

Experimental study on the relation between dissolved sulfur species and sulfur solubility in silicate melts

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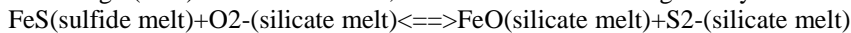
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Experiments on the sulfur solubility in silicate melts were performed using the CCO buffer. In analytical results, the FeO contents controls the sulfur contents in melt with high FeO contents (> 10wt.%), which is good agreement with previous studies. Sulfur contents in melts with low FeO contents (<10wt.%) are dependent on rather the CaO contents than the FeO contents. Analytical results of X-ray chemical shift suggest that sulfate species is more dominant than sulfide species in melts with low FeO contents.

Solubility of sulfur in silicate melts is critical importance on understanding magmatic sulfide ore genesis. Sulfide melts concentrate chalcophile elements in magmas, and forms many magmatic sulfide ore deposits. The source of the metals in sulfide has studied for long time by radiogenic isotope, but little attention of source of sulfur. In order to know physical condition on saturation of sulfur in magmas, it is necessary to quantify sulfur contents at sulfide saturation (SCSS, Shima and Naldrett, 1975). Sulfur species in melts is critical important for fixed quantities of sulfur solubility. Poulson and Ohmoto (1990) predicted that sulfide sulfur species in melts by profile of a large number of experimental data. They suggested sulfide sulfur dissolves as Fe₃SO₂ species in melts with high FeO contents (over 10 wt.%). However, the relation between S and FeO contents in melts with low FeO contents (below 10 wt.%) has been ambiguous. The main focus of this study is to reveal the relation between S solubility and S species in melts under reduced condition.

Experimental condition in this study has performed at 1250 degree centigrade and 1kbar. In this result, the S solubility in melts with high FeO contents depends on FeO contents. However, the S solubility is independent of FeO contents in melts with low FeO contents. In calculated results of a regular solution models for the measured S contents in this study, the relation between S and FeO may occur. S dissolves as sulfate sulfur dominantly by S X-ray chemical shift. Thus the positive correlation between S and CaO contents in melts can be explained by introducing CaSO₄ species, and S solubility is described as the following reactions.

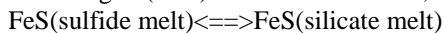
When logX(FeO) is lower than -2.7, sulfide sulfur content is given by the following equation.



The equilibrium constant (logK) is calculated

$$\log K = -6.01$$

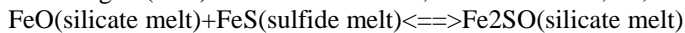
When log X (FeO) is between 1.3 and 2.7, sulfide sulfur content is given by the following equation.



The equilibrium constant (logK) is calculated

$$\log K = -3.31$$

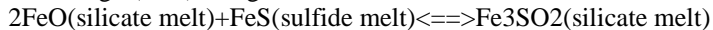
When log X (FeO) is between 1.0 and 1.3, sulfide sulfur content is given by the following equation.



The equilibrium constant (logK) is calculated

$$\log K = -1.91$$

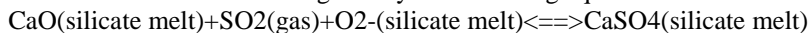
When logX(FeO) is higher than 1.0, sulfide sulfur content is given by the following equation.



The equilibrium constant (logK) is calculated

$$\log K = -0.94$$

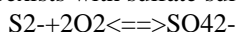
And sulfate sulfur content is given by the following equation.



The equilibrium constant (logK) is calculated

$$\log K = 2.27$$

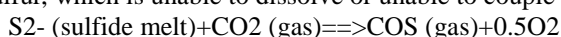
We can make a success of the calculation sulfide sulfur and sulfate sulfur solubility in silicate melts. When sulfide sulfur coexists with sulfate sulfur in silicate melts, the following reaction should forms.



$$\log(\text{XSO}_4^{2-}/\text{XS}_2) = \log K + 2\log f\text{O}_2$$

However, the calculated fO₂ was different from the experimental fO₂. The sulfide to sulfate ratio under the CCO buffer is much higher than the measured ratio.

If Fe²⁺ is very shortage relative to S²⁻ (such as low FeO contents), the ratio of S²⁻/SO₄²⁻ may become large. The sulfide sulfur, which is unable to dissolve or unable to couple with metal ion, may reacts with CO₂ gas;



Thus the ratio of dissolved sulfate sulfur to sulfide sulfur (=X_s(sulfate)/X_s(sulfide)) looks like overestimate.