

LA-ICP-MS analysis on sulfide minerals from the Higashi-Aogashima hydrothermal site to understand the host phase of gold

*Tatsuo Nozaki^{1,2,3,4}, Junji Torimoto¹, Yutaro Takaya^{2,5,1}, Kazuki Kohama⁶, Kotaro Yonezu⁶, Satoshi Okada¹, Takahiro Kuribayashi⁷, Toshiro Nagase⁷, Samuel Morfin⁸, Keiko Hattori⁸

1. JAMSTEC, 2. Univ. of Tokyo, 3. Kobe Univ., 4. Chiba Tech, 5. Waseda Univ., 6. Kyushu Univ., 7. Tohoku Univ., 8. Univ. of Ottawa

The Higashi-Aogashima Knoll Caldera (HAKC) hydrothermal field, locating at 12 km east offshore from Aogashima Island, is a relatively new seafloor hydrothermal field discovered by the research group of The University of Tokyo in 2015. This hydrothermal field occurs at the water depth of ca. 750 mbsl and an abnormal gold (Au) enrichment was reported, especially the average Au concentration of 102 ppm from the mound at the Central Cone Site [1]. Metallogenic study on the HAKC hydrothermal field is still at the beginning stage and bathymetric map, basic petrographic study of mineral deposit and preliminary result of the acoustic plume survey were reported so far [1–3]. We conducted the first multi-disciplinary research cruise (KS-21-20) by R/V Shinsei-maru and ROV HPD at the HAKC hydrothermal field in 2021 and collected rock, seawater, hydrothermal fluid and (micro)biological samples. Here, we report whole-rock geochemical compositions of the mineral deposit and in-situ trace element geochemistry of constituent sulfide minerals determined by LA-ICP-MS.

Bulk Au concentrations of the sulfide/sulfate-rich rock at the HAKC hydrothermal field are 22.54 ± 41.34 ppm ($n = 34$, $\pm 1SD$), ranging from 0.01 to 178.7 ppm. The average Au concentrations at the Central Cone ($n = 26$), Southeast ($n = 5$) and East Sites ($n = 3$) are 25.6, 17.4 and 14.1 ppm, respectively. The maximum Au concentration of 178.7 ppm was observed at the mound of the Central Cone Site (sample no. HPD2136#R05). The Au concentrations show positive correlations with those of Zn ($r = 0.64$), Cd ($r = 0.54$), Te ($r = 0.51$) and Pb ($r = 0.48$), which means that electrum grains are closely associated with sphalerite and galena. In-situ LA-ICP-MS trace element analyses on constituent sulfide mineral ($n = 446$) yielded the Au average concentrations of 12.0 ppm (pyrite; $n = 53$), 4.62 ppm (sphalerite; $n = 176$), 10.0 ppm (chalcopyrite; $n = 105$), 1.33 ppm (galena; $n = 58$), 3.66 ppm (tetrahedrite; $n = 38$), 0.10 (stibnite; $n = 12$), 0.47 (unidentified As-S mineral; $n = 3$) and 4.20 ppm (enargite; $n = 1$), respectively. Analytical data with any inclusions and spikes were already removed. Although the correlation coefficients of the bulk Au concentrations with those of Zn and Pb are highest and fourth highest values, the Au concentrations within sphalerite and galena grains themselves are lower than those of pyrite and chalcopyrite. During the in-situ LA-ICP-MS analyses, Au spikes and enriched parts were often observed at the boundary between sphalerite grain and Cu-Zn-Pb-As-Sb-Ag-rich part (tetrahedrite-like component).

Under the microscope, electrum is associate with sphalerite, galena, chalcopyrite and pyrite. The most electrum-rich part of the mineral deposit is (1) edge of sphalerite and (2) silica (opal) and unidentified clay mineral next to sphalerite. Because electrum grains occur as an aggregate of nano- and micro-particles based on the microscopic observations, electrum is considered to be precipitated after sulfide minerals and trapped in their cracks and defects, and then recrystallized, producing the “apparent” positive correlation ships between the bulk Au and Zn (and Pb) concentrations. Our observation would be direct evidence of the recently observed nano-particle precipitation of electrum through the boiling processes of the hydrothermal fluid [4,5].

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