

# Geochemical Characterization of Subaqueous Molten Sulfur at Active Crater Lakes

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## 1. Introduction

Considerable numbers of molten sulfur flows and pools have been reported at active volcanoes and hydrothermal areas in the world. However, studies on their geochemical implications have been very few, although some works on their isotopic characteristics have been reported for some volcanoes. On the other hand, elemental sulfur deposits along the volcanic gas-rising network underground, and is very likely to occur through interactions between volcanic gas and liquid elemental sulfur. In this paper we discuss the chemical interactions between liquid sulfur and H<sub>2</sub>S, SO<sub>2</sub> gases, and intend to extract some geochemical implications from the published as well as non-published data.

## 2. Gas Solubility

Molten sulfur has been known to dissolve some gases such as H<sub>2</sub>S, SO<sub>2</sub>, CS<sub>2</sub> etc. Among these gases H<sub>2</sub>S dissolves in molten sulfur in a peculiar way as demonstrated by Fanelli et al. (1949). Wiewiorowski and Touro (1966) reasonably interpreted the solubility in terms of sulfane (H<sub>2</sub>S<sub>x</sub>) formation in the liquid. Dissolved H<sub>2</sub>S excluding H<sub>2</sub>S<sub>x</sub> follows Henry's law as normal gas dissolution in liquids.

$$\ln (C/p)_{\text{H}_2\text{S}} = 412/T - 4.13 \quad (1)$$

On the other hand, SO<sub>2</sub> gas in liquid sulfur obeys Henry's law (Touro and Wiewiorowski, 1966),

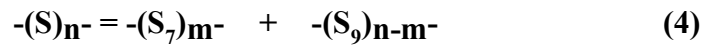
$$\ln (C/p)_{\text{SO}_2} = 931/T - 5.32 \quad (2)$$

The relationships between temperature and the reciprocal of the Henry's constant for the H<sub>2</sub>S and SO<sub>2</sub> gases reveal that in the temperature range of >167°C H<sub>2</sub>S is more soluble than SO<sub>2</sub> in liquid sulfur if the partial pressures of both gases are equal. This suggests a likely process that (SO<sub>2</sub>/H<sub>2</sub>S) ratios of rising volcanic gas may increase through interaction with pre-deposited sulfur liquid along the conduit. Sulfane formation in the liquid sulfur may partly contribute to raise the ratio at elevated

temperature, although rates of its formation and decomposition in the liquid are relatively slow compared with the H<sub>2</sub>S solubility process.

### 3. Homocyclic sulfur in liquid elemental sulfur: Does hydrogen sulfide change the distribution of homocyclic sulfur?

Elemental sulfur once melted has been known to contain the S<sub>x</sub> allotrope (x=6~20) in various concentrations. Among them S<sub>7</sub> is most abundant, often up to a few % (w/w) at ca. 160°C. Takano et al. (1994) found that the S<sub>7</sub>/S<sub>8</sub> ratios of the solidified sulfur are considerably lower than those of pure sulfur melts at the same temperature. In addition, however, the sulfur samples from the Yugama lake showed the S<sub>7</sub>/S<sub>8</sub> ratio similar to the pure sulfur melt when they were re-melted in the atmosphere. Where does this difference come from? We think that the difference between pure sulfur and the molten sulfur in nature is likely to come from the coexistence of H<sub>2</sub>S gas with the natural molten sulfur. The mechanism resulting in the difference in the S<sub>7</sub>/S<sub>8</sub> ratio could be explained by the following reactions:



Hydrogen atoms from H<sub>2</sub>S dissolved in liquid sulfur terminates polymerization of smaller sulfur chains, resulting in lowering of the liquid viscosity. The equations from (1) to (4) may give other sulfanes together with homocycles other than S<sub>7</sub> and S<sub>8</sub>. Blockage of the terminal S radicals (Poulis et al., 1962) in chainlike sulfur molecules resulting from cleavage of S<sub>8</sub> rings (Equation 1) depends upon partial pressure of H<sub>2</sub>S (P<sub>H<sub>2</sub>S</sub>) in rising volcanic gases through the conduit, resulting in reduced populations of the cyclic S<sub>7</sub> in the melt. Thus the linear relationship between temperature and S<sub>7</sub>/S<sub>8</sub> ratio presented by Takano et al. (1994) is significantly lowered than that found for the data by Steudel et al. (1985). Practically the linear relationship between the ratios and temperature is dependent on partial pressure of H<sub>2</sub>S in the environment considered. Isobars of (S<sub>7</sub>/S<sub>8</sub>) ratios should be constructed for temperature estimation by this method.

A similar mechanism with dissolved SO<sub>2</sub> gas is likely to proceed in the molten sulfur, forming polythionic acids in it. However, we think that SO<sub>2</sub> is not likely so much to reduce the formation of sulfur homocycles.

### 4. Conclusion

Elemental sulfur found in volcanic area, particularly molten sulfur from active crater lakes can provide useful information about the *in-situ* volcanic gas, when we get properly quenched sulfur samples, and quick chemical analysis is applicable.