

Interpretation of extreme diagenetic settings with a new thermodynamic activity model

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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 is the incorporation of a comprehensive pressure correction, as well as the flexibility on the choice of input datasets, allowing fine-tuning of the model according to the relevant pTS range. This code is then integrated into our transport-reaction models, allowing for the interpretation of extreme diagenetic settings, where regular seawater models fail.

One such setting is the Mercator mud volcano in the Gulf of Cadiz, where the porewater profiles 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) mud volcano fluids and seawater (S=35). In addition, various types of authigenic gypsum (CaSO₄·2H₂O) and anhydrite (CaSO₄) crystals, typical for evaporitic environments, were found. We show, that here the precipitation of authigenic CaSO₄ minerals is temperature driven and directly related to heat pulses that are typically occurring at mud volcanoes. The composition of the CaSO₄ mineral, in turn, is additionally controlled by the salinity gradient, raising the gypsum-anhydrite transition zone from >1 km to about 500 m sediment depth and during heat pulses (> 30 °C) even to within a few metres below the seafloor.

Another application is the geochemistry of the sediment-hosted natural CO₂ seeps in the southern Okinawa Trough. At the Swallow Chimney, located at 1380 mbsf, liquid CO₂ and CO₂ hydrates are encountered in the top decimetres below the seafloor. Here, the strong CO₂ and concomitant pH gradient induce silicate and complete carbonate dissolution downcore. However, some carbonate is reprecipitated towards the seafloor again, as suggested by the radiogenic and stable Sr isotopy. Our thermodynamic model is used to test this hypothesis and to quantify the diagenetic processes occurring in this extreme geochemical environment.

Carbon isotope gradients in the Eocene as a constraint on the biological pump, atmospheric CO₂ and the ocean's major ion composition

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In the modern ocean surface the δ¹³C of dissolved inorganic carbon (DIC) is high (¹³C-enriched) relative to deep waters, due to isotope fractionation during biological carbon fixation and the subsequent export of organic matter from the surface to sequester ¹³C-deplete carbon at depth, the soft-tissue component of the biological pump. In the Eocene, observations suggest that these isotope gradients were greater than today, leading to the inference that the biological pump was stronger. However, this argument ignores the much greater ocean carbon inventory under high atmospheric CO₂ levels during the Eocene, which would dilute the biologically driven δ¹³C gradients. Box model simulations indicate a number of mechanisms to resolve this discrepancy, including changes in the ocean's major ion composition and meridional temperature gradient. When using observational constraints such as temperature reconstructions, the depth of seafloor carbonate preservation, fluid inclusion data and the absence of large-scale anoxia in the Eocene ocean, we find that the δ¹³C gradients are inconsistent with atmospheric CO₂ levels greater than 1200 ppm. In these Eocene scenarios, the ocean's DIC is similar to today, but pH and buffer capacity are much lower, with implications for marine calcifying organisms.