = 1.05$  and  $1.31$ , respectively from the Greater Olkaria Volcanic Complex and were previously used in phase equilibrium studies (Scaillet & Macdonald, 2001, 2003). The third, EBU, is a pantelleritic obsidian from a welded fall deposit of the Eburru Volcanic Complex, immediately north of Olkaria. It is more strongly peralkaline than the comendites ( $\text{NK}/\text{A} = 1.88$ ) and represents a composition that could have been generated by  $\sim 50\%$  crystallization of Olkaria-type comendites similar to SMN (Scaillet & Macdonald, 2003). These starting melt compositions (Table 1) encompass the entire peralkalinity range displayed by rhyolites associated with flood basalts (Trua *et al.*, 1999; Ayalew *et al.*, 2002; Peccerillo *et al.*, 2003). We restricted our investigations to low-pressure conditions ( $\sim 150$  MPa), thought to be relevant to the production of alkali rhyolites (Mahood, 1984; Scaillet & Macdonald, 2001) and we focused on the role of oxygen fugacity ( $f\text{O}_2$ ), which exerts a strong control on sulphur behaviour in silicic magmas (e.g. Carroll & Webster, 1994; Scaillet *et al.*, 1998; Keppler, 1999).

The experimental procedures are similar to those used in previous studies performed at the ISTO experimental petrology laboratory, such as that by Scaillet *et al.* (1998) and Clemente *et al.* (2004). For each composition, batches of starting glass + sulphur powders with fixed sulphur contents were prepared by weighing 200 mg of glass powder with appropriate amounts of elemental sulphur (1–12 mg added sulphur). The resulting mixture was thoroughly mixed in an agate mortar for several minutes. Most experiments used ND, SMN and EBU batches with bulk sulphur contents of *c.* 1 wt % (1.01, 1.19 and 1.08 wt %, respectively; see Table 1). However, three series with EBU composition were performed with additional bulk sulphur contents of 0.5, 2.01, 3.85 and 6.14 wt % S, so as to explore the effect of sulphur fugacity at fixed  $P$  and  $T$  and  $f\text{H}_2$ . We used Au capsules, which were loaded with

Table 1: Experimental conditions, masses of silicate and volatiles, run products and phase proportions

Charge	$P$ tot (bar)	$f_{H_2}$ (bar)	$f_{H_2O}$ (bar)	$T$ (°C)	$\Delta$ NNO	Duration (h)	S bulk (wt %)	silicate + S (mg)	H <sub>2</sub> O (mg)	sulphur (mg)	fl (wt %)	Po (wt %)	Anhy (wt %)	Ox (wt %)
<i>ND bulk</i>														
ND-1	1520	40.0	1166	803	-1.61	165	1.01	20.20	1.90	0.20	3.89	1.65	—	—
ND-2	1500	7.7	1180	803	-0.17	172	1.01	19.60	2.00	0.20	4.59	1.65	—	—
ND-4	1520	2.5	1170	804	0.82	309	1.01	20.00	2.10	0.20	4.90	1.47	—	—
ND-5	1520	1.3	1177	803	1.37	193	1.01	20.30	2.00	0.20	4.17	1.45	0.80	—
ND-6	1520	0.5	1120	806	2.25	192	1.01	20.30	2.00	0.20	4.63	—	0.94	1.97
ND-3	1500	0.2	1123	808	2.96	188	1.01	30.00	3.00	0.30	4.73	—	1.00	2.17
ND-9	1561	50.0	1295	900	-1.63	96	1.01	20.10	2.00	0.20	4.94	1.38	—	—
<i>SMN bulk</i>														
SMN-1	1520	40.0	1182	803	-1.60	165	1.19	19.80	2.10	0.24	4.92	2.16	—	—
SMN-2	1500	7.7	1149	803	-0.19	172	1.19	20.20	2.00	0.24	4.39	1.93	—	—
SMN-4	1520	2.5	1150	804	0.80	309	1.19	20.70	2.00	0.25	4.23	1.76	—	—
SMN-5	1520	1.3	1120	803	1.33	193	1.19	19.20	2.20	0.23	6.24	—	0.58	2.76
SMN-6	1520	0.5	1098	806	2.24	192	1.19	20.40	2.10	0.24	5.24	—	0.62	5.05
SMN-3	1500	0.2	1098	808	2.94	188	1.19	20.20	2.10	0.24	5.32	—	0.63	5.24
SMN-9	1561	50.0	1299	900	-1.63	96	1.19	20.00	2.00	0.24	4.60	1.65	—	—
<i>EBU bulk</i>														
EBU-1	1520	40.0	1205	803	-1.58	165	1.08	21.00	2.00	0.23	3.78	2.31	—	—
EBU-2	1500	7.7	1181	803	-0.17	172	1.08	20.20	2.00	0.22	4.18	2.06	—	—
EBU-4	1520	2.5	1159	804	0.81	309	1.08	20.60	2.00	0.22	4.23	1.45	—	—
EBU-5	1520	1.3	1104	803	1.32	193	1.08	20.80	2.10	0.22	4.99	—	0.52	5.27
EBU-6	1520	0.5	1074	806	2.22	192	1.08	21.10	1.90	0.22	4.02	—	0.60	5.79
EBU-3	1500	0.2	1093	808	2.94	188	1.08	20.40	2.00	0.22	4.74	—	0.55	5.63
EBU-7-0.5	1500	6.1	1195	801	0.04	214	0.50	20.40	2.10	0.10	4.45	0.82	—	—
EBU-7-2	1500	6.1	1133	801	0.00	214	2.01	20.70	2.00	0.42	4.25	3.66	—	—
EBU-7-4	1500	6.1	1003	801	-0.11	214	3.85	20.10	1.90	0.77	4.94	6.01	—	—
EBU-7-6	1500	6.1	890	801	-0.21	214	6.14	20.00	2.10	1.23	7.43	7.40	—	—
EBU-8-2	1510	44.0	1161	805	-1.70	183	2.01	20.70	2.10	0.42	4.58	4.08	—	—
EBU-8-4	1510	44.0	1047	805	-1.79	183	3.85	21.30	2.10	0.82	5.12	6.51	—	—
EBU-8-6	1510	44.0	825	805	-1.99	183	6.14	21.50	2.00	1.32	6.41	7.31	—	—
EBU-9-0.5	1561	55.0	1353	900	-1.60	96	0.50	21.00	2.00	0.11	3.78	1.00	—	—
EBU-9-1	1561	50.0	1328	900	-1.61	96	1.08	20.00	2.00	0.22	4.35	2.07	—	—
EBU-9-2	1561	50.0	1253	900	-1.66	96	2.01	22.60	2.10	0.45	4.07	3.52	—	—
EBU-9-4	1561	50.0	1119	900	-1.76	96	3.85	20.90	2.00	0.80	5.22	5.71	—	—
EBU-9-6	1561	50.0	934	900	-1.92	96	6.14	20.40	2.00	1.25	7.22	6.56	—	—

S bulk is the wt % content of sulphur of the silicate powder. The mass of sulphur in the charge is given in the column labelled sulphur. The wt % of pyrrhotite (Po), anhydrite (Anhy) and oxide (Ox) are calculated on the basis of condensed phases only (i.e. hydrous glass + minerals). fl is the weight % of fluid at  $P$  and  $T$ .

the glass + sulphur powder (*c.* 20–30 mg, Table 1) plus weighed amounts of distilled water (*c.* 10 wt %, Table 1), and welded shut with a graphite arc welder. Weighing before and after welding, as well as after run completion, was used as a monitor for any volatile loss that occurred at  $P$  and  $T$ . For all charges used in this study, capsule weights remained constant to within 0.2 mg. We used

either cold seal pressure vessels (CSPV) fitted with an H<sub>2</sub> membrane (runs at 800°C) or an internally heated pressure vessel (IHPV) with a drop quench setting (900°C). Errors in quoted temperatures and pressures are  $\pm 8^\circ\text{C}$ , and 2 MPa, respectively. The  $f_{O_2}$  was varied using various Ar–H<sub>2</sub> mixtures as the pressurizing gas. The H<sub>2</sub> fugacity was either read with an H<sub>2</sub>-membrane

(800°C) or known from previous experiments that used the same Ar–H<sub>2</sub> ratio and that were run with an H<sub>2</sub> membrane (900°C). Errors on H<sub>2</sub> fugacities are ±0.01 MPa (800°C), or ±0.5 MPa (900°C), the latter determined by repeat experiments performed with the IHPV while fitted with a H<sub>2</sub> membrane. The  $f_{\text{O}_2}$  of each charge was computed using the dissociation reaction of water (Robie *et al.*, 1979), the  $f_{\text{H}_2}$  and the water fugacity ( $f_{\text{H}_2\text{O}}$ ). The  $f_{\text{H}_2\text{O}}$  of each charge (Table 1) was computed assuming ideal behaviour in the fluid [i.e.  $a_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}_n}$ ,  $X_{\text{H}_2\text{O}_n}$  being the mole fraction of H<sub>2</sub>O in the fluid and  $a_{\text{H}_2\text{O}}$  the activity of water defined as the ratio  $f_{\text{H}_2\text{O}}/f_{\text{H}_2\text{O}}^\circ$ ,  $f_{\text{H}_2\text{O}}^\circ$  being the fugacity of pure water at  $P$  and  $T$  as given by Burnham *et al.* (1969)] and using the calculated fluid composition as determined from mass-balance constraints. The fluid composition was calculated knowing the amounts of dissolved water and sulphur, the amount of sulphur locked into solid phases (sulphide and sulphate) and the bulk content of water and sulphur loaded into the capsules. The water content of quenched melts (glasses) was determined using the by-difference method employing appropriate sets of hydrous glass standards of known H<sub>2</sub>O contents (Scaillet & Macdonald, 2001). For charges with *c.* 1 wt % bulk sulphur, the calculated  $X_{\text{H}_2\text{O}_n}$  of the equilibrium fluid (Table 2) is close to, or higher than, 0.9, with the result that the calculated  $f_{\text{O}_2}$  is only marginally lower than that corresponding to pure H<sub>2</sub>O (the difference is <0.05 log units). For those charges we estimate that the uncertainty on  $f_{\text{O}_2}$  is <0.1 log units. In contrast, charges having bulk sulphur contents in excess of 1 wt % have calculated fluid compositions that are significantly poorer in H<sub>2</sub>O, with  $X_{\text{H}_2\text{O}_n}$  going down to 0.68 (Table 2). As a result, the value of  $f_{\text{O}_2}$  for the sulphur-rich charges is lower than that corresponding to the pure H<sub>2</sub>O case. However, for a fixed set of  $P$ – $T$ – $f_{\text{H}_2}$  conditions (i.e. series EBU-9 in Table 1), the difference in calculated  $f_{\text{O}_2}$  between the sulphur-poor and sulphur-rich charges does not exceed 0.3 log units (Table 1). The main source of uncertainty in S-rich charges comes from the estimate of the amount of H<sub>2</sub>O dissolved in the melt. An error of 1 wt % absolute (i.e. 4.5 wt % instead of 5.5 wt %) produces a change in calculated  $X_{\text{H}_2\text{O}_n}$  of about ±0.07, which in turn induces a change in the calculated log  $f_{\text{O}_2}$  of about ±0.07 units. Overall, for the sulphur-rich charges we estimate that the  $f_{\text{O}_2}$  is known to within 0.3 log units.

Because we use elemental sulphur as a source of sulphur, and not either sulphide or anhydrite (e.g. Luhr, 1990), the initial redox state of the charges is grossly out of equilibrium, as the sulphur in the fluid must be complexed either with O<sub>2</sub> to form SO<sub>2</sub> or with H<sub>2</sub> to produce H<sub>2</sub>S, which are the two dominant fluid species in the fluid at  $P$  and  $T$ , depending on  $f_{\text{O}_2}$  (see Clemente *et al.*, 2004). As long as H<sub>2</sub> from the vessel does not diffuse across the capsule walls (i.e. below 600°C), the redox state of

the charges will be internally controlled to some value that will depend on factors such as the ratio of H<sub>2</sub>O to S loaded, the amount of atmospheric O<sub>2</sub> present in the capsule, and the rates of H<sub>2</sub>O and S dissolution into glass/melt. At 800°C, however, the kinetics of H<sub>2</sub> diffusion even within Au is so fast that osmotic equilibrium in H<sub>2</sub> is attained within a few tens of seconds across the capsule walls (Scaillet *et al.*, 1992), and maintained at a fixed value owing to the large H<sub>2</sub>-buffering capacity of the vessel volume (Schmidt *et al.*, 1995). Both the CSPV and IHPV attain the target temperature in about 20 min, so that the period elapsed at low-temperature conditions, during which transient redox state may occur, is short relative to the total run duration (minimum of 96 h, Table 1). Redox equilibrium will be reached as soon as the dissolution process of volatiles into melt is achieved. Using appropriate diffusivities for H<sub>2</sub>O and S [taken at 800°C as 10<sup>-7</sup> cm<sup>2</sup>/s and 10<sup>-9</sup> cm<sup>2</sup>/s, respectively (Watson, 1994)], it can be calculated that volatile dissolution occurs in a matter of minutes (H<sub>2</sub>O) to a few hours (S) owing to the finely powdered and well-mixed nature of our starting material, which minimizes the diffusion length scale of volatiles to a few tens of microns. None of the charges produced in this study displayed textural evidence of redox disequilibrium, such as sulphide rimmed by sulphate or vice versa, suggesting that either the charge has no time to record redox states radically different from that imposed at run conditions, or any evidence of such variations in  $f_{\text{O}_2}$  during the heating-up period has been erased upon run completion.

