



The rhodochrosite-calcite solid-solution aqueous-solution system at low temperatures

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Sediments are carriers of proxy signals for present and past biogeochemical reactions/microbial activity. In anoxic sediments, the rhombohedral carbonates calcite and rhodochrosite form solid-solutions within a wide compositional range, which have been suggested to be valuable indicators for the characterization of bottom-water redox conditions in the deeps of the Baltic Sea. The formation of rhodochrosite-calcite solid-solutions (RCSS) seems to be related to episodic salt water inflows from the North Sea, followed by intense microbial activity at the sediment-water interface connecting the biogeochemical cycles of manganese, carbon, and sulfur. The exact RCSS formation and stability conditions on a mechanistic and quantitative base, however, are still not fully understood. One important open question is the role of a dolomite-type ordered intermediate, kutnahorite ($\text{CaMn}(\text{CO}_3)_2$), which is found only in natural high-temperature environments, but has not been observed at low temperatures in sediments or experiments. In this presentation, results from experimental studies are summarized on the influence of precipitation conditions on the composition RCSS, their low temperature solubility, and precipitation and dissolution kinetics, reaction paths analyses, as well as stable isotope (C, O) fractionation. The results are compared to experimental studies on the stability and reactivity of ordered kutnahorite. Despite the thermodynamic stability field of kutnahorite, its formation at low temperatures seems to be kinetically inhibited. Finally, field observations from Baltic Sea sediments are discussed in the light of the experimental results.