

Towards a consistent quantitative description of mineral precipitation and dissolution rates

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Knowledge of the mechanisms and rates of mineral dissolution and precipitation, especially at close to equilibrium conditions, is essential for describing the temporal and spatial evolution of natural and industrial processes including weathering, diagenesis, hydrothermal deposit formation, CO₂ sequestration, and radioactive waste disposal. The Surface Complexation approach (SC) combined with Transition State Theory (TST) provides an efficient framework for describing mineral dissolution over wide ranges of solution composition, chemical affinity, and temperature. There has been a large debate for several years, however, about the comparative merits of SC/TS versus classical growth theories for describing mineral dissolution and precipitation at near to equilibrium conditions. The paucity of combined microscopic and macroscopic rate measurements on identical samples has prevented reconciliation of the surface coordination chemistry and crystal growth approaches.

This study considers recent results obtained in our laboratory on quartz, brucite, gibbsite, boehmite, kaolinite, magnesite, dolomite, and hydromagnesite dissolution and precipitation at near to equilibrium conditions via the combination of complementary techniques including batch and mixed flow reactors, hydrogen-electrode concentration cell (HECC), potentiometric titration cell, and hydrothermal atomic force microscopy (HAFM). Results show that the dissolution and precipitation of hydroxides, kaolinite and hydromagnesite powders of relatively high surface area closely follow SC/TST rate laws with a linear dependence of both dissolution and precipitation rates on fluid saturation state even at close to equilibrium ($\Delta G < 500$ J/mol) conditions. This occurs because sufficient reactive sites are available for dissolution and growth (kink, steps, edges) allowing reactions to proceed via the direct and reversible detachment/attachment of reactants at the surface. In contrast, for quartz and magnesite crystals, whose surfaces contain much fewer active sites, crystal growth (and dissolution) rates at near equilibrium conditions exhibit either a parabolic (defect assisted nucleation, spiral growth) or linear (attachment/detachment at reactive sites) dependence on saturation state depending on the treatment of the crystals before the reaction. For example, after extended dissolution (a process that creates active sites) both quartz and magnesite crystals exhibit transient linear growth rates. SC/TST rate laws can thus be applied only to those minerals that have abundant reactive sites density. It follows that determination of the active site density and origin (screw dislocations, preexisting steps...) on mineral surfaces is critical to identifying the mechanism and thus the rate equations that can describe quantitatively mineral dissolution and precipitation rates as a function of fluid composition in natural and industrial processes.

Intact polar tetraether lipids in the Arabian Sea water column and sediments: Implications for TEX₈₆ paleothermometry

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The TEX₈₆ is an increasingly used paleotemperature proxy and relies on the fact that temperature affects the number of cyclopentane moieties in thaumarchaeal membrane lipids (glycerol dibiphytanyl glycerol tetraether lipids, GDGTs). In living Archaea, these lipids are present as intact polar lipids (IPL) with sugar- and/or phosphate-containing head groups attached to the core lipids (CL). Most studies on TEX₈₆, however, have up to now examined (fossil) CL GDGTs rather than IPL GDGTs, derived from living Archaea.

In this study, we examined the distribution and TEX₈₆-values of CL and IPL GDGTs in both the water column and sediment cores of the Arabian Sea, which contains a pronounced oxygen minimum zone. The depth profiles of crenarchaeol core lipid with a phosphohexose or dihexose head group match profiles of (expressed) genes specific for ammonia-oxidizing Thaumarchaeota. However, crenarchaeol with a hexose head group did not match the genetic depth profiles, suggesting that this IPL is partially of fossil origin. Furthermore, the concentration profiles of core lipid crenarchaeol and IPL-derived crenarchaeol showed a second peak in their abundance within the core of the OMZ which was not found in the archaeal gene concentration profiles. This representing additional evidence for a fossil contribution to the IPL pool, specifically for the glycosidic GDGTs. TEX₈₆ values of both fossil core lipid and IPL-derived GDGTs increased from surface waters to the core of the OMZ, below which they decreased again, and did not correlate with *in situ* temperature. TEX₈₆ values of IPL-derived GDGTs did correlate well with the relative amount of glycosidic GDGTs and were consistently higher than that those of CL GDGTs.

We subsequently isolated IPL GDGTs from Arabian Sea sediments to determine cyclopentane distributions and TEX₈₆ of the individual IPL GDGTs. We observed strong differences in GDGT-composition amongst head groups: GDGT-2 and -3 (numbers indicate the number of cyclopentane moieties) are predominantly present as glycolipids, while GDGT-1 is predominantly present as phosphoglycolipid. A similar observation is made for IPL GDGTs of enriched Thaumarchaeota, i.e. GDGT-0, -1 and crenarchaeol predominantly occurring as CL of phosphoglycolipids, and GDGT-2, -3 and -4 as CLs of dihexose GDGTs [1]. As a consequence, in enrichment cultures, the TEX₈₆ shows a relation with the relative amount of dihexose GDGTs, i.e. increasing TEX₈₆ with increasing amount of dihexose GDGTs.

Our results thus suggest that head group composition of IPL GDGTs in Thaumarchaeota and selective preservation of glycosidic GDGTs during diagenesis may strongly impact TEX₈₆ values of produced GDGTs in deep marine waters.

[1] Schouten S., et al. (2008) *Geochim Cosmochim Acta* **74**, pp. 3806 - pp. 3814.