Run products were characterized first by optical inspection with a metallographic microscope and then by electron microprobe analysis (EMPA). Observation under reflected light prior to carbon-coating allowed the oxide to be distinguished easily from sulphide owing to their contrasted colours (grey for oxide vs yellowish for sulphide), as well as shape (rectangular to equant shape for oxide vs pentagonal to rounded shape for smaller individual sulphide grains). Investigation under transmitted light and crossed polars allowed straightforward identification of anhydrite in oxidized charges because of its high birefringence. In anhydrite-bearing charges, anhydrite was fully enclosed by glass, suggesting that it grew from the melt and is not the result of back-reaction of fluid upon cooling, in which case it should have partially filled open cavities representing former gas bubbles. In all cases, optical identification of minerals was confirmed by subsequent EMPA, although owing to their generally small size, most analyses of minerals were contaminated by glass. We used the following conditions to determine the composition of glasses. For major elements, the conditions were: accelerating voltage 15 kV, sample current 6 nA, counting time 10 s on peak for all elements, and a beam defocused to 5 µm. Na and K were analysed first and a ZAF correction procedure applied. Correction

Table 2: Compositions of glasses, coexisting fluid, and calculated fluid/melt sulphur partition coefficients

Charge	SiO <sub>2</sub> (wt %)	Al <sub>2</sub> O <sub>3</sub> (wt %)	FeO (wt %)	MgO (wt %)	CaO (wt %)	Na <sub>2</sub> O (wt %)	K <sub>2</sub> O (wt %)	F (wt %)	Cl (wt %)	NK/A	<i>n</i>	S <sub>melt</sub> (ppm)	S <sub>fluid</sub> (wt %)	XH <sub>2</sub> O <sub>fl</sub>	S <sub>fl</sub> /S <sub>melt</sub>
ND bulk	75-20	12-11	1.81	0.07	0.44	4.59	4.73	0.37	0.22	1.05					
ND-1	77-25 <i>0.18</i>	12-08 <i>0.12</i>	0.39 <i>0.08</i>	0.05 <i>0.03</i>	0.37 <i>0.05</i>	4.54 <i>0.01</i>	5.00 <i>0.08</i>	0.13 <i>0.14</i>	0.13 <i>0.03</i>	1.07	7	268 <i>31</i>	8.2	0.95	307
ND-2	77-18 <i>0.22</i>	12-17 <i>0.13</i>	0.39 <i>0.19</i>	0.05 <i>0.03</i>	0.35 <i>0.05</i>	4.55 <i>0.01</i>	4.98 <i>0.12</i>	0.13 <i>0.10</i>	0.13 <i>0.04</i>	1.06	7	265 <i>34</i>	6.9	0.96	261
ND-4	77-25 <i>0.21</i>	12-19 <i>0.15</i>	0.54 <i>0.17</i>	0.04 <i>0.03</i>	0.30 <i>0.06</i>	4.54 <i>0.01</i>	4.76 <i>0.12</i>	0.18 <i>0.09</i>	0.15 <i>0.04</i>	1.03	12	266 <i>36</i>	7.7	0.96	290
ND-5	77-43 <i>0.08</i>	12-20 <i>0.16</i>	0.56 <i>0.12</i>	0.05 <i>0.02</i>	0.09 <i>0.03</i>	4.53 <i>0.00</i>	4.72 <i>0.08</i>	0.22 <i>0.10</i>	0.08 <i>0.04</i>	1.03	10	329 <i>42</i>	4.8	0.97	147
ND-6	77-43 <i>0.27</i>	12-16 <i>0.13</i>	0.87 <i>0.14</i>	0.03 <i>0.02</i>	0.03 <i>0.03</i>	4.51 <i>0.01</i>	4.55 <i>0.23</i>	0.16 <i>0.13</i>	0.11 <i>0.06</i>	1.02	10	462 <i>27</i>	14.4	0.91	310
ND-3	77-33 <i>0.25</i>	12-19 <i>0.09</i>	0.78 <i>0.13</i>	0.02 <i>0.02</i>	0.01 <i>0.02</i>	4.53 <i>0.01</i>	4.67 <i>0.16</i>	0.25 <i>0.16</i>	0.05 <i>0.03</i>	1.03	6	633 <i>38</i>	13.4	0.92	212
ND-9	76-97 <i>0.23</i>	11-98 <i>0.13</i>	0.63 <i>0.10</i>	0.04 <i>0.03</i>	0.37 <i>0.06</i>	4.55 <i>0.01</i>	4.82 <i>0.12</i>	0.27 <i>0.05</i>	0.12 <i>0.05</i>	1.06	7	303 <i>15</i>	8.9	0.95	294
SMN bulk	74-17	10-89	3.98	0.00	0.29	5.81	4.34	1.00	0.50	1.31					
SMN-1	75-60 <i>0.24</i>	10-67 <i>0.12</i>	2.11 <i>0.23</i>	0.02 <i>0.02</i>	0.06 <i>0.05</i>	5.71 <i>0.01</i>	4.45 <i>0.16</i>	1.07 <i>0.14</i>	0.26 <i>0.08</i>	1.33	7	242 <i>39</i>	6.1	0.97	254
SMN-2	75-14 <i>0.36</i>	10-66 <i>0.12</i>	2.32 <i>0.28</i>	0.01 <i>0.01</i>	0.06 <i>0.04</i>	5.72 <i>0.01</i>	4.42 <i>0.20</i>	1.17 <i>0.20</i>	0.37 <i>0.12</i>	1.33	8	315 <i>24</i>	8.7	0.95	277
SMN-4	75-23 <i>0.22</i>	10-75 <i>0.10</i>	2.46 <i>0.11</i>	0.01 <i>0.01</i>	0.03 <i>0.03</i>	5.70 <i>0.01</i>	4.33 <i>0.12</i>	1.20 <i>0.15</i>	0.22 <i>0.06</i>	1.31	16	351 <i>67</i>	10.3	0.94	293
SMN-5	75-43 <i>0.26</i>	10-53 <i>0.15</i>	2.67 <i>0.25</i>	0.02 <i>0.01</i>	0.03 <i>0.02</i>	5.67 <i>0.01</i>	4.20 <i>0.16</i>	1.09 <i>0.07</i>	0.21 <i>0.06</i>	1.32	10	452 <i>46</i>	14.4	0.91	318
SMN-6	76-51 <i>0.22</i>	10-73 <i>0.15</i>	1.58 <i>0.14</i>	0.00 <i>0.01</i>	0.01 <i>0.02</i>	5.65 <i>0.01</i>	4.24 <i>0.11</i>	1.08 <i>0.10</i>	0.08 <i>0.02</i>	1.29	10	487 <i>37</i>	17.1	0.90	350
SMN-3	76-53 <i>0.25</i>	10-86 <i>0.10</i>	1.49 <i>0.14</i>	0.01 <i>0.01</i>	0.00 <i>0.01</i>	5.67 <i>0.01</i>	4.16 <i>0.12</i>	0.89 <i>0.22</i>	0.15 <i>0.06</i>	1.27	6	550 <i>24</i>	16.7	0.90	303
SMN-9	75-22 <i>0.24</i>	10-49 <i>0.16</i>	2.35 <i>0.21</i>	0.02 <i>0.02</i>	0.06 <i>0.02</i>	5.74 <i>0.01</i>	4.41 <i>0.15</i>	1.05 <i>0.16</i>	0.41 <i>0.05</i>	1.36	8	548 <i>46</i>	11.0	0.94	201
EBU bulk	70-86	8.48	7.17	0.52	0.30	6.68	4.50	0.78	0.43	1.87					
EBU-1	74-09 <i>0.23</i>	8.30 <i>0.10</i>	5.19 <i>0.28</i>	0.01 <i>0.01</i>	0.23 <i>0.05</i>	6.52 <i>0.01</i>	4.41 <i>0.11</i>	0.79 <i>0.19</i>	0.35 <i>0.07</i>	1.87	6	738 <i>65</i>	2.8	0.98	38
EBU-2	73-37 <i>0.32</i>	8.38 <i>0.06</i>	5.40 <i>0.25</i>	0.01 <i>0.02</i>	0.28 <i>0.04</i>	6.54 <i>0.03</i>	4.41 <i>0.08</i>	0.96 <i>0.11</i>	0.36 <i>0.08</i>	1.85	7	897 <i>37</i>	4.3	0.98	48
EBU-4	73-75 <i>0.34</i>	8.29 <i>0.07</i>	5.93 <i>0.25</i>	0.01 <i>0.01</i>	0.14 <i>0.04</i>	6.50 <i>0.01</i>	4.19 <i>0.13</i>	0.82 <i>0.09</i>	0.23 <i>0.04</i>	1.84	11	928 <i>67</i>	9.3	0.95	100
EBU-5	75-37 <i>0.22</i>	8.45 <i>0.06</i>	4.68 <i>0.13</i>	0.02 <i>0.02</i>	0.05 <i>0.02</i>	6.47 <i>0.01</i>	4.03 <i>0.11</i>	0.70 <i>0.14</i>	0.16 <i>0.01</i>	1.77	10	549 <i>25</i>	16.3	0.90	297
EBU-6	75-65 <i>0.22</i>	8.46 <i>0.21</i>	4.43 <i>0.22</i>	0.02 <i>0.02</i>	0.02 <i>0.02</i>	6.46 <i>0.01</i>	4.05 <i>0.09</i>	0.66 <i>0.12</i>	0.12 <i>0.02</i>	1.78	11	368 <i>23</i>	19.9	0.88	542
EBU-3	75-60 <i>0.39</i>	8.50 <i>0.09</i>	4.51 <i>0.28</i>	0.01 <i>0.01</i>	0.04 <i>0.04</i>	6.47 <i>0.01</i>	3.95 <i>0.13</i>	0.78 <i>0.18</i>	0.11 <i>0.05</i>	1.76	5	434 <i>17</i>	17.3	0.90	399
EBU-7-0.5	72-92 <i>0.39</i>	8.13 <i>0.08</i>	6.47 <i>0.26</i>	0.01 <i>0.02</i>	0.26 <i>0.05</i>	6.52 <i>0.02</i>	4.31 <i>0.15</i>	0.87 <i>0.17</i>	0.33 <i>0.04</i>	1.89	11	744 <i>72</i>	2.2	0.99	30
EBU-7-2	75-01	8.43	4.03	0.03	0.21	6.53	4.32	0.89	0.31	1.83	13	1013	10.8	0.94	107



Table 2: Continued

Charge	SiO <sub>2</sub> (wt %)	Al <sub>2</sub> O <sub>3</sub> (wt %)	FeO (wt %)	MgO (wt %)	CaO (wt %)	Na <sub>2</sub> O (wt %)	K <sub>2</sub> O (wt %)	F (wt %)	Cl (wt %)	NK/A	<i>n</i>	S <sub>melt</sub> (ppm)	S <sub>fluid</sub> (wt %)	XH <sub>2</sub> O <sub>fl</sub>	S <sub>fl</sub> /S <sub>melt</sub>
	<i>0.20</i>	<i>0.12</i>	<i>0.14</i>	<i>0.01</i>	<i>0.02</i>	<i>0.01</i>	<i>0.21</i>	<i>0.19</i>	<i>0.09</i>			<i>149</i>			
EBU-7-4	77.29	8.59	2.00	0.02	0.11	6.50	4.44	0.66	0.15	1.81	10	845	26.9	0.83	319
	<i>0.30</i>	<i>0.16</i>	<i>0.16</i>	<i>0.02</i>	<i>0.03</i>	<i>0.01</i>	<i>0.13</i>	<i>0.18</i>	<i>0.03</i>			<i>61</i>			
EBU-7-6	78.70	8.77	0.79	0.01	0.08	6.48	4.39	0.46	0.08	1.76	10	880	39.1	0.74	445
	<i>0.23</i>	<i>0.09</i>	<i>0.11</i>	<i>0.02</i>	<i>0.02</i>	<i>0.02</i>	<i>0.09</i>	<i>0.13</i>	<i>0.01</i>			<i>94</i>			
EBU-8-2	74.92	8.49	3.66	0.02	0.28	6.57	4.48	1.04	0.42	1.84	10	445	7.9	0.95	177
	<i>0.19</i>	<i>0.10</i>	<i>0.15</i>	<i>0.02</i>	<i>0.04</i>	<i>0.01</i>	<i>0.12</i>	<i>0.11</i>	<i>0.07</i>			<i>56</i>			
EBU-8-4	76.83	8.69	1.57	0.01	0.26	6.58	4.53	0.90	0.35	1.81	12	891	22.4	0.86	252
	<i>0.48</i>	<i>0.11</i>	<i>0.18</i>	<i>0.01</i>	<i>0.07</i>	<i>0.03</i>	<i>0.11</i>	<i>0.23</i>	<i>0.10</i>			<i>148</i>			
EBU-8-6	77.49	8.67	0.87	0.01	0.28	6.62	4.54	0.84	0.33	1.82	13	1222	45.7	0.68	374
	<i>0.36</i>	<i>0.18</i>	<i>0.06</i>	<i>0.02</i>	<i>0.07</i>	<i>0.01</i>	<i>0.13</i>	<i>0.15</i>	<i>0.04</i>			<i>180</i>			
EBU-9-0.5	72.66	8.06	6.32	0.02	0.23	6.55	4.30	0.82	0.41	1.92	8	969	2.8	0.98	29
	<i>0.28</i>	<i>0.07</i>	<i>0.14</i>	<i>0.03</i>	<i>0.03</i>	<i>0.00</i>	<i>0.15</i>	<i>0.10</i>	<i>0.03</i>			<i>52</i>			
EBU-9-1	73.34	8.10	5.39	0.01	0.26	6.57	4.37	0.84	0.44	1.92	8	1032	5.9	0.97	58
	<i>0.11</i>	<i>0.13</i>	<i>0.18</i>	<i>0.01</i>	<i>0.04</i>	<i>0.02</i>	<i>0.12</i>	<i>0.04</i>	<i>0.04</i>			<i>25</i>			
EBU-9-2	74.44	8.23	4.15	0.01	0.27	6.58	4.38	0.77	0.42	1.89	8	1193	14.8	0.91	124
	<i>0.35</i>	<i>0.07</i>	<i>0.19</i>	<i>0.02</i>	<i>0.07</i>	<i>0.01</i>	<i>0.11</i>	<i>0.07</i>	<i>0.07</i>			<i>43</i>			
EBU-9-4	76.00	8.45	2.25	0.02	0.25	6.62	4.59	0.71	0.36	1.88	9	1591	28.9	0.81	182
	<i>0.24</i>	<i>0.05</i>	<i>0.17</i>	<i>0.02</i>	<i>0.06</i>	<i>0.02</i>	<i>0.15</i>	<i>0.06</i>	<i>0.06</i>			<i>73</i>			
EBU-9-6	76.39	8.49	1.52	0.02	0.26	6.63	4.54	0.74	0.37	1.87	8	2254	45.8	0.68	203
	<i>0.31</i>	<i>0.03</i>	<i>0.27</i>	<i>0.03</i>	<i>0.03</i>	<i>0.00</i>	<i>0.20</i>	<i>0.13</i>	<i>0.04</i>			<i>47</i>			

Glass compositions have been normalized to 100% anhydrous. Melt water contents determined with the by-difference method range from 5 to 6 wt %. The 1 $\sigma$  standard deviation of each oxide or element analysed is given in italics below the concentration. Reported glass compositions are average of 6–10 electron microprobe analyses. XH<sub>2</sub>O<sub>fl</sub> represents the mole fraction of H<sub>2</sub>O of the coexisting fluid phase that is made of H<sub>2</sub>O and H<sub>2</sub>S (low  $fO_2$ ) or SO<sub>2</sub> (high  $fO_2$ ), and that is determined by mass balance. S<sub>melt</sub> and S<sub>fluid</sub> are the sulphur content of melt and fluid, respectively. *n* is the number of electron microprobe analyses of sulphur. NK/A is the (Na<sub>2</sub>O + K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub> ratio (moles).

factors for Na loss were based on analyses of synthetic peralkaline rhyolitic compositions and a set of metaluminous rhyolitic and dacitic glasses, all of known water content as determined by Karl Fischer titration. Between six and 10 analyses were performed for each glass. The water content of quenched glasses varied between 5 and 6 wt %, except for the two charges with *c.* 6 wt % sulphur, which displayed slightly lower values (between 4 and 5 wt %). Owing to the large uncertainties of the by-difference technique in determining the H<sub>2</sub>O content of quenched glasses (e.g. Devine *et al.*, 1995), in this work we use a fixed melt water content of 5.5 wt % for all charges. The Na+K/Al ratios of quenched glasses do not show any significant departure from that of the starting materials (Table 2). The concentration of total sulphur in glasses was determined by EMPA using three synthetic hydrous dacitic glasses containing 750, 1400 and 1900 ppm sulphur (determined by wet chemistry) as standards (Clemente *et al.*, 2004). The EMPA was run with the following conditions: accelerating voltage 15 kV, sample

current 50 nA, beam diameter 10  $\mu$ m, and a counting time of 60 s. The background was determined by analysing a dry rhyolitic glass without sulphur, using the above analytical procedure. The detection limit under these analytical conditions is about 80 ppm. The sulphur data given in Table 2 are averages of 5–16 analyses.

