S speciation in submarine basaltic glasses as determined by measurements of SKα X-ray wavelength shifts

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Abstract

S occurs in both oxidized (S\(^{6+}\)) and reduced (S\(^{2-}\)) forms in natural silicate liquids. The wavelength of SKα radiation changes as a function of the oxidation state of S and can be used to determine the proportions of sulfide and sulfate in unknown samples by comparison with reference standards of a known valence state. We have measured the wavelength of SKα X-rays in a variety of glassy submarine lavas from spreading centers (Juan de Fuca, Galápagos, Kane, and Southeast Indian Ridge), seamounts (Loihi and Lamont seamounts), and back-arc basins (Lau Basin). The relative \( f_{0\alpha} \) values of these glasses are known from wet-chemical determinations of FeO and Fe\(_2\)O\(_3\) and vary from slightly above the Ni + NiO buffer (NNO) to 3.2 log units below NNO. Measured values of sulfate/S\(_{\text{tot}}\) (S\(^{6+}/S\(_{\text{tot}}\)) vary from 0.02 to 0.25 and increase with increasing relative \( f_{0\alpha} \). Our results demonstrate that the dissolved S in these samples occurs predominately as S\(^{2-}\). Large variations in H\(_2\)O content have no measurable effect on the redox state of S, suggesting that H\(_2\)S or HS\(^-\) are not abundant S species in solution in silicate liquids. Thermodynamic calculations show that the speciation of S in coexisting gas during submarine eruptions of basaltic magma is also dependent on relative \( f_{0\alpha} \). Many lavas from seamounts and back-arc basins are predicted to have S present mainly as SO\(_2\) in coexisting magmatic gas, whereas the lower \( f_{0\alpha} \), of midocean ridge basalts favor H\(_2\)S as the dominant form of gaseous S.

Introduction

S occurs in silicate liquids as both reduced (S\(^{2-}\)) and oxidized (S\(^{6+}\)) species, and the relative proportions of the two appear to be largely controlled by the oxidation state of the liquid (Fincham and Richardson, 1954; Connolly and Haughton, 1972; Nagashima and Katsura, 1973; Katsura and Nagashima, 1974; Carroll and Rutherford, 1988). The effects of other factors such as temperature, pressure, bulk composition, and H\(_2\)O content on the S redox state and speciation are not clear but are important for understanding the stability of S-bearing minerals, sulfide liquid immiscibility, and degassing of S species from active volcanoes. The proportions of oxidized and reduced S (S\(^{6+}/S\(_{\text{tot}}\)) in quenched silicate liquids can be measured by the X-ray spectrometric technique of Carroll and Rutherford (1988). This technique is based on the wavelength shift of SKα radiation that is caused by variation in the S valence state and its effect on bond energies (Wilbur and Gofman, 1965).

Using this technique, we have measured (S\(^{6+}/S\(_{\text{tot}}\)) in 22 rapidly quenched, submarine glasses from a variety of tectonic settings, including spreading centers, propagating ridges, seamounts, and back-arc basins. In our previous work (Wallace and Carmichael, 1992a), we estimated preeruptive equilibration temperatures and the \( f_{0\alpha} \), \( f_{0\beta} \), and \( f_{0\gamma} \) for these samples, which allowed us also to examine any effects that variations in these intensive parameters may have on the S redox state. Our results provide new data on the speciation of S in basaltic magmas and the solution mechanisms by which sulfide dissolves in silicate liquids. Combined with thermodynamic calculations of the speciation of S in a coexisting gas phase, these results provide constraints on the effects of S loss during eruptions of basaltic magma.

Analytical Methods

The glass samples analyzed in this study are largely basaltic and span a wide range of bulk composition, magnetic \( f_{0\gamma} \), S\(_{\text{tot}}\) content, and preeruptive equilibration temperature. They include nepheline-normative alkali basalts, tholeiites, highly differentiated Fe- and Ti-rich basalts, and several andesites from the Lau Basin. Details concerning the major-element compositions of these glasses (except for the Lau Basin samples, which are given in the appendix) are presented in Wallace and Carmichael (1992a), along with information regarding FeO analyses and the calculation of relative \( f_{0\alpha} \).

