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Multi-proxy study of cannon-ball concretions with glendonites from Paleogene-Neogene sediments of Sakhalin Island: implication for concretion growth and ikaite-calcite trans-formation

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The objects of the current study are glendonite pseudomorphs forming the central part of cannon-ball carbonate concretions found within Miocene terrigeneous sediments of Sakhalin island (easternmost part of Russia). Twelve samples of glendonites and host carbonate concretions were examined using optical and cathodoluminescence microscopy, EDX analysis, powder X-ray diffraction and isotopic analysis. The aim of the study is to determine the origin of the concretions and the relationships between the concretion and glendonite occurrence.

Glendonites and host cannon-ball concretions were found within terrigeneous sediments of Bora (Lower Miocene) and Vengeri (Upper Miocene) formations. These formations are composed of laminated sandstones, siltstones, argillites and siliceous rocks. Dropstones are often found within these sediments as well as cannon-ball carbonate concretions, some of them with glendonites in central part. 60-90% of the cannon-ball concretion is occupied by sandy limestone (with high-magnesium calcite) and occasionally contains dolomite and pyrite. Central part of the cannon-ball concretion is occupied by glendonite (single crystal-like or star-like cluster of crystals). Glendonites are composed of several calcite generations. Rosette-like calcite crystals (“ikaite-derived calcite”) are composed of low-magnesium calcite, they are non-luminescent. Needle-like calcite cement is composed of high-magnesium calcite or dolomite and show bright-yellow cathodoluminescence. The rest of the glendonite is occupied with low-magnesium radiaxial fibrous or sparry calcite with dark-red cathodoluminescence.

Isotopic ratios of glendonites are close to those of host concretions. For host concretions $\delta^{13}C$ varies from -20.3 to -14.9 ‰PDB, $\delta^{18}O$ varies from +1.7 to +2.7 ‰PDB; for glendonites $\delta^{13}C$ varies from -18.1 to -1.9 ‰PDB, while $\delta^{18}O$ varies from +0.7 to +3.4 ‰PDB.

Close mineralogical and isotopic composition of the studied glendonites and host cannon-ball concretions suggest they were formed in similar geochemical environment. Association of glendonite occurrence along with dropstones is an indicator of cold conditions, which is well-corresponding with view on glendonites as a proxy for cooling events. Cementation of

surrounding sediment (formation of the cannon-ball concretions) and glendonite formation was simultaneous and occurred during early diagenesis in the sulfate-reduction zone. The source of calcium and magnesium ions was seawater ($\delta^{18}O$ values are characteristic for seawater). Ikaite was replaced with low-magnesium calcite; the replacement was favored by organic matter decay ($\delta^{13}C$ values are characteristic for organic matter). Cementation of the cannon-ball concretion with high-magnesium calcite occurred together with needle-like high-magnesium calcite growth in the glendonite with increasing concentration of magnesium due to calcite extraction from the pore water. The remaining pore space was subsequently filled with radiaxial fibrous or blocky sparry calcite during burial diagenesis.

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