Apart from oxide and sulphur-bearing phases, no other mineral was detected. Two S-bearing phases crystallized: pyrrhotite at NNO < 1 and anhydrite at NNO > 1. At high  $fO_2$ , an oxide co-precipitated with anhydrite. Knowing the amount of sulphur-bearing phases crystallized, and the amount of sulphur dissolved in the melt, the sulphur content of the coexisting fluid is calculated by difference with the known bulk sulphur content, using stoichiometric FeS and CaSO<sub>4</sub> as sulphide or sulphate minerals (e.g. Scaillet *et al.*, 1998). Because, depending on  $fO_2$ , sulphide or sulphate + oxides were the sole phases crystallizing (Table 1), the maximum proportions of sulphur-bearing minerals can be determined by the changes in either FeO<sub>tot</sub> ( $fO_2$  < NNO) or CaO ( $fO_2$  > NNO + 1)

of the quenched glass. This obviously assumes that neither iron or calcium is transported into the fluid (or lost to the capsule in the case of iron) but, under our experimental conditions, sulphur was never detected in Au capsules. If either of these elements is partitioned into the fluid, the amounts of sulphide or sulphate calculated from variations in FeO and CaO abundances in glass will be overestimated, with the consequence that there will be too much sulphur locked in solid phases. As a result, the calculated partition coefficient will be lower than its real value. Conversely, as stated above, we assume that pyrrhotite is end-member FeS. Pyrrhotite departure from FeS stoichiometry can be up to Fe<sub>5</sub>S<sub>6</sub>. An Fe<sub>5</sub>S<sub>6</sub> stoichiometry would decrease our calculated partition coefficients, as it maximizes the amount of sulphur tied up with iron in pyrrhotite and this sulphur is, therefore, no longer available to the fluid. For charges saturated in anhydrite, a problem also arises from the low bulk CaO content of the starting rocks. Generally those charges have melts with CaO contents close to the detection limit. The fact that this extreme depletion in CaO goes along with a decrease in melt Cl content relative to the starting value (see Table 2) suggests that not all the Ca complexes with sulphur to form anhydrite, but that some goes into the fluid, possibly as CaCl<sub>2</sub> species. The concentration of CaO in charges run at low  $fO_2$  remains close to the starting value, although some depletion does occur, possibly also as a result of Ca complexing with Cl. We recognize that partition coefficients of sulphur between fluid and melt determined in this way (by default) can be affected by a number of errors, as illustrated below. However, there is, unfortunately, no straightforward way of assessing this parameter in hydrothermal experiments. In particular, measuring the H–O–S fluid compositions upon quench is unlikely to retrieve the correct numbers, as back-reactions within fluid can alter both its speciation and composition (L. Baker, personal communication, 1996 20XX).

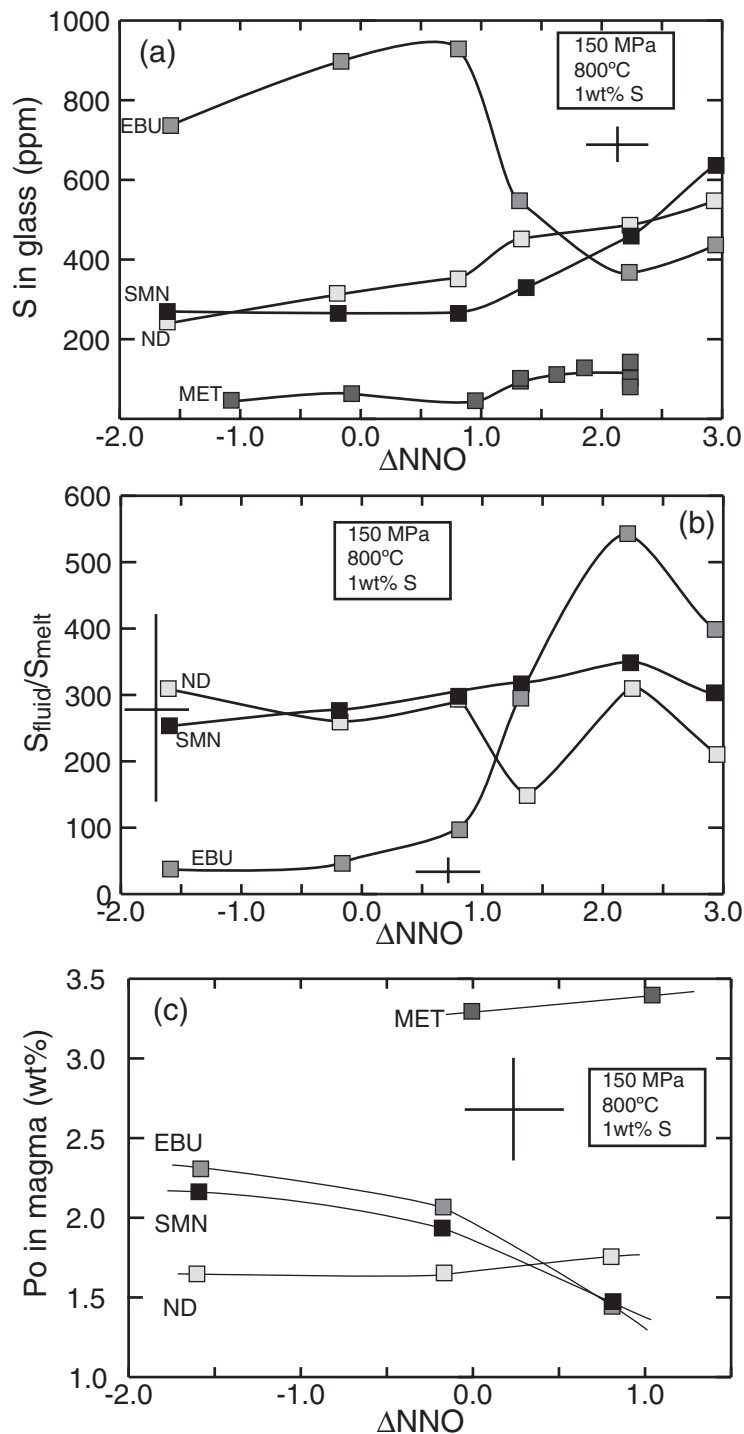
As an example we consider charge ND1 whose partition coefficient,  $D_S$ , calculated using the above assumptions, is 307 (Table 1). This charge consisted of 20.2 mg of silicate powder with 1.01 wt % S (0.2 mg), and 1.9 mg of H<sub>2</sub>O. The bulk FeO is 1.81 wt % (0.37 mg) and after the run the hydrous glass (5.5 wt % or 1.11 mg H<sub>2</sub>O) has 0.39 wt % FeO<sub>tot</sub> (0.08 mg). The difference in FeO content in glass before and after the run (0.2867 mg) implies that 0.00399 millimoles of Fe is sequestered in pyrrhotite (0.2867/71.85). Assuming stoichiometric pyrrhotite this implies in turn that 0.128 mg (32 × 0.004) of sulphur is locked up in pyrrhotite. Knowing that the glass has 268 ppm dissolved sulphur, corresponding to 0.0054 mg sulphur, this leaves 0.07 mg sulphur for the fluid (or 0.074 mg H<sub>2</sub>S). The amount of water in the fluid is 0.79 mg (1.9–1.11), which implies that the mole fraction of H<sub>2</sub>O in the fluid,  $X_{H_2O}$ , is 0.95, and that the

amount of fluid at  $P$  and  $T$  is 0.864 mg (0.79 + 0.074), which corresponds to 3.9 wt % fluid in the system [0.864/(20.2 + 1.9)], the fluid having 8.2 wt % sulphur. The amount of pyrrhotite is 1.65 wt %, calculated on the basis of condensed phases only (hydrous glass + pyrrhotite).

We now explore the individual effect of the main parameters that affect the calculated  $D_S$ , namely glass iron content, pyrrhotite stoichiometry, iron loss toward the capsule, and glass water content. If, instead of 0.39 wt % FeO, the glass contains 0.49 wt % (i.e. the amount of iron is allowed to increase by 1 $\sigma$  of EMPA), this increases  $D_S$  from 307 to 342. Similarly, if instead of FeS a stoichiometry of Fe<sub>5</sub>S<sub>6</sub> is taken (1.2 mole of S for 1 mole of Fe), this means that 0.15 g of sulphur is locked into pyrrhotite, which decreases  $D_S$  to 202, or by 30%. Alternatively, if we assume that the Au capsule has dissolved 100 ppm Fe [corresponding to a loss of 8 wt % of iron relative to bulk content, as observed in supra-liquidus charges by Scaillet & Macdonald (2004)], then this will increase  $D_S$  to 394. Finally, if the amount of H<sub>2</sub>O dissolved is 4 wt % instead of 5.5 wt % (which would correspond to the possible melt H<sub>2</sub>O content of the charges with 6 wt % sulphur),  $D_S$  decreases to 227. There is clearly a considerable uncertainty on our fluid/melt partition coefficients, yet each parameter taken in isolation affects  $D_S$  by less than 40% when allowed to vary within a reasonable range. Our assumptions of stoichiometric pyrrhotite and fixed melt water content, if incorrect, lead to an overestimation of the calculated  $D_S$ . Conversely, other assumptions (in particular no Fe or Ca loss toward the fluid), if properly evaluated, would yield an underestimation of partition coefficients (i.e. real values are higher than the values listed in Table 2). This is, in fact, the main source of uncertainty in the present work, as we have no control on the amount of dissolved fluid species other than H<sub>2</sub>O and S. However, the work of Scaillet *et al.* (1998), using the same procedure, yielded partition coefficients for sulphur in silicic arc magmas that agree within a factor of two with those derived independently from remote sensing of volcanic plumes. We note in passing that this study explored the effect of CO<sub>2</sub> and concluded that this volatile species has no detectable effect on the partition behaviour of sulphur between fluid and melt in silicic magmas in the  $fO_2$  range explored. We, thus, conclude that the partition coefficients reported here are accurate to within 50%, and the proportions of sulphide/sulphate are known to within 15%.

## RESULTS

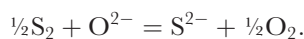
The experimental conditions together with run products and phase proportions are listed in Table 1. The melt compositions together with the calculated partition coefficients are listed in Table 2. Variations in melt sulphur



**Fig. 1.** Sulphur behaviour in peralkaline rhyolites with 1 wt % sulphur at 800°C and 150 MPa. (a) Melt sulphur content as a function of  $fO_2$  for the three rhyolite compositions of increasing peralkalinity (ND < SMN < EBU) used in the experiments (Table 2). Also shown are the sulphur contents of metaluminous silicic melts (MET) held under similar  $P$ - $T$ - $S_{bulk}$  conditions (Luhr, 1990; Scaillet *et al.*, 1998). The maximum error on  $fO_2$  is 0.3 log unit. (b) Variations in the  $S_{fluid}/S_{melt}$  partition coefficient with  $fO_2$  for the three peralkaline rhyolites with *c.* 1 wt % bulk sulphur. Two error bars are shown, one for partition coefficients lower than 100 (bottom part) and one for partition coefficients at around 300 (middle part). Each error bar represents an uncertainty of *c.* 50%. For clarity, the error bar corresponding to the EBU datum at 550 ( $\pm$  275) is not reported. (c) Variation of the proportion of sulphide [wt % Po = mass Po/(mass of Po + mass of hydrous melt)] with  $fO_2$  ( $\Delta NNO$ ) in the three peralkaline rhyolites. Also shown is the proportion of sulphide in the Pinatubo dacite (MET) with *c.* 1 wt % bulk sulphur held over the same  $fO_2$  range at 780°C (Scaillet *et al.*, 1998). The cross represents the typical error on calculated wt % Po and experimental  $fO_2$ .