Measurements of the wavelength of SKα radiation (\( \Delta \lambda(\text{SKα}) \)) for the glass samples were conducted using both an eight-channel ARL SEMQ electron microprobe at the
University of California at Berkeley and a four-channel Cameca SX-50 electron microprobe at the University of Chicago. With the former instrument, analyses were performed using ADP and PET crystals on two spectrometers, allowing two independent measurements to be made simultaneously, whereas the Cameca SX-50 was equipped with PET crystals on each of three spectrometers. Analyses performed with the two instruments yielded similar results. Operating conditions were an accelerating voltage of 15 kV, a beam current of 25–30 nA, a beam diameter of 10 μm, and a counting time of 20–40 s per spot for the glass samples and 5–10 s for the standards. Following the techniques of Carroll and Rutherford (1988), measurements of λ(\(\text{SKα}\)) in FeS were performed before and after each unknown, and all wavelength shifts are calculated relative to this standard. For each wavelength scan the spectrometers were moved through a total range of 0.005 sin θ units in 100 steps of 0.00005 sin θ units per step. For the glass samples the electron beam must be moved to a new spot after each step in the scan. Leaving the electron beam in a single spot longer than about 15 min causes an apparent increase in λ(\(\text{SKα}\)) of the sample relative to FeS (Wallace and Carmichael, 1992b), perhaps due to electron beam damage of the glass, diffusion in the sample and consequent charge-balance effects, or charge build-up. Reference samples containing S of known valence state are similar to those employed by Carroll and Rutherford (1988) and include Canyon Diablo troilite and pyrrhotite (FeS) for S\(^{2-}\) and anhydrite (CaSO\(_4\)) for S\(^{4+}\). In addition we have measured SKα wavelength shifts for pyrite (FeS\(_2\)) and barite (BaSO\(_4\)).

For each sample, λ(\(\text{SKα}\)) was determined by fitting the wavelength scan data with a Gaussian function to estimate the SKα peak center, from which the wavelength can be calculated using Bragg's law. Average values for wavelength shifts relative to FeS (Δλ(\(\text{SKα}\))) for the standards are listed in Table 1, and for the glass samples, in Table 2. The total SKα wavelength shift between sulfide and sulfate for both anhydrite and barite agree within error and are consistent with previous determinations (Carroll and Rutherford, 1988). The value of Δλ(\(\text{SKα}\)) for pyrite (S\(^{4+}\)) is approximately 1/3 of the total shift between S\(^{2-}\) and S\(^{4+}\), consistent with a linear increase of SKα energy with an increasing S valence state (Kucha et al., 1989).

