Transformation of arsenic phase and detection of monothioarsenate in the hydrothermal water from Iwo-Yama , Kirishima volcanoes

*Keigo Mori[1], Harue Masuda[1], Jun-ichiro Ishibashi[2], Takeshi Matsushima[2], Katsunori Yanagawa[3], Syogo Oshima[4], Yasuhisa Tajima[5], REO IKAWA[6]

1. Osaka City University, 2. Kyushu University, 3. The University of Kitakyushu, 4. West Japan Engineering Consultants, Inc, 5. Nippon Koei Co., Ltd, 6. AIST

Since phreatic eruptions occurred on the two craters (south (Y2) and west (W4)) of Iwo-yama, Kirishima active volcanoes, on April 19 and 20, 2018, and active hydrothermal activities with fumarole emanation have continued at the two craters and surroundings. In this study, high temperature hydrothermal waters and low-temperature spring and river waters were taken during July 2018 and December 2019. The major chemical components, hydrogen and oxygen stable isotope ratios of water, total arsenic concentration and the chemical species of arsenic were analyzed in order to clarify the behavior of arsenic in the Iwo-Yama hydrothermal system. The water samples collected in November and December 2019 were subjected to speciation and quantitative analysis of different chemical forms of arsenic by IC-ICP-MS. Also, the mineral composition was analyzed for the hydrothermal sediments from the two craters.
Magmatic fluid (andesite fluid) flew out from the two craters after the eruption. During the sampling campaign, the hydrothermal water containing the highest contribution of magmatic fluid was taken from W4 in July 2018; $\delta^{2}H$ = -15~-10 ‰, $\delta^{18}O$ = +5 ‰, pH<1, high chloride concentration >300 mM and Cl/S ratio >1.5. Total arsenic concentration was ~5500 ppb, which was the maximum among the studied sample waters, in this water.
The magmatic fluid has been constantly issuing from W4 and the arsenic concentration ranged from 2800 to 5500 ppb. In the Y2, chloride concentration decreased with time and and the contribution of the fumarolic components separated from the magmatic fluid became high. The arsenic of hydrothermal fluids had a positive linear relation to the chloride ion concentration but not to the sulfate concentration. Thus, the arsenic may have the similar origin to chlorine in this hydrothermal system. Speciation analysis revealed that the arsenite accounts >95% for the water from W4 in the November and minor arsenate peak was detected. Alunite and cristobalite were the minerals detected by XRD for the hydrothermal precipitate. Steam fraction became dominant in the Y2 water with time, especially after March 2019 plausibly due to boiling beneath the creter. Total arsenic concentration of the sample collected from Y2 in the November and December 2019 was about 50-180 ppb, and arsenite was aboundant compared with arsenate. It is notable that the unidentified arsenic (peak X) occupied 35 to 67% of total arsenic. Peak X was not caused by the isobaric interference. This peak was identified as monothioarsenate, which was evidenced when comparing the retention time of monothioarsenate synthesized according to the method of Schwedt (1996). The small peak X was detected in the water from W4 taken in the December. Mineral compositions of the hydrothermal sediments taken with these waters were alunite, native sulfur, quartz and cristobalite. Since the presence of native sulfur corresponds to the detection of monothioarsenate, the monothioarsenate would be formed via the redox reaction between native sulfur and arsenite as the followings.
$2H_2S+SO_2 \rightarrow 3S+2H_2O$
$S+H_3As^{(III)}O_3 \rightarrow H_3As^{(V)}O_3S$
The arsenic concentration in the low-temperature spring water located on the north slope of the Iwo-Yama was about 10 ppb, and >95% was arsenate, indicating oxidation of arsenite and monothioarsenate in the underground paths of hydrothermal fluids when contacting aerobic shallow groundwater. Monomethylarsonic acid, dimethylarsinic acid and arsenobetaine were detected in this

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water, and the former two arseno-organic acids were detected in some of the hydrothermal water from the Y2. These organo-arsenic compounds must be formed via microbial activity inside of the shallow part of the volcano. Detection of small amounts of organo-arsenic compounds in the high temperature hydrothermal water suggests the contamination of shallow groundwater with microbially mediated arsenic compounds and short retention time in the high temperature condition.

Keywords: Iwo-Yama, hydrothermal water, speciation and quantitative analysis

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