content ( $S_{\text{melt}}$ ) with  $fO_2$  (here expressed in log units notation relative to the NiNiO solid buffer, such that  $NNO - 1$  means one log unit below NNO) are shown in Fig. 1a. Also plotted is the  $S_{\text{melt}}$  of synthetic metaluminous silicic melts held under similar  $P$  and  $T$  and bulk S content ( $S_{\text{bulk}}$ ) conditions (Luhr, 1990; Scaillet *et al.*, 1998). The sulphur solubility of rhyolite melts is strongly dependent on their NK/A ratio, in addition to  $fO_2$ . At 800°C, under reduced conditions ( $<NNO$ ),  $S_{\text{melt}}$  rises from *c.* 50 ppm in metaluminous rhyolite to nearly 1000 ppm in strongly peralkaline rhyolite (Fig. 1a). In the two less peralkaline compositions (ND and SMN), an increase in  $fO_2$  produces a smooth increase in  $S_{\text{melt}}$ , which broadly conforms with observed behaviour in other silicate melt compositions (e.g. Carroll & Webster, 1994). In contrast, in the most peralkaline composition EBU, the increase in  $S_{\text{melt}}$  peaks at around  $NNO + 1$  and then sharply decreases, so that at higher  $fO_2$  the relative order of sulphur enrichment for the three peralkaline rhyolites is opposite to that observed below NNO. The enhanced sulphur solubility of peralkaline rhyolites at low  $fO_2$  is in part related to the higher iron content (Table 2), which complexes with S (Carroll & Webster, 1994), but may also be due to the greater proportion of oxygen anions in peralkaline melts relative to metaluminous varieties, as oxygen anions are believed to substitute for S (Carroll & Webster, 1994) via the following reaction:



This reaction makes no assumption as to the nature of the element complexed to sulphur in the melt. It simply states that, at fixed  $fS_2$ , an increase in the activity of free oxygen will increase the amount of sulphur dissolved. Given that peralkaline melts have more free oxygen than metaluminous ones (e.g. Mysen, 1988), this could be one explanation for their enhanced sulphur solubility at low  $fO_2$ . At high  $fO_2$ , the opposite, and thus peculiar, trend displayed by EBU warrants further discussion. The above reaction predicts that an increase in  $fO_2$  decreases the sulphur solubility, if again it is assumed that  $fS_2$  does not change across the interval of  $fO_2$  shown in Fig. 1. However, rigorously evaluating the reason for such a trend would require us to know the exact values of intensive parameters other than  $fO_2$ ; namely,  $fS_2$  and the activities of oxygen and sulphur anions in the melt, all of which is unknown in our experiments (and in almost all experimental work so far done at high  $P$  on aluminosilicate melts of geological interest). One possibility would be that our oxidized experiments with the EBU composition did not reach anhydrite saturation, and, thus, that the anhydrite in these charges represents a quench phase and that the drop in solubility observed at high  $fO_2$  simply reflects the fact that sulphur is being increasingly partitioned toward the fluid as  $fO_2$  increases. We do not agree with such an interpretation

because of the textural evidence given above. In addition, the experimental conditions adopted in our study are similar to those of other experimental work aimed at defining the stability of anhydrite in silicate melts, in particular hydrous melts (e.g. Carroll & Rutherford, 1985; Luhr, 1990; Scaillet *et al.*, 1998; Scaillet & Evans, 1999; Clemente *et al.*, 2004), as are the criteria used to define anhydrite stability domains in magmas. In other words, if anhydrite is a quench product in our experiments, so it is in other experimental studies, in which case conclusions derived from those experiments about the stability field of anhydrite in magmas should be revised. Rather, we suggest that the trend shown by the EBU melt composition is a real feature that reflects the fundamental structural changes that occur in strongly peralkaline silicic liquids relative to metaluminous types, as noted in the Introduction, and the control that  $fO_2$  exerts upon them. By analogy with what we observe at low  $fO_2$ , we can only speculate that the increase in  $fO_2$  dampens the role of oxygen anions in peralkaline melts, which results in a decreased  $S_{\text{melt}}$  (at fixed  $fS_2$ ).

More generally, if sulphur solubility in hydrous silicic melts is a simple linear function of their iron content (at low  $fO_2$ ), as conventional wisdom would predict, then there would be no reason to have the huge difference between metaluminous and peralkaline compositions that we document here (Fig. 1a). The very fact that  $S_{\text{melt}}$  increases by a factor of *c.* 5 between standard metaluminous rhyolitic and slightly peralkaline melts with similar iron contents indicates that the FeO content is not the sole parameter affecting sulphur behaviour in the studied compositions, unlike in dry basaltic systems (O'Neill & Mavrogenes, 2002). This is also shown by the three series of experiments carried out with various amounts of sulphur, in which the melt iron content decreases whilst the amount of sulphur dissolved in the melt increases (Table 2, series EBU 7, 8 and 9). For instance, at 900°C, the melt with 969 ppm dissolved sulphur has an FeO content of 6.32 wt %, whereas that with 2254 ppm of sulphur has an FeO content of 1.52 wt %. This trend is clearly due to our procedure of adding elemental sulphur, which forces the system to crystallize FeS, which in turn removes FeO from the melt. It shows, however, that the FeO content and dissolved sulphur in hydrous silicic melts are not simply correlated. In this respect, the experimental study of Clemente *et al.* (2004) has clearly shown that in metaluminous rhyolites, the iron control on sulphur solubility is not straightforward, and that variations in  $fS_2$ ,  $fH_2S$  and  $fSO_2$  affect predominantly  $S_{\text{melt}}$ . This study has shown that in hydrous silicate melts, the  $S_{\text{melt}}$  can be modelled as the result of two dissolution reactions, one involving  $H_2S$  and the other  $SO_2$ , as proposed by Burnham (1979). Given the hydrous character of our experiments, it can be anticipated that the fugacities of sulphur-bearing species will exert a role, possibly a

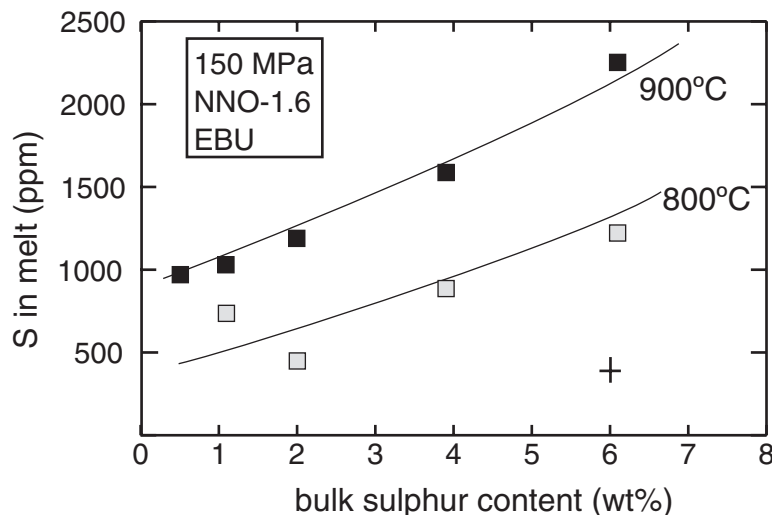


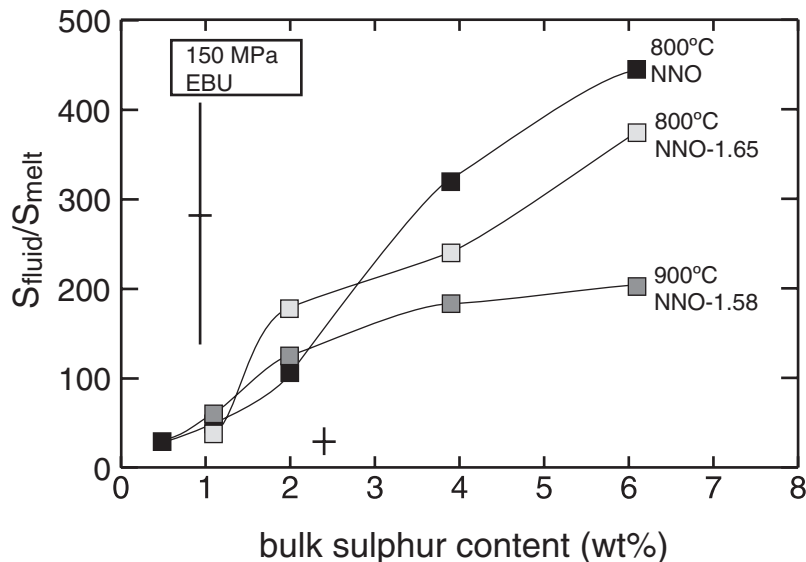
Fig. 2. Variation in the melt sulphur content of EBU rhyolite with the bulk S content for two temperatures, both at an  $fO_2$  of  $c.$  NNO – 1.6.

predominant one, on  $S_{\text{melt}}$  in peralkaline rhyolites as well. Direct comparison of our results with experimental studies bearing on the sulphur solubility of anhydrous melts is, therefore, to a large extent meaningless (or of any anhydrous vs hydrous studies), because in the latter the dissolution reactions of S-bearing species cannot account for the role of H-bearing ones (i.e.  $H_2S$ ), leaving aside the profound structural changes produced by the incorporation of water into silicate melts. In particular, the presence of hydrogen opens the possibility that Fe is not the element with which S preferentially complexes in silicate melts, but instead that H plays that role, as proposed by Burnham (1979), based on theoretical and experimental considerations, a hypothesis that is in agreement with the findings of Clemente *et al.* (2004). In other words, because both the nature and abundances of dissolving species ( $H_2S$  vs  $S_2$  or  $SO_2$ ) and the sulphur complexes in the melt ( $H_2S$  vs  $FeS$ ) are likely to differ between hydrous and anhydrous melts, there is no reason to expect that results gathered from the study of sulphur in anhydrous melts can be directly applicable to hydrous melts. If this statement could be rigorously demonstrated, there would be no reasons for performing the present experimental work.

Whatever the mechanism of sulphur dissolution, our results show that at all values of  $fO_2$ , the sulphur-carrying capacity of peralkaline rhyolites is 5–20 times greater than their metaluminous equivalents. Increasing the temperature to 900°C increases the  $S_{\text{melt}}$  by a factor of two, other parameters being kept equal (Fig. 2). Similarly, varying  $S_{\text{bulk}}$  from 0.5 to 6 wt % increases  $S_{\text{melt}}$  by 2–2.5 times, as a result of increasing sulphur fugacity (Fig. 2). The increase may also reflect the fact that the melt composition is changing when sulphur is added, as it removes part of the iron in solution to produce sulphide.

Variations with  $fO_2$  in the sulphur content of fluid ( $S_{\text{fluid}}$ ) over  $S_{\text{melt}}$ , or the partition coefficient  $D_S$ , are shown in Fig. 1b for rhyolite melts having 1 wt % of  $S_{\text{bulk}}$ . Here again, the two less peralkaline compositions (ND, SMN) show little variation in  $D_S$  with  $fO_2$ ,  $D_S$  being  $\approx 270$ , except at around NNO + 1 when anhydrite and pyrrhotite crystallize together, such as in charge ND5, which has a slightly lower  $D_S$  (Table 1). In the most peralkaline melt (EBU), however, the partition coefficient rises abruptly at  $fO_2 > \text{NNO} + 1$ , behaviour similar to that found in silicic magmas from volcanic arcs (Scaillet *et al.*, 1998). The reason for the limited variation in  $D_S$  in the two less peralkaline melts is that the increase in sulphur solubility with  $fO_2$  is compensated by crystallization of lower proportions of anhydrite at high  $fO_2$  relative to pyrrhotite at low  $fO_2$  (Table 1). In contrast, the increase in  $D_S$  in the most peralkaline melt is because it crystallizes slightly higher proportions of sulphide at low  $fO_2$ , whereas at high  $fO_2$  this composition does not crystallize anhydrite in higher modal amounts than ND and SMN. Because its solubility decreases beyond NNO + 1, this results in an overall increase in the partition coefficient as  $fO_2$  rises.

A comparison with experimental results obtained on a natural metaluminous dacite (Scaillet *et al.*, 1998) shows that, under the same  $T$ – $fO_2$  conditions, a peralkaline rhyolite (SMN) with bulk iron and sulphur contents similar to those in the dacite crystallizes  $\sim 30$ – $40$  % less sulphide (Fig. 1c). Even the most peralkaline rhyolite, with 7 wt %  $FeO_{\text{tot}}$  (EBU, Table 1), crystallizes less sulphide than the metaluminous dacite, which has 4.4 wt %  $FeO_{\text{tot}}$ . We interpret this as resulting from the fact that, when held at the same  $fO_2$ , the  $Fe^{2+}/Fe^{3+}$  ratio is lower in peralkaline than in metaluminous melts (Gwinn & Hess, 1989; Gaillard *et al.*, 2001), such that there is less



**Fig. 3.** Variation in the  $S_{\text{fluid}}/S_{\text{melt}}$  partition coefficient with increasing bulk S content for the EBU rhyolite at 800 and 900°C at three  $fO_2$  conditions. Two error bars are shown, one for partition coefficients lower than 100 (bottom part) and one for partition coefficients at around 300 (middle part). Each error bar represents an uncertainty of  $\approx 50\%$ . For clarity, the error bar corresponding to data at  $\approx 400$  is not reported.

$Fe^{2+}$  available for sulphur complexation in the melt and consequently for sulphide crystallization. The lower modal proportion of sulphide in peralkaline rhyolites results in elevated fluid/melt partition coefficients, in particular for moderately peralkaline melts, even at low  $fO_2$ , differing in this respect from metaluminous melts (Scaillet *et al.*, 1998). The partition coefficient steadily increases for  $S_{\text{bulk}}$  between 1 and 6 wt %, but remains broadly constant for  $S_{\text{bulk}}$  between 0.5 and 1 wt % (Fig. 3). As for the solubility trend, this reflects an increase in  $fS_2$  perhaps coupled to a change in melt chemistry (which becomes iron-poor as the bulk sulphur content increases). At bulk sulphur contents lower than 4 wt %, a rise in temperature from 800 to 900°C decreases  $D_S$  by only 10%, as a consequence of the modest increase of sulphur solubility with temperature (Fig. 3). Our results show, therefore, that any petrogenetic process favouring the formation of peralkaline over metaluminous silicic melts will minimize the possibility of sulphur loss via sulphide fractionation.

