New occurrences of silica clathrate minerals in Sakhalin

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Silica clathrate minerals are rare minerals containing various gas molecules  $(CH_4, C_2H_6, CO_2, H_2S, N_2 etc.)$  in their cage-like framework structures constructed of pure silica. Three types of silica clathrate minerals have been hitherto known in nature. They are structurally analogous to gas hydrates. In fact, the three minerals, melanophlogite, chibaite, and bosoite are isostructural with three types of natural gas hydrates, i.e., sI, sII, and sH hydrates, respectively. The source of gas molecules in silica clathrate minerals is also considered to be common with one type of natural gas hydrates having thermogenic origin.

We recently noticed two specimens of quartz pseudomorphs from Sakhalin in old mineral collection of the National Museum of Nature and Science. They are labeled as quartz pseudomorphs after fluorite or apophyllite because they have truncated octahedral shape. However, they look identical to quartz pseudomorphs after chibaite occurred in Chiba and Nagano prefectures. These specimens motivated us to field investigation of Sakhalin. The two specimens are from "Souni misaki" (Kuznetsova) and "Bisyasan", the most southwest part of Sakhalin where Miocene sedimentary rocks and volcanic rocks are exposed. Unfortunately, we could not approach these places during the field survey in 2015 but we discovered new locality of melanophlogite at Nevelsk. Melanophlogite is associated with fossils of various chemosynthetic shells in calcareous concretion of mudstone of Miocene age. The concretions are abundantly distributed as veins or pipes mostly parallel to the bedding plane, or some of them look like isolated nodules of diameters up to several meters. Among these concretions, melanophlogite only occurs in the one containing massive amount of shells and voids. Melanophlogite occurs in these voids as aggregates of cubic crystals of sizes up to 0.1 mm, associated with chalcedony and small quartz crystals.

Keywords: silica clathrate minerals, methane seep, chemosynthetic community