### RESULTS

The measured values of Δλ(\(\text{SKα}\)) for the glasses in Table 2 are shown in Figure 1 as a function of relative magmatic f\(_0\). They vary from 0.05 × 10^{-3} to 0.75 × 10^{-3} Å, all of which are small compared with the total wavelength shift between sulfide (S\(^{2-}\)) and sulfate (3 × 10^{-3} Å). For f\(_0\) between 3.2 and 0.1 log units below NNO (ΔNNO = -3.2 to -0.1), Δλ(\(\text{SKα}\)) remains relatively constant, showing a slight overall increase with increasing ΔNNO. Three of the most oxidized samples have significantly higher values.
In order to interpret the wavelength shift data as a quantitative determination of the proportion of oxidized S ($S^{6+}/S_{\text{tot}}$), we have assumed that $\Delta \lambda(SK\alpha)$ increases linearly with $S^{6+}/S_{\text{tot}}$. Carroll and Rutherford (1988) have demonstrated that this assumption gives results that agree with the data of Nagashima and Katsura (1973) and Katsura and Nagashima (1974). In these last two studies, melts equilibrated at known $f_{\text{O}_2}$ values were analyzed for sulfide and sulfate using wet-chemical methods. It should also be noted that we are assuming that all of the S occurs as $S^{2-}$ and $S^{6+}$. The data shown in Figure 1 clearly indicate that a substantial amount of S occurs as $S^{2-}$ because all but a few of the most oxidized samples have $\Delta \lambda(SK\alpha) < 0.3 \times 10^{-3}$ Å, smaller than the value for S of $0.39 \times 10^{-3}$ Å determined by analyzing pyrite (Table 1). In principle the $\Delta \lambda(SK\alpha)$ data for these samples could be interpreted as being a mixture of $S^{2-}$ and $S^{6+}$, but the vacuum distillation analyses of Sakai et al. (1984) for basalt glass samples of similar $f_{\text{O}_2}$ show that some sulfate is also present under these conditions. Their data are consistent with ours results only if most or all of the reduced S occurs as $S^{2-}$. Similarly, the data of Carroll and Rutherford (1988) for samples equilibrated at high $f_{\text{O}_2}$ show that most of the S occurs as $S^{2-}$, although the presence of some sulfite ($S^{4+}$), especially at intermediate $f_{\text{O}_2}$, cannot be ruled out. Thus the SK\alpha wavelength shift and vacuum distillation data are consistent with $S^{2-}$ and $S^{6+}$ as the major forms of dissolved S in silicate liquids. If some sulfite is present, it will not significantly affect our estimates of the proportions of oxidized and reduced S because $S^{4+}$ has $\Delta \lambda(SK\alpha)$ much closer to that of sulfate ($S^{6+}$) than to $S^{2-}$ (Kucha et al., 1989).

Calculated values of $S^{6+}/S_{\text{tot}}$ for the submarine glasses vary from 0.02 to 0.25 (Table 2), indicating that the majority of the S in these samples is present as $S^{2-}$. These data are plotted in Figure 2 as a function of the relative $f_{\text{O}_2}$ of the sample. Shown for reference are the data of Carroll and Rutherford (1988) for glasses that were equilibrated at known $f_{\text{O}_2}$ values. Our data for submarine glasses are in excellent agreement with the relationship that they found between relative $f_{\text{O}_2}$ and $S^{6+}/S_{\text{tot}}$. This is significant, given the large differences in H$_2$O contents, bulk compositions, and equilibration temperatures between the two sample sets. Calculated equilibration temperatures for the submarine glasses vary from 1250 to 1055 °C, whereas the experimental glasses were largely equilibrated at temperatures between 1025 and 920 °C. Within the range of our data, there are no other consistent relationships between $S^{6+}/S_{\text{tot}}$ and other variables (e.g., temperature, Fe content, silica activity). There is some correlation of $S^{6+}/S_{\text{tot}}$ with $f_{\text{O}_2}$, $f_{\text{SO}_2}$, and $f_{\text{O}_3}$, but this is probably due to the relationships among $f_{\text{O}_2}$, $f_{\text{SO}_2}$, and $f_{\text{O}_3}$ for basaltic melts that are saturated with immiscible monosulfide Fe-S-O liquid (Wallace and Carmichael, 1992a). Therefore we conclude that $f_{\text{O}_2}$ is the dominant parameter controlling $S^{6+}/S_{\text{tot}}$ in silicate liquids and that other variables have no measurable effect. Carroll and Rutherford (1988) arrived at the same conclusions on the basis of their experimental data, and our new results extend this relationship over a wider range of compositions and temperatures.

**DISCUSSION**

**Sulfide-sulfate equilibrium in silicate liquids**

The S oxidation reaction in silicate liquids can be expressed as

$$S^{2-}_{\text{melt}} + 2O_{(\text{g})} = SO^{2-}_{\text{melt}}$$  \hspace{1cm} (1)
with

\[ K_1 = \frac{a_{SO_3}^{\text{mol}}}{a_{SO_3}^{\text{aq}}} f_{O_2}^3. \]  

