## *Genesis of Sulfate in Acid Hot Spring*

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Acid hot springs contain generally large amounts of sulfate ion, and it has been usually considered that most of them are formed by the oxidation of hydrogen sulfide or other sulfides with oxygen from the air at or near the ground surface¹⁾.

However, this explanation is not always acceptable, when their high discharges and the chemical composition of gases accompanied with the acid hot springs are taken into consideration.

Fumarolic gases from active volcanoes contain usually hydrogen sulfide, sulfur dioxide,

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1) E. T. Allen and A. L. Day, "Hot Springs of the Yellowstone National Park" Carnegie Inst. Washington Pub. (1935); D. E. White, *Bull. Geol. Soc. Am.*, **68**, 1637 (1957) etc.

Table I

| Silicate rock | Condition | $H_2SO_3$(mM) Residual | $H_2SO_4$(mM) Found | S(mM) Found | $H_2SO_4$/S |
|---|---|---|---|---|---|
| None | A | 6.51 | 2.36 | 1.10 | 2.1 |
|  | B | 3.43 | 3.79 | 1.80 | 2.1 |
| Basalt | A | 0.69 | 5.96 | 2.38 | 2.5 |
|  | B | 0.36 | 5.68 | 2.69 | 2.1 |
| Andesite | A | 0.26 | 5.89 | 2.75 | 2.1 |
|  | B | 0.14 | 5.25 | 2.95 | 2.1 |
| Granite | A | 1.03 | 5.60 | 2.70 | 2.1 |
|  | B | 2.68 | 3.89 | 1.72 | 2.3 |

hydrogen chloride and carbon dioxide in the same order of amounts, and nitrogen in a smaller amount, but scarcely any oxygen and sulfur trioxide.

On the other hand, gases from region of the acid hot springs consist of carbon dioxide and hydrogen sulfide as the major components, and of nitrogen as the minor components, and of sulfur dioxide, hydrogen chloride and oxygen as the trace components. Therefore, the most important chemical species for the formation of sulfate would not be hydrogen sulfide, but sulfur dioxide.

When volcanic gases are condensed by cooling under the ground, hydrogen chloride and sulfur dioxide would dissolve into the condensed water to form hydrochloric and sulfurous acids. Then sulfuric acid may be formed from this sulfurous acid, liberating sulfur by the following self oxidation-reduction reaction.

$$3H_2SO_3 = 2H_2SO_4 + S + H_2O \qquad (1)$$

In order to confirm this new hypothesis, some experiments were carried out as follows. Two grams of the powdered silicate rock were taken into an ampoule (50 ml.) and 20 ml. of 0.5 M sulfurous acid solution (condition A) or 20 ml. of the mixed solution consisting of 0.5 M sulfurous acid and 0.5 M hydrochloric acid (condition B) were added. Then each ampoule was sealed in the atmosphere of carbon dioxide and kept at 105°C. After about three days, some droplets of sulfur were observed on the surface of the solution into which andesite or granite was added. After a week, all ampoules were cooled to room temperature and the amount of each reaction product was determined (Table I).

It is clear that, as shown in Table I, the self oxidation-reduction reaction of sulfurous acid is mainly based on Eq. 1 under these conditions and this reaction proceeds easily in the presence of hydrochloric acid or silicate rock. Under natural circumstances where higher pressure and temperature are expected, this reaction would proceed more easily and the sulfur formed may contribute to the formation of some ores such as pyrite and native sulfur impregnated with wall rocks.

It is concluded that the principal source of sulfate in the acid hot spring may be sulfur dioxide from volcanic gas and the formation of sulfate may be based on the self oxidation-reduction of sulfurous acid.

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