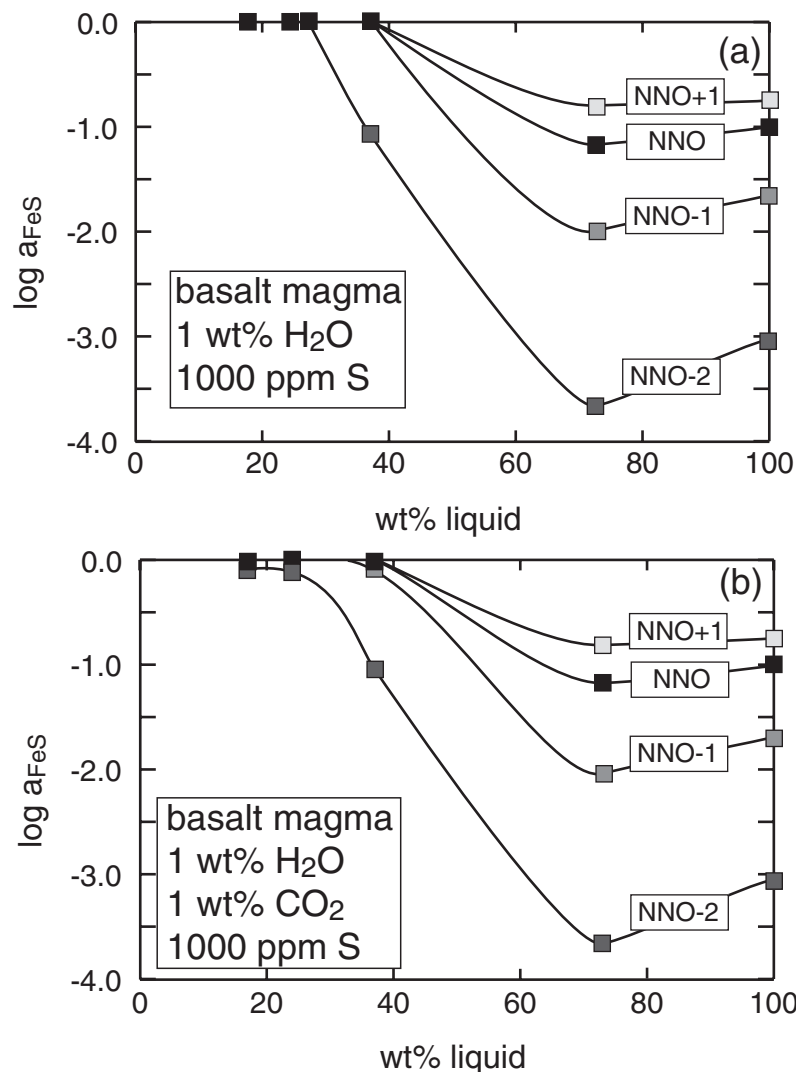
The increased solubility of sulphur in peralkaline melts is consistent with the apparent scarcity of modal sulphides in peralkaline rhyolites. We are aware of three occurrences. Crisp & Spera (1987) recorded scarce pyrrhotite microphenocrysts in comendites and pantellerites of the Tejada volcano, Gran Canaria. Mungall & Martin (1996) noted rare pyrite phenocrysts in pantellerites of the Pico Alto volcano on Terceira Island, Azores. Lowenstern *et al.* (1993) found phenocrysts of pyrrhotite and molybdenite in pantellerites and pantelleritic trachytes from Pantelleria, Italy, the occurrence

of molybdenite being apparently unique in a silicate magma.

## SULPHUR CONTENT OF CRUSTALLY AND MANTLE-DERIVED RHYOLITES

### General

Before using the above experimental results to constrain the atmospheric sulphur yields of rhyolites associated with flood basalts, we need to fix possible limits on the bulk sulphur contents of rhyolites, which will depend on their source region. Two end-member petrogenetic models have been proposed bearing on sulphur enrichment in magmas: crystal fractionation of basaltic magmas, e.g. the Ethiopian ignimbrites (Ayalew *et al.*, 2002), and partial melting of the lower–middle continental crust (albeit with variable mantle input), e.g. the Paraná–Etendeka deposits (Bellieni *et al.*, 1986; Garland *et al.*, 1995; Harris & Milner, 1997; Ewart *et al.*, 1998, 2004). The Ethiopian rhyolites are peralkaline, whereas the felsic magmas of the Paraná–Etendeka province are predominantly metaluminous, being in addition slightly less silicic and more  $K_2O$ -rich than those in Ethiopia. Both types of magma have high iron contents, however, which is usually attributed to low  $fO_2$  during magma genesis (Ewart *et al.*, 1998, 2004). Whatever their mode of origin, the sulphur content of silicic magmas is controlled by the source composition during partial melting and by subsequent evolutionary processes. Sulphur in a magma can reside in fluid, melt and solids, the last being mostly sulphides



**Fig. 4.** Variations in sulphide activity [in log scale,  $\log(a_{\text{FeS}})$ ] in the melt during the crystallization of a basalt magma for different  $f_{\text{O}_2}$  values. (a) With 1 wt % H<sub>2</sub>O and 1000 ppm sulphur. The decrease of  $a_{\text{FeS}}$  observed at high melt fractions is due to the fact that intermediate compositions are Fe-rich compared with the parent magma, and thus have a higher sulphur solubility (which consequently induces a decrease in  $a_{\text{FeS}}$ ) than the totally molten starting magma. (b) With 1 wt % H<sub>2</sub>O, 1 wt % CO<sub>2</sub> and 1000 ppm sulphur. It should be noted that, at NNO - 2, the magma does not reach sulphide saturation even after 80% crystallization. In all calculations we assume that, once stable, the sulphide melt is made of pure FeS and we thus neglect the role of Ni.

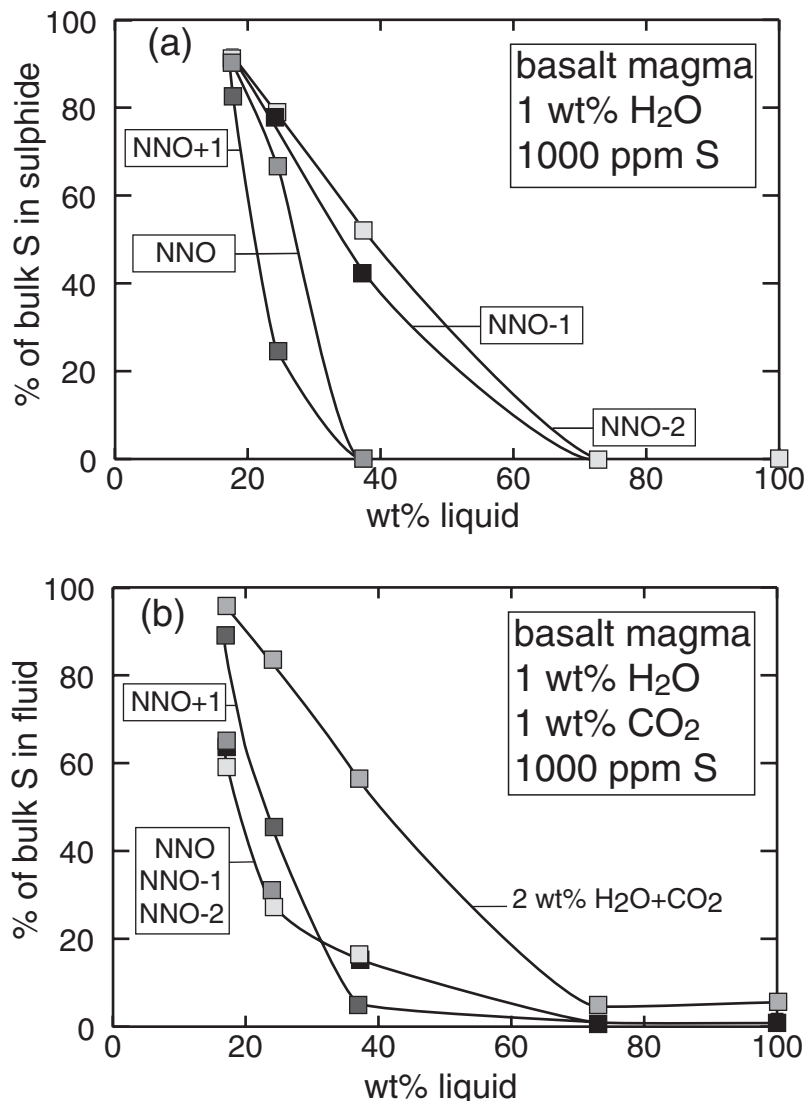
under the low  $f_{\text{O}_2}$  thought to prevail in basalts and in the lower crust. In the following discussion we first consider a mantle origin (i.e. basalt fractionation) and then a crustal origin for rhyolites associated with trap sequences.

### Mantle origin

#### Method

In basalts, sulphide stability largely dictates the possibility of generating a sulphur-rich silicic derivative because, given their high density, sulphides can easily settle out from the host magma. Thus, to produce a sulphur-rich rhyolite supposes that during fractionation the basalt

does not crystallize significant amounts of sulphide. Generation of peralkaline rhyolites by fractionation of alkali basalt requires 80–90% crystallization (e.g. Barberi *et al.*, 1975; Ayalew *et al.*, 2002). Alkali basalts typically have bulk H<sub>2</sub>O contents of at least 1 wt %, CO<sub>2</sub> contents sometimes higher than 1 wt %, and sulphur contents that can exceed 1000 ppm (Clocchiatti *et al.*, 1992; Dixon *et al.*, 1997; Bureau *et al.*, 1999; Wallace, 2002). They evolve at  $f_{\text{O}_2} \leq \text{NNO}$  (Dixon *et al.*, 1997). We have, therefore, calculated the conditions under which alkali basalts become saturated in sulphide during crystallization, for bulk H<sub>2</sub>O–CO<sub>2</sub> contents of 1–2 wt % as inferred from studies of modern analogues



**Fig. 5.** Relative amounts of sulphur hosted in the sulphide and in the fluid in a crystallizing basalt with 1000 ppm sulphur. (a) Proportion of bulk sulphur locked in sulphide during the crystallization of a hydrous basalt (1 wt % H<sub>2</sub>O), calculated for four  $f_{O_2}$  values. Under these conditions (i.e. no CO<sub>2</sub> present) there is no fluid phase so the remaining sulphur is in the residual melt. (b) Proportion of bulk sulphur dissolved in the fluid during the crystallization of a H<sub>2</sub>O–CO<sub>2</sub>-bearing basalt calculated for various  $f_{O_2}$  values. The presence of CO<sub>2</sub> promotes early fluid saturation and, as a result, a significant part of the sulphur present in the system goes into the fluid phase. The curve labelled 2 wt % H<sub>2</sub>O + CO<sub>2</sub> corresponds to the case where the bulk H<sub>2</sub>O and CO<sub>2</sub> are each set at 2 wt % . All other curves are for 1 wt % H<sub>2</sub>O and 1 wt % CO<sub>2</sub>.

(Dixon *et al.*, 1997; Gerlach *et al.*, 2002; Lange, 2002), using a  $S_{\text{bulk}}$  of 0.1 wt %, and over a range of plausible redox conditions from NNO – 2 to NNO + 1 (Fig. 4). We also have calculated the corresponding proportions of bulk sulphur partitioned into sulphide and fluid phases (Fig. 5).

*Melt compositions used.* We used the basalt–rhyolite sequence of the Boina centre in the Afar rift (Barberi *et al.*, 1975) as a proxy for the evolution of liquid compositions in a fractionating, mildly alkaline basalt series. Although we could have used a thermodynamic model to simulate this evolution, available models still fail to

reproduce the transition from metaluminous to peralkaline melts, a feature that is critical for the understanding of sulphur behaviour, as shown below. The petrological and geochemical study of the Boina volcano concluded that the silicic magmas were derived from fractional crystallization of transitional basalt (Barberi *et al.*, 1975). Five representative compositions were used here: G485, S52, D237, D210, D224B (Barberi *et al.*, 1975) (see Table 2). The degree of crystallization was determined using the K<sub>2</sub>O content, assuming perfectly incompatible K<sub>2</sub>O behaviour during crystallization, a reasonable assumption except for composition D224B



Table 3: Melt compositions used in the calculations

Boina	$T$ (°C)	Melt fraction (wt %)	SiO <sub>2</sub> (wt %)	Al <sub>2</sub> O <sub>3</sub> (wt %)	FeO (wt %)	MnO (wt %)	MgO (wt %)	CaO (wt %)	Na <sub>2</sub> O (wt %)	K <sub>2</sub> O (wt %)	TiO <sub>2</sub> (wt %)	Total (wt %)	H <sub>2</sub> O (wt %)	S (ppm)	S max (ppm)	NK/A
G485	1200	100.00	46.75	13.93	10.96	0.19	9.75	10.08	2.70	0.80	2.30	97.46	1.00	1000	1000	0.38
S52	1088	72.73	46.03	14.80	13.67	0.12	6.04	10.36	3.00	1.10	2.50	97.62	1.38	1375	1375	0.41
D237	942	37.21	56.81	13.88	10.00	0.29	2.13	5.04	5.00	2.15	1.76	97.06	2.69	2688	1290	0.76
D210	890	24.46	59.44	15.00	7.26	0.21	1.76	4.00	4.97	3.27	1.82	97.73	4.09	4088	850	0.78
D224B	861	17.70	69.91	13.14	4.07	0.14	0.01	0.71	5.95	4.52	0.43	98.88	5.65	5650	480	1.12

Melt compositions from Barberi *et al.* (1975). Column melt fraction gives the amount of residual melt calculated assuming that liquid G485 is parental to all others and that K<sub>2</sub>O behaves as a perfectly incompatible element. Column H<sub>2</sub>O gives the H<sub>2</sub>O content of the residual melt in the case of a basalt melt crystallizing without CO<sub>2</sub>. Column S gives the melt sulphur content if sulphur behaves as a perfectly incompatible element (no sulphide crystallization and no fluid saturation). Column S max gives the melt sulphur content corrected for sulphide crystallization ( $a_{\text{FeS}} = 1$ ) for an  $f_{\text{O}_2}$  at NNO – 2 and with no CO<sub>2</sub> present. Column NK/A is the (Na<sub>2</sub>O + K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub> molar ratio of melts.

in which K-feldspar crystallizes, and thus for which the extent of crystallization relative to the parent basalt G485 is a minimum. The following proportions of residual liquids were calculated: S52, 73%; D237, 37%; D210, 24%; D224B, 18%. This natural liquid line of descent shows that peralkaline rhyolites can be produced from basalt crystallization after *c.* 80 wt % crystallization (Table 3, composition D224B). Temperatures were calculated assuming a linear relationship between melt fraction and  $T$ , and using a liquidus of 1200°C for basalt G485 and 890°C for the rhyodacite D210 (Table 3). Clearly, such an approximation is unlikely to be valid in detail. We are, however, interested in fixing the general behaviour of C–H–O–S volatiles in a crystallizing basalt, for which we need to know the approximate amount of residual melt available at each temperature in order to calculate the partitioning of each volatile species between melt and fluid using mass-balance constraints and solubility laws (see below). Any departure from a linear trend will either promote or delay the attainment of volatile and sulphide saturation. This will not affect, however, the general conclusion derived from our analysis, which concerns the importance of the role of CO<sub>2</sub>. In addition, we note that our assumption of linearity predicts a temperature of 861°C for the peralkaline rhyolite D224B, which is in reasonable agreement with available estimates for such compositions (Bizouard *et al.*, 1980; Ayalew *et al.*, 2002; Nekvasil *et al.*, 2004). All calculations described below were performed for a pressure of 150 MPa, as our experimental results were collected at this pressure.