If the ratio of the activity coefficients modifying the mole fractions \((X)\) remains constant, then the sulfate to sulfide ratio in silicate liquids can be represented by

\[ \log(X_{SO_3}^{\text{aq}}/X_{S_2}^{\text{aq}}) = \log K + 2 \log f_{O_2} \]  

where \(K\) is modified from Equation 2 to incorporate the activity coefficients. The data of Carroll and Rutherford (1988) show that the ratio \(X_{SO_3}^{\text{aq}}/X_{S_2}^{\text{aq}}\) (which can be calculated from \(S^{6+}/S_{\text{aq}}\)) is dependent on the relative \(f_{O_2}\), suggesting that the temperature dependence of \(K_1\) is similar to that of other redox reactions such as Ni + NiO (NNO) or fayalite + magnetite + quartz (FMQ). Using linear regression their data can be fitted to an expression based on Equation 3:

\[ \log(X_{SO_3}^{\text{aq}}/X_{S_2}^{\text{aq}}) = a \log f_{O_2} + b/T + c \]  

where \(a = 1.02, b = 25410\) K, and \(c = -10.0\). The temperature coefficient \((b)\) is taken from the Ni + NiO reaction (Huebner and Sato, 1970), multiplied by 1.02, so that \(X_{SO_3}^{\text{aq}}/X_{S_2}^{\text{aq}}\) is only dependent on relative \(f_{O_2}\). We also note that the value for \(a\) is considerably lower than the value of 2 predicted by Equation 3.

Values of \(S^{6+}/S_{\text{aq}}\), calculated from Equation 4 are shown in Figure 2. The calculated values fit most of the experimental and natural data within error, although it appears that at high and low \(f_{O_2}\), Equation 4 may slightly overestimate and underestimate, respectively, the actual value of \(S^{6+}/S_{\text{aq}}\). This may indicate that the ratio of the activity coefficients of \(SO_3^{2-}\) and \(S^{2-}\) does not remain constant over the entire range of \(f_{O_2}\), or that \(\log(X_{SO_3}^{\text{aq}}/X_{S_2}^{\text{aq}})\) is not a simple linear function of \(\log f_{O_2}\) (i.e., the \(a\) coefficient varies with relative \(f_{O_2}\)).

The relationship of \(S^{6+}/S_{\text{aq}}\) to relative \(f_{O_2}\), makes it possible to estimate relative magmatic \(f_{O_2}\), using Equation 4, together with measured values of SKα wavelength shifts. \(S^{6+}/S_{\text{aq}}\) changes rapidly over the interval from NNO - 1 to NNO + 2, making it a sensitive indicator of \(f_{O_2}\) for samples in this range. As an example, it may be possible to use this method on glass inclusions in phenocrysts from volcanic rocks for which other means of estimating \(f_{O_2}\) (e.g., Fe-Ti oxides or FeO/FeO analysis) are not suitable.

**Role of H\(_2\)O in S speciation**

Measurements of \(S^{6+}/S_{\text{aq}}\) in silicate glasses provide constraints on the speciation of S in magmas and the mechanisms by which these species dissolve. Of particular importance is the role of \(H_2O\) in the dissolution of sulfide in hydrous melts. One possibility is that sulfide dissolves by forming \(H_2S\) or \(HS^-\) through equilibria such as

\[ \text{H}_2\text{O}_{\text{melt}} + \text{SO}_3^{\text{aq}} = \text{H}_2\text{S}_{\text{melt}} + 2\text{O}_2\text{gas} \]  
\[ \text{OH}_{\text{melt}} + \text{SO}_3^{\text{aq}} = \text{HS}_-^{\text{aq}} + 2\text{O}_2\text{gas}. \]

