

Geochemical modeling of the influence of silicate mineral alteration on alkalinity production and carbonate precipitation

Gerhard Herda (1), Stephan M. Kraemer (2), Susanne Gier (1), Patrick Meister (1,3)

(1) Department of Geodynamics and Sedimentology, University of Vienna, Vienna, Austria (jerry.herda@gmail.com), (2) Department of Environmental Geosciences and Environmental Science Research Network, University of Vienna, Vienna, Austria (stephan.kraemer@univie.ac.at), (3) Department of Lithospheric Research, University of Vienna, Vienna, Austria (patrick.meister@univie.ac.at)

High CO₂ partial pressure (pCO₂) in deep rock reservoirs causes acidification of the porefluid. Such conditions occur during injection and subsurface storage of CO₂ (to prevent the release of greenhouse gas) but also naturally in zones of strong methanogenic microbial activity in organic matter-rich ocean margin sediments. The acidic fluids are corrosive to carbonates and bear the risk of leakage of CO₂ gas to the surface. Porefluid acidification may be moderated by processes that increase the alkalinity, i.e. that produce weak acid anions capable of buffering the acidification imposed by the CO₂. Often, alkalinity increases as a result of anaerobic microbial activity, such as anaerobic oxidation of methane. However, on a long term the alteration of silicates, in particular, clay minerals, may be a more efficient mechanism of alkalinity production. Under altered temperature, pressure and porefluid composition at depth, clay minerals may change to thermodynamically more stable states, thereby increasing the alkalinity of the porefluid by partial leaching of Mg-(OH)₂ and Ca-(OH)₂ (e.g. Wallmann et al., 2008; Mavromatis et al., 2014). This alteration may even be enhanced by a high pCO₂. Thus, silicate alteration can be essential for a long-term stabilization of volatile CO₂ in the form of bicarbonate or may even induce precipitation of carbonate minerals, but these processes are not fully understood yet.

The goal of this study is to simulate the alkalinity effect of silicate alteration under diagenetic conditions and high pCO₂ by geochemical modeling. We are using the program PHREEQC (Parkhurst and Appelo, 2013) to generate high rock/fluid ratio characteristics for deep subsurface rock reservoirs. Since we are interested in the long-term evolution of diagenetic processes, over millions of years, we do not consider kinetics but calculate the theoretically possible equilibrium conditions. In a first step we are calculating the saturation state of different clay minerals as well as carbonates in porefluids under different pCO₂ levels. In a second step, we will let the minerals react to a thermodynamically stable state and thereby observe the resulting alkalinity effect and the effect on carbonate precipitation.

So far, modeling showed that saturation states of some of the most common clay minerals, including kaolinite, illite, montmorillonite and chlorite in a standard seawater solution strongly depend on silica and aluminum concentrations, but they show very little dependence on the pH. This is understandable since a congruent dissolution of clay minerals does not significantly increase or decrease the alkalinity. However, partial leaching of structural ions by incongruent dissolution/precipitation should have a strong effect on porewater alkalinity. Hence, substitution reactions will have to be simulated as part of this study. Calculated mineral alteration and rock-fluid interactions in deep sediments will contribute to a better understanding of carbonate diagenesis but also of long-term effects in subsurface CO₂ storage reservoirs.

Mavromatis et al. (2014) *Chem. Geol.* 385, 84–91.

Parkhurst, D.L., and Appelo, C.A.J. (2013) *U.S Geological Survey Techniques and Methods*, book 6, chap. A43, 497 p.

Wallmann et al. (2008) *Geochim. Cosmochim. Acta* 72, 3067–3090.