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Mineralogical and geochemical facets of the massive deposition of stibnite-metastibnite at a seafloor hydrothermal field (Wakamiko Crater, Kagoshima Bay, Ryukyu Volcanic Arc)

Vesselin Dekov[1,*], Yukako Furuma[1], Bleuenn Guéguen[2,3], Lukas Klose[4], Kazutaka Yasukawa[5,6], Motoaki Morita[7], Dan Asael[8], Toshiro Yamanaka[1], Luca Bindi[9,†], Andrea Koschinsky[4], Bernhard Pracejus[10], and Yasuhiro Kato[5,6,11,12]

[1]Department of Ocean Sciences, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan
[2]CNRS, University Brest, UMR 6538 Laboratoire Géosciences Océan, F-29280 Plouzané, France
[3]CNRS, University Brest, UMS 3113, F-29280 Plouzané, France
[4]Department of Physics and Earth Sciences, Constructor University Bremen gGmbH, Campus Ring 1, 28759 Bremen, Germany
[5]Frontier Research Center for Energy and Resources, School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
[6]Department of Systems Innovation, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[7]Department of Marine Electronics and Mechanical Engineering, Tokyo University of Marine Science and Technology, 2-1-6 Etchujima, Koto-ku, Tokyo 135-8533, Japan
[8]Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06520, U.S.A.
[9]Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via Giorgio La Pira 4, I-50121, Firenze, Italy
[10]Department of Earth Sciences, Sultan Qaboos University, PO Box 36, 123 Al-Khoud, Muscat, Sultanate of Oman
[11]Ocean Resources Research Center for Next Generation, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, Japan
[12]Submarine Resources Research Center, Research Institute for Marine Resources Utilization, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan

Abstract

Stibnite precipitates in the form of massive boulders at two active hydrothermal mounds in the submarine Wakamiko Crater (Ryukyu Volcanic Arc) as opposed to commonly observed accessory stibnite in the seafloor hydrothermal deposits. The stibnite dimorph, metastibnite, found here for the first time on the seafloor, appears to always form whenever stibnite is precipitated under submarine hydrothermal conditions. Our study shows that hydrothermal conditions of low temperatures (<50 °C) and low values of pH (<6) are favorable for the precipitation of stibnite on the seafloor. The stibnite probably does not precipitate at the measured vent fluid temperatures (i.e., 177.6–187.0 °C) along the chimney conduits, but rather at temperatures <50 °C and at slightly reduced to slightly oxic conditions (*Eh* = –0.5 to +0.5 V) within the chimney walls and hydrothermal mounds. Metastibnite deposition appears to be the result of rapid quenching of hot hydrothermal fluid when mixed with cold seawater and rapid precipitation at the interface between stibnite and vent fluid. The low concentrations (usually below detection limits) of the trace elements (Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, P, Pb, Sr, V, Zn) in the stibnite deposits from Wakamiko Crater are likely a result of the decreased metal-transporting capacity of the precipitating vent fluid due to its low chlorinity. Low-chlorinity venting implies sub-seafloor boiling and phase separation of the hydrothermal fluid. Sluggish hydrothermal fluid/seawater mixing within the walls of the chimneys and mounds favors the reduction of sulfate dissolved in the hydrothermal fluids and results in a heavy S isotope composition of the sulfate in the vent fluids. Sulfate reduction and disproportionation of magmatic SO_2, both leading to heavy S isotope composition of sulfate in the vent fluids, seem to be common processes in volcanic arc/back-arc submarine hydrothermal settings.

Keywords: Hydrothermal, metastibnite, stibnite, sulfate reduction, Wakamiko Crater