These equilibria predict that at constant \(f_{O_2}\), increases in \(H_2O\) content should increase the proportion of sulfide (present as \(H_2S\) or \(HS^-\)) by reduction of \(S^{6+}\) in the melt. \(H_2O\) contents for glasses from the same regions and of the same general compositions as our samples are commonly <0.5 wt% \(H_2O\) (Muenow et al., 1990, and references therein), but in some (e.g., Lau Basin), the \(H_2O\) content may be as high as 1.5 wt%. In contrast, the compositions investigated by Carroll and Rutherford (1988) were chosen to be representative of the types of \(H_2O\)-rich magmas that erupt along continental margins and were equilibrated at \(H_2O\)-saturated conditions at pressures of 1–4.5 kbar. The total range of \(H_2O\) contents covered by their data set and ours translate into variations in \(f_{H_2O}\) that range over three orders of magnitude and should cause large increases in the amount of reduced S if \(H_2S\) or \(HS^-\) are abundant sulfide species in silicate melts. Instead, within the precision of the \(S^{6+}/S_{\text{aq}}\) data (ca. 10–15% absolute), there is no measurable effect.

An alternative to Equations 5a and 5b is that \(S^{2-}\) dissolves in silicate liquids by forming a complex with Fe through equilibria such as

\[ \text{CaSO}_4_{\text{melt}} + \text{FeO}_{\text{melt}} = \text{FeS}_{\text{melt}} + \text{CaO}_{\text{melt}} + 2\text{O}_2\text{gas} \]
\[ \text{SO}_4^{2-}_{\text{aq}} = \text{S}^{2-}_{\text{melt}} + 2\text{O}_2\text{gas}. \]

Under reducing conditions, where sulfide is the dominant S species, it has been demonstrated experimentally in anhydrous silicate liquids that increases in \(H_2O\) content cause an increase in the amount of S that dissolves, which is likely to be caused by the formation of a complex of \(Fe^{2+}\) and \(S^{2-}\) (Haughton et al., 1974). At high \(f_{O_2}\) values, where oxidized S is the dominant S species, anhydrite precipitates from S-saturated silicate liquids (Carroll and Rutherford, 1985, 1987; Luhr, 1990), suggesting that CaSO\(_4\) may be an important melt species for sulfate. Other network-modifying cations are probably also involved to a lesser extent in the formation of sulfide and sulfate complexes in silicate liquids. If Equation 6a is applicable, then variations in \(a_{\text{FeO}}\) should also have an effect on \(S^{6+}/S_{\text{aq}}\). Although the samples in Table 2 cover a wide range of FeO contents (7.3–15.8 wt%), the consequent values of \(a_{\text{FeO}}\) for this range vary only by a factor of 2 (calculated from Snyder and Carmichael, 1992), and therefore, any effect of \(a_{\text{FeO}}\) would be much less than that caused by variations in \(f_{H_2O}\). No correlation is observed between \(a_{\text{FeO}}\) and \(S^{6+}/S_{\text{aq}}\) for the data in Table 2, but that is not surprising, given the small range of variations in \(a_{\text{FeO}}\) and the errors of the \(S^{6+}/S_{\text{aq}}\) measurements. In conclusion, with the absence of a measurable effect of large variations in \(f_{H_2O}\) on the redox state of S, it seems probable that \(H_2S\) or \(HS^-\) are not abundant species by which sulfide dissolves in silicate liquids.

**Fugacities of S species in basaltic magmas and the effects of degassing**

Basaltic magmas are typically saturated with CO\(_2\)-rich gas during ascent and eruption on the sea floor (Moore et al., 1977). Although the dominant forms of dissolved S in silicate liquids are \(S^{2-}\) and \(S^{6+}\), the S species that are
present in coexisting magmatic gas are \( \text{H}_2\text{S},\ \text{S}_2,\ \text{and SO}_2 \). The fugacities of these species are related through the following equilibria:

\[
\begin{align*}
0.5\text{S}_2 + \text{O}_2 &= \text{SO}_2 \\
\text{H}_2\text{S} + 1.5\text{SO}_2 &= \text{SO}_2 + \text{H}_2\text{O}.
\end{align*}
\]

(7)  (8)