*Solubility and activity models.* For a given initial volatile content and residual melt fraction, the amount of volatiles dissolved in the melt was calculated using the solubility models for H<sub>2</sub>O and CO<sub>2</sub> of Dixon *et al.* (1995). In the absence of appropriate solution models for both H<sub>2</sub>O and CO<sub>2</sub> in intermediate melt compositions, those for basalt were used. For sulphur we use the solubility model of

Scaillet & Pichavant (2005). The latter is an empirical model that allows us to relate the melt sulphur content to the sulphur fugacity, for a variety of melt compositions, including hydrous basalts. This model was derived in an attempt to evaluate the behaviour of sulphur in hydrous mafic magmas, for which there are few experimental data [apart from those of Luhr (1990)]. The model has the form

$$\log S = aP + bT + c\Delta\text{NNO}^3 + d\Delta\text{NNO}^2 + e\Delta\text{NNO}\Delta\text{FFS} + f\Delta\text{FFS} + \sum g_i W_i \quad (1)$$

where  $S$  is the total sulphur concentration in ppm,  $P$  the pressure in bars,  $T$  the temperature in °C,  $\Delta\text{NNO}$  and  $\Delta\text{FFS}$  are the referenced  $f_{\text{O}_2}$  and  $f_{\text{S}_2}$  against the Ni–NiO and Fe–FeS solid buffers respectively,  $W_i$  represents the weight % of oxide  $i$ , and  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ ,  $f$  and  $g_i$  are fitted parameters (Table 4) that were obtained by linear regression of the experimental databases of Luhr (1990), O'Neill & Mavrogenes (2002) and Clemente *et al.* (2004). The summation is carried out over all major oxides, including FeO, Fe<sub>2</sub>O<sub>3</sub>, OH<sup>–</sup> and H<sub>2</sub>O. This third-order polynomial function is necessary to reproduce the inverted bell-shaped pattern of sulphur solubility in silicate melts (e.g. Carroll & Webster, 1994; Clemente *et al.*, 2004), and the crossed  $f_{\text{O}_2}$ – $f_{\text{S}_2}$  term is needed to take into account the effect of varying  $f_{\text{S}_2}$  on the relationship between  $f_{\text{O}_2}$  and  $S$  in melt (Clemente *et al.*, 2004). This model encompasses a large SiO<sub>2</sub> range (35–80 wt %), and reproduces measured  $f_{\text{S}_2}$  within an average of 0.65 log unit, over more than 15 log units when normalized to the FFS solid buffer. Finally, it should be noted that the model of Scaillet & Pichavant (2005) is calibrated only for metaluminous compositions, which implies that sulphur solubilities of intermediate or silicic peralkaline compositions corresponding to any given  $f_{\text{S}_2}$  are underestimated by this model and thus that

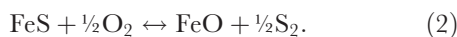
Table 4: Regression coefficients for the empirical model of sulphur solubility

$P$	7.28E-06
$NNO^3$	0.00488128
$NNO^2$	0.0818873
$NNOFFS$	-0.0224068
$T$	0.00084107
$FFS$	0.22801636
$SiO_2$	-0.012467
$Al_2O_3$	-0.0015766
$Fe_2O_3$	0.37362348
$FeO$	0.0674383
$MgO$	0.01121929
$CaO$	0.02000831
$Na_2O$	0.05644745
$K_2O$	-0.0248037
$TiO_2$	0.00672403
$H_2O$	0.06868295
$OH$	0.05778453

From Scaillet & Pichavant (2005).

sulphide activities calculated here for those melts are overestimated (see below).

For any  $fO_2$  and  $fS_2$ , the activity of FeS in the melt was calculated from the following equilibrium, using thermodynamic data from O'Neill & Mavrogenes (2002):



The activity of FeO in the melt was calculated by determining the  $Fe^{2+}/Fe^{3+}$  ratio of the melt using the Kress & Carmichael (1991) method and an activity coefficient for FeO of 1.4 (O'Neill & Mavrogenes, 2002). For any melt in which the calculated FeS activity was found to exceed unity, the melt sulphur content was fixed to that corresponding to an  $a_{FeS} = 1$ , and the excess sulphur was converted to sulphide (we thus neglect the role of additional elements such as Ni or Cu that could promote early saturation in sulphide).

The fluid phase composition was calculated using a Modified Redlich–Kwong type equation of state (MRK), using as input parameters  $fH_2O$ ,  $fCO_2$  and  $fS_2$ . It must be stressed that, regardless of our current knowledge or body of experimental constraints on the sulphur content of fluids in magmas, the sulphur content of a fluid coexisting with a silicate melt can be calculated using a thermodynamic approach, provided that appropriate solubility laws exist for the main volatile species. This stems from the fact that in the C–O–H–S system, once  $fH_2O$ ,  $fCO_2$  and  $fS_2$  are fixed (at  $P$  and  $T$ ), the fugacities of all other volatile species are fixed as well (Holloway,

1987; Scaillet & Pichavant, 2003, 2004). In other words, the composition of the fluid is uniquely defined, including its sulphur content. This allows us to compute the partition coefficients of sulphur between fluid and melt, as the melt sulphur content is fixed by  $fS_2$  (and  $fO_2$ ). The accuracy of such an approach relies, among other things, on our knowledge of the thermodynamic properties of C–O–H–S fluids, which appear to be reasonably well known (e.g. Shi, 1992), at least in the low-pressure range (<1000 MPa). Using this approach, Scaillet & Pichavant (2003) showed that there was a good overall agreement between calculated and measured fluid compositions for silicic arc magmas. The same method has been applied to active basaltic volcanoes (Scaillet & Pichavant, 2005), for which remote sensing of volcanic gases can be used to constrain the gas chemistry at depth. In this case too, generally good agreement is observed (Scaillet & Pichavant, 2005). Therefore, although we recognize that the current experimental database on the sulphur content of fluids of mafic magmas is almost non-existent, this gap can be partly circumvented by using a thermodynamic approach, which, when compared with independent estimates, appears to retrieve the correct order of magnitude in terms of the sulphur content of magmatic fluids.

*Procedure.* For any given initial  $H_2O$ ,  $CO_2$  and S contents, the equilibrium distribution of those volatiles between melt, fluid and sulphide was calculated via an iterative procedure by finding the fugacities that satisfy the following two sets of conditions: first, the condition of chemical equilibrium:

$$fH_2O_{melt} = fH_2O_{fluid} \quad (3)$$

$$fCO_{2melt} = fCO_{2fluid} \quad (4)$$

$$fS_{2melt} = fS_{2fluid}; \quad (5)$$

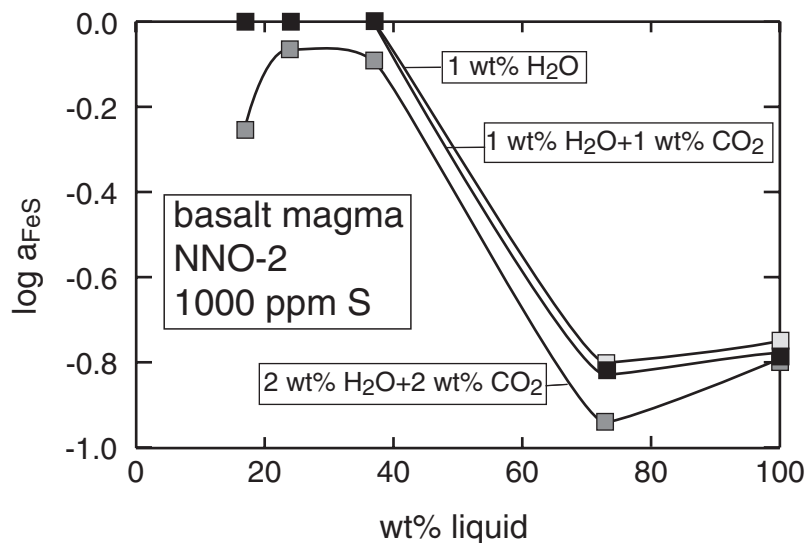
second, the mass-balance constraints:

$$H_2O_{total} = H_2O_{melt} + H_2O_{fluid} \quad (6)$$

$$CO_{2total} = CO_{2melt} + CO_{2fluid} \quad (7)$$

$$S_{total} = S_{melt} + S_{fluid} + S_{sulphide}. \quad (8)$$

The mass-balance equations also take into account the amounts of C, S and H in other species such as  $H_2S$ ,  $SO_2$ ,  $CO$  and  $CH_4$ . In the  $H_2O$ -only case, with a bulk  $H_2O$  content of 1 wt %, we considered that the crystallizing basalt does not reach fluid-saturated conditions, as the  $H_2O$  content of the residual melt reached after 82% crystallization is 5.65 wt % (Table 3), which is on the verge of  $H_2O$  saturation of rhyolitic melts at



**Fig. 6.** Effect of bulk H<sub>2</sub>O and CO<sub>2</sub> contents on the sulphide activity (log scale) of a crystallizing basalt at an  $fO_2$  of NNO – 2. It should be noted that when there is a large amount of CO<sub>2</sub> in the magma (i.e. the 2 wt % case), the coexisting fluid can scavenge a significant proportion of the bulk sulphur such that the system does not reach saturation in sulphide even after 80% of crystallization.

150 MPa (e.g. Zhang, 1999). In this case, the sulphur was partitioned between melt and sulphide only.

Let us consider, as an example of the calculation procedure, the case of a basalt carrying only H<sub>2</sub>O and sulphur crystallizing at an  $fO_2$  of NNO – 2. At 890°C, the basalt has 24.46 wt % residual liquid with a composition of D210 (Table 3). If sulphur had a perfectly compatible behaviour (bulk S of 1000 ppm), then the melt composition D210 would have 4088 ppm of dissolved sulphur (1000/0.2446). Using the model of Scaillet & Pichavant (2005), this amount of dissolved sulphur would correspond to an  $fS_2$  of 0.035 MPa, or to an  $aFeS = 18$  when calculated using equilibrium (2) and the assumptions given above. Clearly, there is too much sulphur in solution and some of it must be withdrawn to decrease the  $aFeS$  to unity, because by definition the activity of FeS cannot increase beyond unity (for appropriate standard states for solids and liquids at  $P$  and  $T$ ). The next step is thus to remove the excess sulphur in solution in the melt until the calculated  $fS_2$  corresponds to an  $aFeS = 1$ , and convert that excess sulphur into immiscible/solid sulphide [considering also the constraints set out in equations (3)–(8)]. For that specific case, using equation (1), we calculate that saturation of melt composition D210 with sulphide ( $aFeS = 1$ , because we perform an equilibrium calculation,  $aFeS$  in the silicate liquid is equal to that in the sulphide) is achieved when  $fS_2 = 10^{-4}$  MPa at 890°C and NNO – 2, which corresponds to a melt sulphur content of 850 ppm. In other words, this means that of the 1000 ppm sulphur dissolved in the molten basalt at 1200°C, 208 ppm ( $850 \times 0.2446$ ) are dissolved in the residual melt at 890°C, the remainder (792 ppm =  $1000 - 208$ ) being locked up in sulphide, as under these

conditions no fluid is present [Table 3; the melt water content is below the saturation value of an andesitic melt at 150 MPa (Burnham, 1979)]. The introduction of CO<sub>2</sub> into the system promotes early fluid saturation and thus the sulphur content of melt at 890°C (i.e. when there is only 24.46 wt % residual melt) must be lower than when only H<sub>2</sub>O is present. For instance, implementing the example above with addition of CO<sub>2</sub> (i.e. a basalt with 1 wt % H<sub>2</sub>O and 1 wt % CO<sub>2</sub> at NNO – 2), we calculate that at 890°C the sulphur content of the residual melt is 635 ppm. Finally, as noted above, peralkaline melts dissolve more sulphur than metaluminous types, so our calculated sulphide proportions should be considered maxima for the most fractionated melt (D224B, Table 3). Assuming, on the basis of our experimental results, that the peralkaline melt D224B dissolves five times more sulphur than that calculated by the model of Scaillet & Pichavant (2004), or 4250 ppm, then it follows that such compositions would be barely saturated at NNO – 2, the proportion of sulphide being low. This implies that the amounts of CO<sub>2</sub> needed to scavenge the sulphur toward the fluid, which under our  $P$ – $T$  conditions is calculated to be 2 wt % (see below), must be considered maximum values where peralkaline derivatives are produced.

### Results

The results of our calculations are shown on Figs 4–6. We have considered three cases corresponding to different bulk volatile contents: case (1), 1 wt % H<sub>2</sub>O and 1000 ppm sulphur; case (2), 1 wt % H<sub>2</sub>O, 1 wt % CO<sub>2</sub> and 1000 ppm sulphur; case (3), 2 wt % H<sub>2</sub>O, 2 wt %

CO<sub>2</sub> and 1000 ppm sulphur. Figure 4a shows the evolution of  $a_{\text{FeS}}$  of a basalt with degree of crystallization, calculated at four  $f_{\text{O}_2}$  values. An H<sub>2</sub>O-bearing (1 wt %) but CO<sub>2</sub>-free alkali basalt crystallizing at or above NNO – 1 is sulphide-saturated after *c.* 60% of crystallization. At NNO – 2, saturation in sulphide is slightly delayed, to 70% crystallization. Figure 5a shows the evolution of the proportion of bulk sulphur sequestered in sulphide with degree of crystallization, corresponding to the calculations shown in Fig. 4a. By the time the residual melt is peralkaline (20–30% liquid; see Table 2), it can be seen that 90 wt % of  $S_{\text{bulk}}$  is locked up in sulphide (Fig. 5a). Further crystallization results in massive sulphide precipitation; after 82% crystallization more than 80 wt % of  $S_{\text{bulk}}$  is locked up in sulphide. The calculations corresponding to case (2) illustrate the role of CO<sub>2</sub>. When this volatile is introduced, the sulphur behaviour is dramatically altered because fluid saturation occurs at an early stage, owing to the low solubility of CO<sub>2</sub> in silicate melts (e.g. Dixon *et al.*, 1995) and chemical equilibrium demands that sulphur is also partitioned into the fluid, thus lowering  $S_{\text{melt}}$  and the activity of sulphide. With a bulk CO<sub>2</sub> content of 1 wt % and 1 wt % H<sub>2</sub>O [case (2)], similar to the bulk content inferred for Kilauean or Etnean basalts (Clocchiatti *et al.*, 1992; Gerlach *et al.*, 2002), the calculations show that sulphide saturation is slightly delayed compared with the H<sub>2</sub>O-only case (Fig. 4). However, the main difference relative to the CO<sub>2</sub>-free situation [case (1)] is that after 80% crystallization, at least 60% of  $S_{\text{bulk}}$  is in the fluid phase, whatever the prevailing redox conditions, rising to 90% for  $f_{\text{O}_2} = \text{NNO} + 1$  (Fig. 5b). Finally, case (3) shows that at  $f_{\text{O}_2} = \text{NNO} - 2$ , for initial CO<sub>2</sub> and H<sub>2</sub>O contents of 2 wt % each, a crystallizing alkali basalt remains below sulphide saturation, even after 80% crystallization when derivative liquids are rhyolitic (Fig. 6). Under these conditions 95% of  $S_{\text{bulk}}$  is hosted by the fluid, even after 80 wt % of crystallization (Fig. 5b).

