Diagenesis in organic-poor systems: Sediment geochemistry and nutrient fluxes in Lake Superior

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In organic-poor sediments, such as in oligotrophic lakes or the deep Arctic Ocean, the position of the redox boundary is highly sensitive to the sedimentation flux of organic matter. Small changes to the balance between the fluxes of organic carbon and electron acceptors can shift the redox boundary vertically by 10s of centimetres [1], affecting the fluxes of nutrients across the sediment surface. In oligotrophic Lake Superior, sediment oxygen penetration varies between 2 and 18 cm, and nitrate penetration between 5 and >20 cm. The water-column N:P ratio nears 10,000 [2], and there is a concern that the deep penetration of oxidants may limit the sediment remobilization of phosphorus, which strongly binds to the authigenic Fe oxyhydroxides. Using a compilation of data from several distinct basins of the lake, and with the help of a diagenetic reaction-transport model LSSE-Mega [1], we investigate the links among the geochemical cycles of organic carbon, O_2, N, Fe, and P. We identify the characteristic diagenetic regimes, determine the sensitivity of the O_2, N, and P fluxes to factors such as the sedimentation flux of organic carbon, and investigate the possibilities for regime switches, such as a reversal of the sediment-water NO_3^- fluxes.

[1] Katsev *et al*. (2006) *Limnol. Oceanogr.* **51**, 1581-1593. [2] Sterner *et al*. (2007) *Geophys. Res, Lett.* **34**, L10406-10.

Precipitation and mixing properties of the "disordered" (Mn,Ca)CO$_3$ solid solution

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Following a protocol fully described in Fernández-González *et al*. [1], the mixing properties of the calcite-rhodochrosite solid solution were determined by calorimetric measurements of the heat of precipitation of several $Mn_xCa_{1-x}CO_3$ compositions at 25°C.

An extended study of the broadening of the diffraction peaks showed that the precipitates were compositionally homogeneous. The X-Ray diffraction patterns did not comprise additional reflections that could be assigned to the ordered phase of kutnahorite [$MnCa(CO_3)_2$] and, therefore, long-range disorder could be assumed in all precipitates. The calculated positive values of the enthalpy of mixing (ΔH^m) of the Mn-bearing calcites are in agreement with the absence of long-range ordering and suggest a non-ideal solid solution with tendency to exsolve. However, the proposed miscibility gap can be considered "metastable" as it covers a compositional range in which ordered kutnahorite is the stable phase. Despite the predicted unmixing process, the complete series of the solid solution has been obtained but most of the precipitates correspond to metastable compositions that exceed the thermodynamic miscibility range.

Based on the experimental data, we propose a thermodynamic model for the "disordered" solid solution in which the excess free energy of mixing (ΔG^{ex}) has been estimated assuming completely random mixing. The obtained mixing properties have been used to calculate the aqueous solubility of this solid solution and the results are in good agreement with a series of experimental measurements reported in the literature [2, 3].

[1] Fernández-González *et al*. (2007) *Cryst. Growth Des*. **7**, 545-552. [2] Mucci (2004) *Aquat. Geochem.* **10**, 139-169. [3] Böttcher (1997) *Marine Chem.* **57**, 97-106.