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The effect of strong salinity and temperature gradients on transport processes and the formation of bathyal authigenic gypsum at a marine mud volcano

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A thermodynamic activity model (Pitzer approach) applicable to extreme environmental pTS-conditions (up to 1000 bar, 200 ˚C and 6 M NaCl) coupled to an extensive mineral database has been developed. The advantage of this code over existing ones, such as Phreeqc, Wateq, Minteq, is the additional integration of a comprehensive pressure correction, as well as the flexibility on the choice of input datasets, allowing fine-tuning of the model according the relevant pTS range.

An example of the successful application of the model is the interpretation of near-surface pore water profiles from the Mercator mud volcano in the Gulf of Cadiz. These profiles are intriguing for two reasons. First, they are characterised by a strong salinity gradient in the upper 1-2 mbsf created by the mixing of upward advecting hypersaline (halite and gypsum saturated, S=360) mud volcano fluids and seawater (S=35) and, second, the pore water profiles encompass various types of authigenic gypsum ($CaSO_4{\cdot}2H_2O$) and anhydrite ($CaSO_4$) crystals, which usually form only in evaporitic environments.

It was found that while high Ca and SO_4 concentrations from dissolution of an underlying diapir provide gypsum saturated fluids, the occurrence of supersaturation and thus authigenic gypsum (or anhydrite) precipitation is only possible through the reduction of temperature. In addition to the strong temperature control, the salinity has an important impact on the resultant composition of the precipitating $CaSO_4$ minerals. Increasing salinity significantly lowers the activity of water, thereby raising the gypsum-anhydrite transition zone from $>$1 km to about 500 m sediment depth at the MMV and during heat pulses ($>$ 30 ˚C) even to within a few metres below the seafloor.

Another effect of the strong salinity gradient is its influence on the diffusive transport of solutes. When comparing the activity and concentration profiles of dissolved species at the Mercator mud volcano, it becomes obvious that here the true transport property, the chemical potential, respectively activity, of a species has to be considered, i.e. the Maxwell-Stefan equation. An interpretation solely based on Fick's law using the concentration profiles would lead to erroneous results.