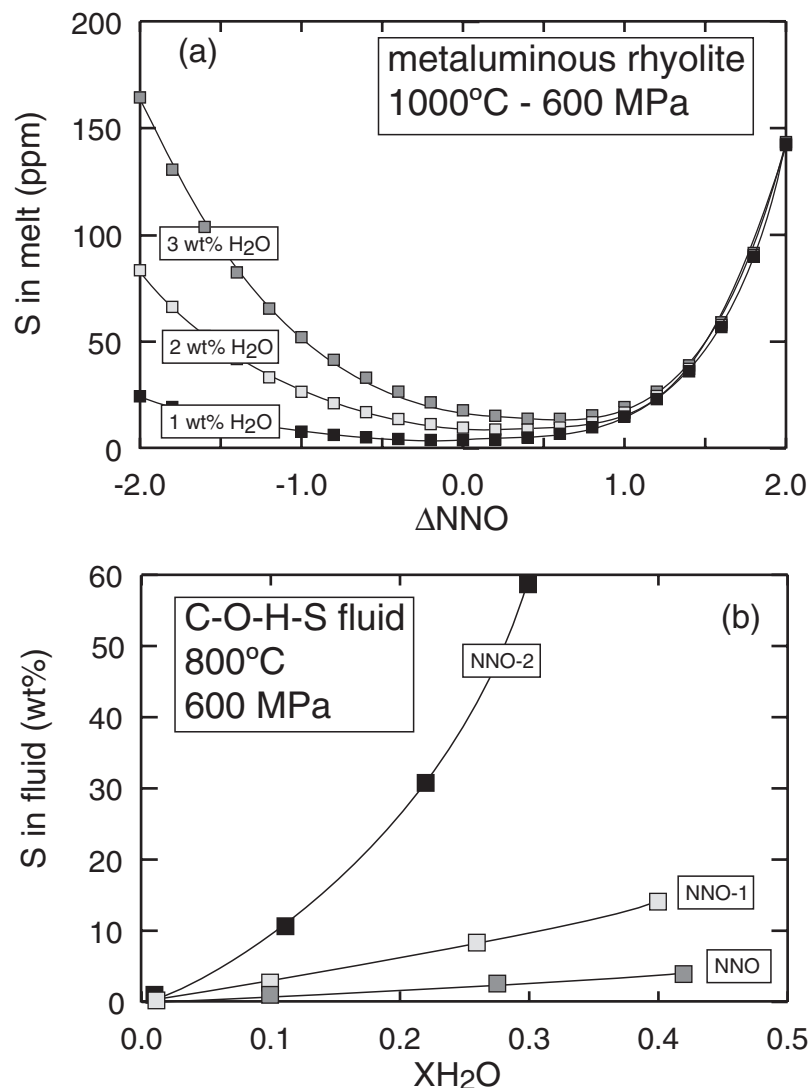
We stress that such elevated bulk volatile contents have been inferred for some alkali basalts (Dixon *et al.*, 1997), including those in flood sequences (Lange, 2002). In addition, recent experimental data on the generation of silica-saturated alkalic suites from alkali basalts suggest that the latter contain at least 0.5 wt % H<sub>2</sub>O, and possibly up to 2 wt % (Nekvasil *et al.*, 2004), which reinforces the view that trap basalts may be considerably richer in fluids than those at mid-ocean ridges. The above calculations show that, provided they are CO<sub>2</sub>- and H<sub>2</sub>O-rich, basaltic magmas can readily produce sulphur-rich derivatives, regardless of the imposed redox conditions. The amount of CO<sub>2</sub> appears to be the key parameter, as it triggers early volatile exsolution, which prevents sulphide precipitation. Without CO<sub>2</sub>,  $f_{\text{O}_2}$  exerts a prime control on the amount of sulphide crystallization in basalt with a certain initial sulphur content. A reduced CO<sub>2</sub>-poor

basaltic magma will yield silicic derivatives that are sulphur-poor owing to extensive sulphide precipitation, whereas a basalt crystallizing at or above NNO + 1, as in arc settings, may give rise to sulphur-rich silicic magmas (Scaillet & Pichavant, 2003; Scaillet *et al.*, 2003). The presence of CO<sub>2</sub> in large amounts significantly reduces this  $f_{\text{O}_2}$  control. If alkali basalts are CO<sub>2</sub>-rich, they can release >90% of their  $S_{\text{bulk}}$  during crystallization. After the stage of rhyolite production, the ultimate fate of sulphur will be dictated by the composition of the melt, particularly its NK/A ratio (in addition to  $f_{\text{O}_2}$ ; Scaillet *et al.*, 1998). As our experimental data show, metaluminous felsic magmas can carry less sulphur in solution than peralkaline types, especially at low  $f_{\text{O}_2}$ . We conclude that if alkali basalt fractionation produces peralkaline rhyolites, these may well be sulphur-rich, concentrating a significant proportion of the original sulphur content of the parent magma.

## Crustal origin

### Method

To constrain the sulphur content of silicic melts produced by partial melting of the lower crust, we have calculated the sulphur contents of (1) anatectic melts and (2) metamorphic fluids in the amphibolite–granulite facies. The sulphur content of crustal melts can be calculated using the solubility model for sulphur of metaluminous rhyolites derived by Clemente *et al.* (2004), as dehydration melting of mid- to lower crustal lithologies produces dominantly metaluminous or peraluminous silicic melts (Clemens & Vielzeuf, 1987). The ambient  $f_{\text{S}_2}$  conditions during crustal melting are likely to be controlled by sulphide equilibria, such as pyrite–pyrrhotite (Poulson & Ohmoto, 1989). Under lower crustal conditions, this equilibrium fixes  $f_{\text{S}_2}$  at *c.* 0.1 MPa (Shi, 1992). Therefore, the calculations were performed by fixing  $f_{\text{O}_2}$ ,  $f_{\text{H}_2\text{O}}$  and  $f_{\text{S}_2}$ , at  $f_{\text{O}_2}$  ranging from NNO – 2 to NNO + 2, which are likely to encompass redox conditions in the lower crust. We explored specifically the sulphur solubility for three melt H<sub>2</sub>O contents, 1, 2 and 3 wt %, as we are interested in anatectic melts that are relatively dry (see below). At any  $f_{\text{O}_2}$ , fixing the melt water content fixes  $f_{\text{H}_2\text{O}}$  [using the thermodynamic model of H<sub>2</sub>O solubility of Zhang (1999)] and thus  $f_{\text{H}_2}$ . Given that we set  $f_{\text{S}_2}$  as constant, this allows us to calculate  $f_{\text{SO}_2}$  and  $f_{\text{H}_2\text{S}}$ , which are then used as input parameters in the thermodynamic model of Clemente *et al.* (2004), from which the amount of sulphur dissolved in the rhyolitic melt arising from the additive contributions of H<sub>2</sub>S and SO<sub>2</sub> species is derived. For metamorphic fluids, we have calculated the sulphur content of a C–O–H–S fluid phase likely to be present in the mid- to lower crust, assuming again an  $f_{\text{S}_2}$  controlled by the pyrrhotite–pyrite equilibrium (i.e.  $f_{\text{S}_2} = 0.1 \text{ MPa}$ ).



**Fig. 7.** Sulphur content of crustal melts produced during partial melting of previously dehydrated hot lower crust, such as proposed for the origin of the Paraná–Etendeka flood rhyolites. (a) Variation with  $f_{\text{O}_2}$  ( $\Delta\text{NNO}$ ) of the melt sulphur content of H<sub>2</sub>O-poor metaluminous rhyolitic magmas, calculated for three bulk melt water contents, using the solubility model of Clemente *et al.* (2004). In all cases the sulphur fugacity has been set at 0.1 MPa. (b) Sulphur content of a C–O–H–S metamorphic fluid, calculated for various mole fractions of H<sub>2</sub>O (i.e. various  $f_{\text{H}_2\text{O}}$ ) in the fluid, three  $f_{\text{O}_2}$  values and an  $f_{\text{S}_2}$  of 0.1 MPa, which corresponds to the pyrite–pyrrhotite equilibrium (Shi, 1992). The calculations are done using an MRK equation of state (Holloway, 1987). The difference to 100% on the ordinate scale corresponds to fluid species other than S and H<sub>2</sub>O, i.e. CO<sub>2</sub>, CO, CH<sub>4</sub>. The sulphur contents of the fluid are intended to model the sulphur content of putative metamorphic fluids that have scavenged the lower crust of most of its volatiles prior to widespread melting.

To this end we have used the MRK equation of state introduced above and explored various  $f_{\text{O}_2}$  conditions likely to encompass crustal redox states as well as various water activities (expressed as  $X_{\text{H}_2\text{O}}$  in Fig. 7b). As detailed for the basalt above, we fix  $f_{\text{O}_2}$ ,  $f_{\text{H}_2\text{O}}$  and  $f_{\text{S}_2}$  as input parameters to calculate the fluid phase composition. The temperature at which we calculate the composition of metamorphic fluids, 800°C, is lower than that considered for anatexis (1000°C), as we are interested in the amount of sulphur that can be transported in

metamorphic fluids prior to widespread partial melting. In summary, as for the crystallization of basalt detailed above, we have calculated the equilibrium sulphur contents of a fluid and a rhyolitic melt, under  $P$ – $T$ – $f_{\text{O}_2}$ – $f_{\text{S}_2}$  conditions considered likely to prevail in the lower crust. By comparing the sulphur contents of crustally derived metaluminous melts with those of metamorphic fluids, we aim to constrain the overall behaviour of sulphur in hot mid- to lower crust flushed by melts or fluids.



## Results

Figure 7a shows that the sulphur content of silicic melts for melt water contents  $\leq 3$  wt % and  $fO_2$  in the range  $NNO - 2$  to  $NNO + 1$ , all calculated for an  $fS_2$  of 0.1 MPa, does not exceed 200 ppm. In contrast, the sulphur content of metamorphic fluids under similar  $P$ – $T$ – $fO_2$  conditions is strongly dependent on  $fO_2$  and water fugacity, and it reaches several wt %, except for nearly dry conditions (Fig. 7b). From Fig. 7a, we conclude that silicic melts produced in the mid- to lower crust are unlikely to reach values of  $S_{melt}$ , and thus  $S_{bulk}$  if extracted from their source, much higher than 200 ppm. This value should be considered as a maximum for the following reasons. First, the sulphur content of the lowercrust is estimated to be *c.* 400 ppm (Wedepohl, 1995), which indicates a rather small sulphur buffering capacity during melting. Second, crustal melts associated with flood basalts record temperatures in the range 900°C to >1100°C (Bellieni *et al.*, 1986; Harris & Erlank, 1992; Garland *et al.*, 1995; Harris & Milner, 1997; Ewart *et al.*, 1998, 2004), which has led to the suggestion that such felsic magmas were produced from previously dehydrated crust (Kilpatrick & Ellis, 1992). The dehydration event could have involved fluids and/or melts but in any case, in view of the sulphur content of such melts/fluids (Fig. 7), such a dehydration event is likely to have removed most of the sulphur budget of the crustal protolith. Subsequent partial melting of dehydrated lower crust is, thus, unlikely to produce sulphur-rich magmas.

## Summary

We thus envisage basalt-derived rhyolites as magmas that can potentially carry several thousands of ppm of sulphur, either dissolved in the melt or in a separate fluid phase, with only minor amounts trapped in coexisting sulphide, especially when they are peralkaline. In contrast, the sulphur content of crustally derived melts is calculated to be less than 200 ppm, especially if formed from dehydrated lower crust.

## DISCUSSION

### Sulphur yields of Ethiopian, Deccan and Paraná–Etendeka silicic rocks

We first address the Ethiopian sequences for which the pre-eruptive sulphur contents are reasonably well known, melt inclusion analyses having yielded  $S_{melt}$  in the range 400–500 ppm (Ayalew *et al.*, 2002). The NK/A ratios of Ethiopian rhyolites range from *c.* 1 to 1.4, which corresponds to the two less peralkaline samples used in our experiments. Pre-eruptive temperatures have been estimated at 740–900°C. The pre-eruptive water content is not well known but similar rhyolites from the Ethiopian rift

had melt  $H_2O$  contents of 4–8 wt % (Webster *et al.*, 1993). Redox states are poorly constrained, yet such rhyolites are generally inferred to evolve at  $fO_2 < NNO$  (e.g. Mahood, 1984; Scaillet & Macdonald, 2001; White *et al.*, 2005). High water contents are consistent with 80–90% crystallization of parent alkali basalts (Ayalew *et al.*, 2002) with an initial bulk  $H_2O$  content of 1 wt %. If fractionation occurs at shallow levels (<200 MPa), then  $H_2O$  saturation of the liquid will occur after 80% crystallization if no  $CO_2$  is present, or earlier with  $CO_2$ . At 150 MPa, a basalt with 1 wt %  $H_2O$  initially can yield a rhyolite magma with 5–6 wt % dissolved  $H_2O$  coexisting with 4–6 wt % fluid, provided that both melt and fluid have left their source. The amount of free fluid might well be larger, however, as this estimate does not include  $CO_2$ . Using a conservative bulk initial S content of 1000 ppm for the parental basalt, then rhyolite produced after 90% crystallization will potentially carry up to 1 wt % sulphur. With this  $S_{bulk}$  and at  $fO_2 < NNO$ , moderately peralkaline rhyolites dissolve 200–300 ppm sulphur at 800°C, or 400–500 ppm at 900°C (Fig. 1a). The sulphur content of the coexisting fluid phase ranges between 6 and 10 wt % (Table 1). The fact that the sulphur contents of both natural and experimental melts compare closely indicates that the chosen experimental conditions broadly correspond to those of magma storage before eruption.

