Solubility measurement of monohydrocalcite; Monohydrocalcite is 3rd stable calcium carbonate at lower temperature.

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Monohydrocalcite (MHC) is rare mineral in geological settings. It is metastable with respect to calcite and aragonite. The transformation of MHC in aqueous solution is inhibited by phosphate ion that prevents the crystallization of the more stable anhydrous form of CaCO3. There have been two reports of the solubility of MHC. One was given by Hull and Turnbull, (1973) who determined the solubility at 25 degree C (log Ksp = -7.6). Another was measured by Kralj and Brecevic, (1995), who determined the solubility at temperature range of 15 to 50 degree C (log Ksp = 7.050 + 0.000159T2. The latter showed that the solubility decreases with temperature same as anhydrous calcium carbonates such as calcite and aragonite. However, the temperature dependence is opposite in sing to ikite (hexahydrate) which is also hydrous calcium carbonate (Bischoff et al. 1992). Although it is recognized that MHC formation is favor at low temperature (Dahl, K. and Buchardt, B.), there is no MHC solubility date at the temperature lower than 15 degree C. In the present study, we determined MHC solubility between 5 to 40 degree C in order to understand the reliable stability relationships of calcium carbonate minerals under low temperature.

Solubility measurements were conducted in polycarbonate vessel covered with silicon cap with portals for the gas-dispersion tube, pH electrode with thermometer. High purity CO2-gas was bubbled through the reaction vessel after first passing through ion exchanged water kept at same temperature to pre-saturate the gas with water vapor. The MHC (200mg) was added to preheated or cooled 0.01M NaCl electrolyte solutions containing Na2HPO4 (200˜800µM) as the inhibiter. The attainment of equilibrium was evaluated with the fixed pH. After the equilibrium, the suspension were collected from the reaction vessel by preheated or cooled syringe, and filtered through a 0.2µm membrane. The mineralogy of air-dried solids and total calcium concentration in solutions were analyzed by X-ray diffraction and ion-chromatography respectively. Solubility products of MHC based on CO2 partial pressure, total calcium concentration, and pH were calculated by Visual MINTEQ ver.2.51.

X-ray diffraction indicated that MHC was not altered under all experimental conditions. The phosphate as inhibitor does not influence on the solubility data. The solubility product of MHC as function of temperature is expressed in figure 1. The solubility of MHC increases with the temperature. MHC is stable at lower temperature. The temperature dependence of MHC solubility was opposite in sign to that of earlier study (Kralj and Brecevic, 1995) which become increasingly soluble at lower temperatures. In addition, the solubility of MHC becomes lower than vaterite at the temperatures lower than 10 degree C. The present study indicates that MHC is possibly third stable calcium carbonate at lower temperature.