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Trace element and stable isotope behaviour, and reaction rates upon experimental low-temperature dissolution of kutnahorite, CaMn(CO3)2

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Sediments are carriers of proxy signals for present and past biogeochemical reactions. In anoxic sediments, the rhombohedral carbonates calcite and rhodochrosite form solid-solutions within a wide compositional range, which are valuable proxies for the characterization of bottom-water paleo redox dynamics (e.g. Huckriede & Meischner, 1996). One important open question is the low-temperature role of the dolomite–type ordered intermediate, kutnahorite (CaMn(CO3)2), which in nature is only found in natural high-temperature environments and has not been observed at low temperatures in sediments or experiments. Despite the thermodynamic stability field of kutnahorite, its formation at low temperatures seems to be kinetically inhibited. At low temperatures, a complex dissolution-reprecipitation behaviour of kutnahorite was suggested previously (Mucci, 1991).

In the present study, the dissolution behaviour of ordered natural kutnahorite (Ca0.45Mn0.52Mg0.017Zn0.017Fe0.003CO3; Sterling Hill mine, USA) has been investigated in free-drift batch-type experiments, open and closed with respect to gaseous carbon dioxide, and flow-through reactors. The focus was set on the partitioning of minor and trace elements (Sr2+, Ba2+, Mg2+, Zn2+, Fe2+) and stable isotopes (13C and 18O).

The low-temperature (20° - 30°C) dissolution in aqueous solutions has been found to be congruent with respect to major, minor and trace elements. Extrapolation of experimental results gives a solubility product at 20°C (pKLP) of 21.21 +/- 0.14. No influence was found by the presence of a number of foreign trace salts (2-4 mM; NaCl, KCl, LiCl, RbCl, MgCl2, CaCl2; BaCl2), with the exception of MnCl2, that led to the incongruent dissolution of kutnahorite accompanied by the precipitation of Ca-rhodochrosite, as expected from partition coefficient studies (Böttcher, 1998). The development of 13C contents of DIC upon flow-through dissolution of kutnahorite was congruent and can be explained according to the closed-system mixing model (Deines et al., 1974).

The experimental data upon congruent dissolution followed a rate law depending on the relative undersaturation according to: R = k (1 - (IAP / KLPm))n; with R is the dissolution rate, k the rate constant (in mol / cm2 / s), IAP the ion activity product, m the number of ionic units in the dissolving solid, and n the reaction order. Values of -8.6 and -9.1 were found for pk in experiments open and closed to (20°C; initial PCO2 = 0.98 atm), with respective empirical reactions orders of 11 and 7. The dissolution rate of kutnahorite decreased far from equilibrium, as previously shown in experimental studies of dolomite dissolution (Busenberg & Plummer, 1982; Kirchhoff, 1988), and is much smaller than the rates found for pure calcite and rhodochrosite, or selected calcite-rhodochrosite solid solutions under the same experimental conditions. The low rates for kutnahorite may partly be explained by an inhibiting effect caused by liberated trace elements.