Thus the values of \( f_{\text{H}_2\text{S}}, f_{\text{S}_2}, \) and \( f_{\text{SO}_2} \) are dependent not only on temperature and pressure, but also on \( f_{\text{O}_2} \) and \( f_{\text{H}_2\text{O}} \). Even though \( \text{H}_2\text{S} \) is not an abundant melt species, it may be a significant component of the gas, especially at high \( f_{\text{H}_2\text{O}} \) or low \( f_{\text{O}_2} \) (Eq. 8). Values of \( f_{\text{H}_2\text{O}} \) for basaltic magmas can be calculated from magmatic \( \text{H}_2\text{O} \) contents using the methods of Dixon (1992). Most midocean ridge basalts (MORB) contain \( \leq 0.4 \) wt% \( \text{H}_2\text{O} \) (Muenow et al., 1990), whereas the lavas of Loihi seamount contain 0.3–0.8 wt% (Byers et al., 1985), and those of the Lau Basin may contain as much as 1.0 wt% or more (Aggrey et al., 1988). It is important to note that at pressures relevant to submarine eruptions of basaltic magma (\( \leq 500 \) bars) \( f_{\text{H}_2\text{O}} \) is not dependent on pressure (Dixon, 1992), and therefore, at a given \( f_{\text{O}_2} \) and \( \text{H}_2\text{O} \) content, \( f_{\text{SO}_2}/f_{\text{H}_2\text{S}} \) calculated from Equation 8 will not vary as a function of pressure.

Shown in Figure 3 are values of \( \log(f_{\text{SO}_2}/f_{\text{H}_2\text{S}}) \) in a coexisting magmatic gas phase at 1200 °C calculated as a function of magmatic \( \text{H}_2\text{O} \) content and relative \( f_{\text{O}_2} \). \( \text{SO}_2 \) is the major \( S \) species for basaltic magmas that are more oxidized than FMQ (NNO – 0.7) and contain \( \leq 1.0 \) wt% \( \text{H}_2\text{O} \) conditions that are appropriate for many lavas from seamounts and back-arc basins (Fig. 3). Under the more reducing conditions that are typical of MORB, \( \text{H}_2\text{S} \) is the dominant \( S \) species in the coexisting gas, even for magmas with very low \( \text{H}_2\text{O} \) contents (e.g., 0.1 wt% \( \text{H}_2\text{O} \) and \( f_{\text{O}_2} \) below NNO – 2). Similar calculations using Equation 7 demonstrate that for low magmatic \( \text{H}_2\text{O} \) contents, \( \text{SO}_2 \) is an important species between NNO – 2 and NNO – 1. As an example, a magma with 0.1 wt% \( \text{H}_2\text{O} \) at 1200 °C and NNO – 2 will have approximately equal proportions of \( \text{SO}_2,\ \text{H}_2\text{S}, \) and \( \text{S}_2 \) in coexisting gas. Decreasing temperature at constant relative \( f_{\text{O}_2} \) shifts Equation 8 to the left, as does increasing \( f_{\text{H}_2\text{O}} \), so that lower temperature \( \text{H}_2\text{O}-\text{rich} \) magmas such as andesites and rhyolites have lower \( f_{\text{SO}_2}/f_{\text{H}_2\text{S}} \) than the values depicted in Figure 3.

During submarine eruptions of basaltic magma, \( S \) is not strongly partitioned into the coexisting gas phase (Moore, 1970; Moore and Schilling, 1973), but, during low-pressure eruptions (subaerial and shallow subma-

...
S\(^+\)/S\(_{w}\) of subaerial Kilauea lavas suggests that these reactions do not cause significant changes in relative f\(_{O_2}\) of either gas or lava.

**CONCLUSIONS**

Measured values of S\(^+\)/S\(_{w}\) vary from 0.02 to 0.25 and increase with increasing relative f\(_{O_2}\) in accordance with the experimentally derived relationship of Carroll and Rutherford (1988). S\(^+\)/S\(_{w}\) can be used to estimate f\(_{O_2}\) for glassy lavas that are in the range of NNO - 1 to NNO + 2.

Dissolved S in these samples occurs predominately as S\(^2-\). Large variations in H\(_2\)O content and f\(_{O_2}\) have no measurable effect on the redox state of S, suggesting that H\(_2\)S or HS\(^-\) are not abundant in silicate liquids.

