Geochemistry of monohydrocalcite and its potential as proxy

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Elemental and isotopic composition of calcite and aragonite are widely used as proxies of palaeo-environment and palaeo-climate. In contrast, a quantitative understanding of geochemistry of the metastable hydrous carbonates, like monohydrocalcite is yet lacking. This is remarkable, as monohydrocalcite is often found in saline lakes, cold springs, speleothems, marine cold-water settings and deep sediments, [1]. Consequently, occurrence of monohydrocalcite indicates very specific formation conditions like high alkalinity, elevated salinity and low temperature [1] [2].

Here we investigate the precipitation and transformation of metastable calcium carbonate phases. First, we applied an experimental approach at 10°C in solutions with a defined Mg/Ca ratio of 3 and different saturation indices of 0.8, 1.1 and 1.4 with respect to monohydrocalcite. The formation of monohydrocalcite depends strongly on the saturation state and precipitation time. Higher degrees of supersaturation resulted in longer stability of the mineral. Next, we investigated the geochemical signatures of obtained precipitants. We find that for oxygen isotopic fractionation the factor between monohydrocalcite and water ($\alpha_{Mhc\text{-}H2O} = 1.029$) is similar to that of aragonite, but larger than that of amorphous calcium carbonate ($\alpha_{ACC\text{-}H_2O} = 1.026$) and calcite ($\alpha_{Cc\text{-}H_2O} = 1.025$). Monohydrocalcite formed in our experiments incorporates only little Mg and Sr. The distribution coefficient of Mg between monohydrocalcite and water is 0.001 and therefore smaller than that for aragonite (0.007), calcite (0.015) and amorphous calcium carbonate (0.03) at 10°C and rapid mixing. Also the distribution coefficient of Sr between monohydrocalcite and water is 0.1 and therefore smaller than that for calcite (0.49), amorphous calcium carbonate (0.7) and aragonite (1).

Knowing formation conditions of monohydrocalcite as well as the elemental and isotopic composition will provide important paleoenvironmental information. Occurrence of monohydrocalcite indicates unaltered sediments due to its high potential of transformation.

[1] Solotchina et al., 2009, *Quaternary International* **205**, 38-52. [2] Li et al., 2008, *Quaternary International* **187**, 105-116.