

## Precipitation condition of stibnite at Wakamiko submarine Hydrothermal system in Kagoshima Bay, Japan

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Active hydrothermal venting have been occurred on a shallow-seafloor in the most inner part of Kagoshima Bay, Southern Kyushu, Japan. That area is called Wakamiko hydrothermal field and at least three active vents with chimneys are recognized. Those chimneys are standing on sulfide mounds, which almost consist of stibnite. The previous studies suggested that those sulfide deposits possibly ejected from beneath the seafloor where they once formed. Therefore, it is likely that those sulfides may form ore body below seafloor.

In this study, to confirm prevailing favorable condition for stibnite precipitation below the seafloor, mineral paragenesis, elemental analysis using EPMA, and stable isotope analysis were performed together with thermodynamic calculations based on chemical and physical data obtained from previous studies at the area.

From the microscopic and EPMA analysis, pyrite, sphalerite, chalcopyrite, and galena were found as minor components in the sulfide deposits. Sulfur isotope compositions of stibnite were almost uniform among the samples ( $\delta^{34}\text{S} = +2.3$  to  $+3.3\%$ ), while those values of co-occurred pyrite were relatively variable (from  $+1.7$  to  $+7.0\%$ ). It suggests that source of sulfide to form pyrite is variable. Therefore, it was considered that most of them were not paragenetic relation with stibnite. The FeS contents of sphalerite measured by EPMA showed significant variations ranging from 0.5 to 41.0 mole percent. It may suggest that sphalerite precipitate at variable redox condition. Sulfur isotope geothermometer (Ohmoto and Goldhaber, 1997) suggests that precipitation temperature of stibnite is ranging from 110 to 220 degree-C.

Thermodynamic calculation with respect to antimony suggested that the element dissolved in the fluid as several complexes, such as  $\text{H}_2\text{Sb}_2\text{S}_4$ ,  $\text{HSb}_2\text{S}^-$ ,  $\text{Sb}_2\text{S}_4^{2-}$ , and  $\text{Sb}(\text{OH})_3$ . Those solubility is not likely affected by redox condition and sulfide concentration of fluid. Furthermore pH condition of the fluid is expected to be strongly constrained approx. 6 due to high concentration of dissolved  $\text{CO}_2$ , so the effect of pH to solubility is not considered. Under such condition, at the high temperature ( $>200$  degree-C) sufficient antimony (1ppm) can be dissolved in the fluid, while at the low temperature ( $<170$  degree-C) the solubility is estimated dramatically decrease. This estimation is almost consistent with that of the sulfur isotope geothermometer.

Drop of the fluid temperature is occurred by conductive cooling or mixing with cool seawater. According the calculation, both cooling is effective to stibnite mineralization. Mixing with seawater involve oxidation of the fluid. Some hydrothermal clay minerals contained magnesium have been observed in the core sediment obtained around the vent sites, and the formation temperature was estimated around 130 degree-C. It may suggest that mixing with seawater is a plausible cause of cooling the fluid. Those sulfide deposits contained significant amount of gold (up to 500 ppm), it's mineralization may also occur due to cooling and oxidation of the fluid.

Accordingly, temperature is the main control factor for stibnite precipitation in the Wakamiko system, and it may suggest that slow temperature dropping of fluid temperature in sedimentary layer relative to fluid venting from the chimney is favorable to form massive stibnite deposit below seafloor.

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