Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

BCG28-08 Room:105 Time:May 26 15:15-15:45

Formation condition of monohydrocalcite (CaCO3.H2O)

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Monohydrocacite (MHC: $CaCO_3.H_2O$) is one of calcium carbonates and is metastable phase with respect to calcite and aragonite. MHC was frequently found in the saline environments such as saline lake, cold spring and cold seawater. The solubilities of the minerals formed in saline conditions are usually high. For example, that of gypsum ($CaSO_4$), which can be frequently found in saline lake, is $10^{-4.6}$. On the other hand, that of MHC is not so high ($10^{-7.7}$) which is 1000 times lower than gypsum. Why MHC, which is not soluble phase, is frequently found in saline conditions?

MHC is rare in nature. On the other hand, MHC can be easily synthesized in laboratory. For example, the simple addition of sodium carbonate (Na_2CO_3) to seawater leads to the immediate formation of MHC. Seawater is mixture of various components. Among them, magnesium is known as the essential component for the formation of MHC. The coordination number of magnesium is six in ambient conditions. On the other hand, that of calcium in monohydrocalcite is eight. Therefore, magnesium cannot be incorporated into the MHC structure. Why the MHC formation requires the coexisting magnesium?

We examined the formation conditions of MHC by the laboratory synthesis experiments by mixing the $CaCl_2$, $MgCl_2$ and Na_2CO_3 solutions in various ratio (Nishiyama et al. 2013). The results showed that the MHC can form from the solutions of which the calcium concentrations were higher than the carbonate concentration in the presence of a certain amount of magnesium. The reacted solutions after MHC formations were equilibria with MHC as well as hydrous magnesium carbonate (nesquehonite: $MgCO_3.3H_2O$). According to the experimental results, the formation conditions of MHC can be considered as the conditions which allow the formation of hydrous magnesium carbonate after the consumption of calcium and carbonate from solutions for the formation of MHC.

Based on the formation conditions, we can answer the mysteries in regard with MHC formation. Although the solubility of MHC is not so high, that of the coexisting hydrous magnesium is relatively high ($10^{-5.3}$ for nesquehonite). Consequently, the formations of MHC have been frequently found in the saline conditions such as saline lakes.

The motivation to study MHC was the finding of MHC in the long sediments core from Lake Hovsgol (largest fresh water lake in Mongolia). Although MHC was not observed in the surface parts of the sediments, it was found in the depths corresponding to the past glacial periods. The presences of MHC in the layer indicates that the water qualities of the lake was salty during the glacial periods. The formation conditions of MHC obtained from the present study enables the quantitative reconstruction of the past water quality in Lake Hovsgol.