Thermodynamic calculations of S speciation in coexisting gas during submarine eruptions of basaltic magma show that S may be present mainly as H\(_2\)S or SO\(_2\), depending largely on magmatic f\(_{O_2}\). Many lavas from seamounts and back-arc basins are predicted to have molar SO\(_2\)/H\(_2\)S > 1 in coexisting magmatic gas, whereas the lower f\(_{O_2}\) values of mid-ocean ridge basalt favor H\(_2\)S as the dominant form of gaseous S.

**ACKNOWLEDGMENTS**

We would like to thank the following people for kindly providing the samples used in this study and access to unpublished data: J. Pearce (Lau Basin), E. Kappel and E. Klein (Southeast Indian and Juan de Fuca Ridges), C. Langmuir and J. Bender (Kane fracture zone), M. Perfit and D. Fornari (Galapagos 85\(^\circ\)W), D. Clague (Loihi seamount), D. Christie (Galapagos 95\(^\circ\)W), and J. Allan (Lamont seamounts). We would also like to thank D. Christie and J. Allan for preparing many of the samples and J. Donovan and I. Steele for assistance with the electron microprobes. Reviews by J. Luhr and M. Rutherford and discussions with A.T. Anderson, Jr., and D. Snyder led to significant improvements. This research was supported in part by National Science Foundation grant EAR-91-05231. P.W. acknowledges the financial support of A.T. Anderson, Jr., during the final stages of this work.

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**APPENDIX TABLE 1.** Sample locations, depths of recovery, analytical data, and calculated intensive parameters for Lau Basin glasses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Depth</th>
<th>Mg$^+$</th>
<th>FeO</th>
<th>FeO$_{int}$</th>
<th>Fe$^{3+}$/Fe$_{int}$</th>
<th>$T$ (°C)</th>
<th>Log $f_{O_2}$</th>
<th>Log $f_{H_2O}$</th>
<th>Log $f_{SO_2}$</th>
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<tbody>
<tr>
<td>10-1-3</td>
<td>19.14°S</td>
<td>176.53°W</td>
<td>2260</td>
<td>28.8</td>
<td>14.64</td>
<td>17.28</td>
<td>0.153</td>
<td>1089</td>
<td>−9.34</td>
<td>0.35</td>
<td>0.90</td>
</tr>
<tr>
<td>12-5-3</td>
<td>19.89°S</td>
<td>176.55°W</td>
<td>2350</td>
<td>33.2</td>
<td>9.34</td>
<td>11.64</td>
<td>0.198</td>
<td>1083</td>
<td>−8.85</td>
<td>0.15</td>
<td>1.37</td>
</tr>
<tr>
<td>20-5-1</td>
<td>19.49°S</td>
<td>175.95°W</td>
<td>2640</td>
<td>20.4</td>
<td>9.45</td>
<td>11.72</td>
<td>0.194</td>
<td>1056</td>
<td>−9.14</td>
<td>0.33</td>
<td>1.45</td>
</tr>
<tr>
<td>22-6-2</td>
<td>19.69°S</td>
<td>175.99°W</td>
<td>2730</td>
<td>56.5</td>
<td>9.73</td>
<td>10.92</td>
<td>0.109</td>
<td>1181</td>
<td>−9.35</td>
<td>−1.00</td>
<td>−0.66</td>
</tr>
<tr>
<td>41-3-2</td>
<td>19.28°S</td>
<td>176.17°W</td>
<td>3050</td>
<td>66.4</td>
<td>7.76</td>
<td>9.08</td>
<td>0.145</td>
<td>1247</td>
<td>−7.87</td>
<td>−0.99</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Note: depth is in meters. Mg$^+$ is the molar ratio 100Mg/(Mg + Fe$^{3+}$). FeO determined by colorimetry using a technique of Carmichael (see Christie et al., 1986). FeO$_{int}$ is Fe$_{int}$ determined by electron microprobe. Intensive parameters are calculated as described in Wallace and Carmichael (1992a).