We can now evaluate the potential sulphur delivery to the atmosphere by the Ethiopian rhyolites, whose estimated volume is 60 000 km<sup>3</sup> (dense rock equivalent or DRE, Ayalew *et al.*, 2002). Assuming that such magmas coexisted with 5 wt % fluid, the bulk sulphur erupted ranges from  $4.3 \times 10^{17}$  g for an  $S_{fluid}$  of 6 wt % to  $7.3 \times 10^{17}$  g for  $S_{fluid}$  of 10 wt %. These estimates are one order of magnitude higher than previous figures (Ayalew *et al.*, 2002), basically because the fluid contribution, in which 90% of the sulphur in melt + fluid is stored, has been taken into account.

Evaluation of the sulphur yield of the Paraná–Etendeka silicic eruptives is somewhat simpler. The magmas have been inferred to be nearly dry, on the basis of elevated temperature estimates and lack of hydrous phenocrysts (Ewart *et al.*, 1998, 2004), indicating that they were probably not fluid-saturated at depth. This essentially restricts their atmospheric sulphur yield from melt degassing during ascent to the surface. Using an estimated volume of 20 000 km<sup>3</sup> (Harris & Milner, 1997) and a conservative pre-eruptive  $S_{melt}$  content of 100 ppm, we calculate that these silicic magmas were capable of delivering no more than  $4.6 \times 10^{15}$  g of sulphur to the atmosphere when fully degassed, or almost two orders of magnitude less than the Ethiopian contribution, for comparable volumes of erupted magmas.

The Deccan flood basalts are associated with minor amounts of silicic rocks, estimated to reach 500 km<sup>3</sup>

(Lightfoot *et al.*, 1987). Although a partial melting origin from basalt protoliths has been advocated (Lightfoot *et al.*, 1987), the Deccan rhyolites share most of the major element characteristics of the Ethiopian sequences. In particular, they are strongly peralkaline, which is marked, *inter alia*, by very high Zr concentrations compared with metaluminous rhyolites. The high solubility of Zr in peralkaline rhyolites is a well-established feature (e.g. Watson, 1979; Linnen & Keppler, 2002; Scaillet & Macdonald, 2003).

Assuming that the sulphur yield of Deccan rhyolites scales with that of the Ethiopian rhyolites, between  $3.6 \times 10^{15}$  and  $6.1 \times 10^{15}$  g of sulphur could have been emitted. However, pre-erosional volumes of silicic magmas may have been much larger than the current outcrop (Bryan *et al.*, 2002). Javoy & Courtillot (1989), for example, have suggested that a short-term variation in the seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio at the Cretaceous–Tertiary boundary could have been due to intense silicic volcanism related to the Deccan basalts, and estimated their volume to about  $50\,000\text{ km}^3$ , which is comparable with that of the Ethiopian rhyolites. If it is assumed that Deccan basalts were somehow able to produce peralkaline derivatives at the same yield as in Ethiopia (thereby producing roughly twice the Ethiopian silicic volumes), the Deccan rhyolites could have produced  $0.9 \times 10^{18}$  to  $1.5 \times 10^{18}$  g of S, comparable with the estimate for the basalt emissions alone (Wignall, 2001).

### Environmental consequences

The most common explanation for the formation of Large Igneous Provinces, including continental flood basalt sequences (Coffin & Eldholm, 1994), is that they result from periodic mantle–core instability that generates hot mantle plumes, which, via adiabatic melting, lead to a widespread but short-lived melting episode when the plume reaches shallow mantle levels. Much recent interest in flood basalt activity has stemmed from the recognition that there is a strong correlation between periods of major basalt eruption and worldwide environmental crises such as mass extinctions and oceanic anoxic events (e.g. Courtillot & Renne, 2003). A causal link between those two events has, therefore, been claimed (e.g. Vogt, 1972; Morgan, 1981; Courtillot, 1999; Rampino & Self, 2000; Courtillot & Renne, 2003). Establishing whether such a causal link indeed exists rests primarily on (1) obtaining precise timing constraints for the geological events and (2) evaluating the volatile contributions of flood events to the atmosphere, as it is thought that massive emissions of climate-sensitive volatile species are a major contributing factor to global climate change. In particular, the volcanic hypothesis of mass extinctions hinges critically on the injection of massive amounts of volcanic sulphur

into the atmosphere, which, in addition to  $\text{CO}_2$ , is one of the controlling factors of climate variability (Robock, 2000).

Whereas decisive progress has been made in recent years with respect to the effects of  $\text{CO}_2$  (see Courtillot & Renne, 2003), our ability to analyse the role of S emissions has been less successful. Sulphur emissions of past flood events have been largely evaluated using simple scaling arguments, which assume that present-day magmas have a sulphur content comparable with those erupted during flood eruptions, basically because, in most instances, it is the only approach that can be applied, especially when the events considered are old, in which case critical data needed to assess sulphur yield, in particular glassy melt inclusions, are lacking. For instance, the 1783–1784 Laki fissure eruption on Iceland and its climate aftermath (Métrich *et al.*, 1991; Thordarson *et al.*, 1996; Thordarson & Self, 2003) is often taken as a representative, yet smaller-scale, scenario for the environmental consequences of flood basalt emissions (e.g. Eldholm & Thomas, 1993; Stone, 2004). For silicic compositions, it is well established, however, that such an approach can lead to dramatic under- or over-estimations of the sulphur content of the original magmas (Scaillet *et al.*, 1998). As shown for andesite and rhyolite in arc settings, the sulphur content at the time of eruption can differ by orders of magnitude between magmas having similar compositions but different redox states (Scaillet *et al.*, 1998). The present study illustrates an additional factor to be considered when assessing the sulphur yield of silicic magmas; that is, their Na + K/Al ratio. For mafic magmas, given the vagaries of melt generation, storage and evolution in the mantle, there is no *a priori* reason to ascribe to flood basalts a common value for their sulphur content, and it remains to be established whether the scaling-up procedure yields correct numbers, although in most cases this is perhaps the only approach that we can use. Our analysis shows that the ultimate fate of sulphur in basalt will be heavily dependent on the bulk  $\text{CO}_2$  content of the system. It shows, though, that under near-liquidus conditions, most of the sulphur remains dissolved in the melt, even when the basalt coexists with considerable amounts of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . For instance, in Fig. 5b the case of a basalt at NNO – 2 with 2 wt %  $\text{H}_2\text{O} + \text{CO}_2$  shows that at near-liquidus conditions (i.e. more than 80% melt) the magma has less than 10% of its sulphur hosted by the fluid, the remaining sulphur being dissolved in the melt, as no sulphide is present under such conditions (i.e.  $a_{\text{FeS}} < 1$ , Fig. 6). This implies that, for eruptions involving crystal-poor basaltic magmas, estimates of atmospheric sulphur yields relying on the difference in sulphur contents between melt inclusions and matrix glasses (i.e. estimates that ignore the fluid contribution) will obtain figures which are close to real values, as

illustrated for recent basaltic eruptions for which independent estimates of sulphur yields using remote sensing methods are available (Sharma *et al.*, 2004).

In addition to these evaluation problems, the causal link between volcanoes and climate has been criticized on several grounds (Wignall, 2001), and in particular on the fact that volatiles emitted during effusive basaltic eruptions are unable to reach the upper atmosphere. Although theoretical studies have shown that flood activity can lead to stratospheric loading of magmatic volatiles (Woods, 1993), the effusive nature of basalt is still considered as a major shortcoming of the flood-basalt driven mass extinction hypothesis (Wignall, 2001). This is unlike the case for their silicic counterparts, which, owing to their explosive nature, are able to result in major stratospheric sulphur loading with regional to hemispheric dispersion (Rampino & Self, 1992). However, all studies aimed at evaluating such a hypothesis have exclusively considered flood volcanic activity and its attendant environmental impact to be due to basalt emissions and have ignored the role of associated silicic magmas. In fact, the generation of copious amounts of silicic magmas by melting of continental crust should be an expected consequence of plume impingement at the base of the continental crust (Javoy & Courtillot, 1989). Recent detailed thermal modelling studies have indeed confirmed that widespread production of felsic magmas, either via crystal fractionation of basalt magma or via partial melting of the surrounding crust, is an inescapable by-product of basalt intrusion in the lower crust (Annen & Sparks, 2002; Annen *et al.*, 2006). Thus, there exists the possibility that the overall volcanic events had a global, long-lasting, impact on climate through their silicic emissions. In this paper, we have attempted to evaluate the contribution of the silicic end-members of flood activity to atmospheric sulphur release and have shown that, in some cases at least, it may have been volumetrically as large as the associated basalts.

The Ethiopian Traps flood sequences coincided with a worldwide oceanic cooling event (Rochette *et al.*, 1998; Touchard *et al.*, 2003), whereas the Paraná–Etendeka eruptives are the only flood sequence not synchronous with a documented major environmental change or mass extinction event (Courtillot & Renne, 2003). Our results offer one explanation, namely the contrasted sulphur yields of the silicic activity. Besides this parameter, factors controlling eruption dynamics may also have played an important role. Water is critical in producing the high and sustained eruptive columns (Sparks *et al.*, 1997) that are required for global dispersion of volcanic volatiles via injection of magmatic volatiles into the stratosphere. The Ethiopian rhyolitic magmas were possibly cooler and richer in water than the Paraná–Etendeka rhyolites. We, thus, speculate that in the former case, the conditions of explosive eruption were easily achieved, and the

recent discovery of ash layers at several places in the Indian Ocean having the correct age and composition (Touchard *et al.*, 2003) is circumstantial evidence that at least part of the Ethiopian rhyolites were emitted during highly energetic eruptions. In contrast, the high to very high pre-eruption temperatures inferred for the Paraná–Etendeka silicic deposits point to rather low magma viscosity which, together with their anhydrous character, could have favoured a mostly effusive regime (Kirstein *et al.*, 2001), with much less potential for hemispheric stratospheric loading of its volatiles. Lastly, the recent thermal simulation results of Annen *et al.* (2006) of basalt intrusion at the base of the crust show that rhyolite production via fractionation of basalt occurs before that due to partial melting of the crust. In detail, the time interval between the onset of basalt intrusion (and emission) and the widespread production of silicic magmas is dependent on a number of factors (depth of intrusion, fertility of the crust, emplacement rate of basalt, ambient geotherm) and varies between 0.02 Myr and several million years in the case of slowly intruded mafic magmas. Yet, results show that rhyolite floods originated via partial melting will be erupted later than those produced by basalt fractionation. In addition to this incubation time, modelling shows clearly that the basalt fractionation mechanism for rhyolite generation has a higher productivity than partial melting of the crust. For instance, intrusion at 30 km depth of basalts with 2.5 wt % H<sub>2</sub>O, with 50 m thick sills injected every 10 kyr, is able to produce *c.* 18% of silicic melts via fractionation (18% relative to the total volume of intruded basalt) 500 kyr after the onset of the process, whereas, within the same time interval, partial melting of overlying amphibolite crust is able to yield only 3% of silicic melt (Annen *et al.*, 2006, fig. 10). The above lines of evidence (higher sulphur yield and explosivity, shorter incubation time and greater productivity) all combine to suggest that flood rhyolites formed via basalt fractionation are more likely to have a greater environmental impact than those that result from partial melting of the crust.

The foregoing discussion suggests that magmatic traps associated with silicic emissions can be tentatively classified into two main groups: those having produced dominantly metaluminous magmas and those associated with peralkaline rhyolites *sensu lato*. Given the generally poor preservation of silicic flood sequences (Bryan *et al.*, 2002), we can only speculate at this stage as to their classification. Silicic traps associated with the Karoo basalts are similar to those of Paraná–Etendeka (Harris & Erlank, 1992) and are associated with an extinction event that is minor considering the volume of erupted basalt (Wignall, 2001). On the other hand, the Emeishan Trap basalts, which are broadly coeval with the massive Permian–Triassic mass extinction, are associated with scarce silicic

eruptives of possible peralkaline affinity (Xu *et al.*, 2001). Given that most provinces display both metaluminous and peralkaline felsic rocks (Bryan *et al.*, 2002), it is also important to evaluate the proportions of each magma type.

Finally, we note that melting of crust in back-arc settings may be a particularly favourable locus for the generation of voluminous amounts of silicic magmas with only minor basalts, e.g. the Sierra Madre Occidental in western Mexico and Chon Aike in South America (Bryan *et al.*, 2002). Such rhyolites may have formed by crustal melting following protracted subduction zone magmatism, the latter having extensively hydrated the lower crust. Such a process could conceivably increase the sulphur content of the lower crust, given the high sulphur contents of arc magmas (Scaillet *et al.*, 2003). Melting of such protoliths may produce silicic melts rich in water and perhaps in sulphur.

## CONCLUSIONS

Our study shows that rhyolite magmas may act as an important conveyor of mantle sulphur toward the atmosphere, especially when their parental basalts are rich in volatiles, particularly CO<sub>2</sub>. We do not dismiss the important role played by the basaltic component in terms of volatile output. Our study simply suggests that, in addition to volumes of erupted basalt and the duration of peak activity, the environmental consequences of flood magmatism may or may not be greatly enhanced by their silicic component. When voluminous peralkaline derivatives are produced, their explosive emission may give the coup de grâce to the worldwide changes triggered by early basaltic emissions. We note that an alternative scenario to the conventional core–mantle origin of flood sequences is that trap basalts are rooted in an anomalously volatile-rich sublithospheric mantle (Anderson, 1994). Although still scanty, available evidence suggests that trap basalts are indeed richer in volatiles than those erupted at oceanic ridges (e.g. Lange, 2002; Rodriguez Durand & Sen, 2004). Given the generally poor preservation of silicic members, in particular in old sequences, we suggest that future studies aimed at evaluating the environmental consequences of flood activity focus on the evaluation of the volatile contents of basalts. In addition, a better petrogenetic understanding of the processes leading to peralkaline derivatives in bimodal suites is highly desirable.

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