



Effects of microbial activity and silicate alteration on porefluid alkalinity and carbonate diagenesis in a deep methanogenic zone at the Peru Margin (ODP Site 1230)

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The formation of early diagenetic carbonates is of interest as it affects the geological record and preserves and/or alters geochemical signatures indicative of past environments and life. An important factor for carbonate precipitation is alkalinity production by microbial activity, such as sulfate reduction (SR) and anaerobic oxidation of methane (AOM). In contrast, production of CO₂ by fermentative processes, such as methanogenesis, cause acidification of the porefluid and counteract the formation of carbonates. Partial dissolution of silicates seems to have an influence on fluid alkalinity during burial diagenesis, and it has been suggested that the additional alkalinity from clay mineral alteration may drive carbonate precipitation even in strongly methanogenic zones.

We simulate alkalinity production by microbial activity and clay mineral alteration using a reaction-transport model in combination with a mineral equilibration model (PhreeqC). The resulting alkalinity profiles are compared to measured profiles of porewater chemistry at Ocean Drilling Program (ODP) Site 1230, where an alkalinity of 150 mmol/l is reached ~150 m below seafloor (mbsf).

By fitting the simulated ammonium concentration profile, as indicator of total dissimilatory microbial activity to measured concentrations, 115 mmol/l alkalinity was calculated. The resulting profiles showed that calcite is slightly oversaturated between 30 and 140 mbsf, despite a contribution of up to 240 mmol/l of dissolved CO₂. This is largely due to additional alkalinity produced due to ammonium remineralization during methanogenesis. It is consistent with the occurrence of small amounts of calcite between 60 and 140 mbsf which is deep in the zone of methanogenesis where conditions were thought to be corrosive for carbonates due to acidification by CO₂.

XRD-analysis of the samples revealed the minerals illite, kaolinite, smectite, chlorite, quartz, feldspar and calcite. In addition, amorphous opal is present. 48 scenarios including all thermodynamically possible combinations of observed minerals, and assuming porewater composition calculated from the reaction-transport model and normal seawater salt concentrations with 10 mM Ca²⁺ and 50 mM Mg²⁺, resulted in strongly different alkalinity production. One scenario including only chlorite, calcite and opal-A reproduced the measured [Ca²⁺], [Mg²⁺], DIC and alkalinity profiles of Site 1230 best. All other scenarios including more than one clay minerals resulted in unrealistically high alkalinity. The main insight gained from this study is that despite the clay minerals being far from thermodynamic equilibrium with marine porewaters they have not equilibrated during several million years. The processes are largely inhibited or slow. Any effect that could help to lower the kinetic barriers with respect to congruent or incongruent clay mineral dissolution could strongly affect carbonate diagenesis. Such effects would be appreciated for application of CO₂ capture and storage in suitable porous rock reservoirs as it could help buffering acidification and induce carbonate precipitation to permanently trap and store CO₂ as carbonate rock.