

## Modeling mineral aging in the Critical Zone

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Mineral aging is a widely recognized process affecting chemical weathering and element cycling in the Critical Zone, and yet quantitative models for it are rarely described or used. Mineral aging may involve changes in thermodynamic stability for secondary phases that are important in regulating the overall rate of chemical weathering and element cycling by controlling undersaturation with respect to primary phase(s). These changes in stability often follow the Ostwald Step Rule, with a sequence of progressively more stable phases developing over time. Or the progression may involve a single phase that gradually reorders and/or ripens with time to a larger and thermodynamically more stable phase, although the latter can often be represented operationally as a process similar to the classical Ostwald Step Rule. Or the progression may involve a series of changes taking place at equilibrium that reflect the relative stability of phases with size-dependent solubilities, as suggested by Navrotsky in recent publications. In order to capture these transformations, it is normally necessary to track changes in crystal size over time, a capability that is normally not found in any of the commonly available hydrogeochemical transport codes suitable for simulating the Critical Zone. In this work, we compare the various approaches for modeling secondary mineral thermodynamic transformation in terms of their ability to describe observations of kaolinite aging at the Santa Cruz chronosequence.

Mineral aging may also involve changes in reactivity over time. Although this may apply to both primary and secondary phases in the Critical Zone, the issue is most important for primary phases whose reactivity is observed to decrease by orders of magnitude over geological periods of time. Part of the challenge here is to resolve the discrepancies between rates obtained in kinetic experiments involving suspensions of minerals and rates determined on single step faces or reactive sites, particularly since the abundance of reactive sites may change over time. To address this issue, a multi-rate model based on individual, time-dependent reaction mechanisms and sites is proposed for use at the continuum scale

## Silica solubility and transport in saline, immiscible fluids: Application of the Si-Cl geothermobarometer to sub-seafloor hydrothermal systems

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Liquid-vapor immiscibility and phase separation are widely recognized processes that influence the evolution of seafloor hydrothermal systems, including the vent fluid chemistry. Seafloor hydrothermal vent fluids are considered to represent the low-salinity vapor portion of an immiscible fluid pair generated at depth. Estimation of P-T conditions at depth in the sub-seafloor hydrothermal system based on measured vent ('vapor') salinity requires that either the temperature or pressure at depth is known [e.g. 1]. The dissolved silica content of vent fluids provides an additional constraint on the P-T conditions of liquid-vapor equilibrium at depth. Experimental studies have shown that hydrothermal fluids in sub-seafloor systems reach quartz saturation, and quartz solubility varies systematically with pressure, temperature and salinity (X). Therefore, by combining known phase relations of the H<sub>2</sub>O-NaCl system with a quartz solubility model for the H<sub>2</sub>O-NaCl-SiO<sub>2</sub> system, a unique P-T-X condition is defined that is consistent with liquid-vapor-quartz equilibrium and with the measured vent salinity and dissolved silica content [2].

Application of Si-Cl thermobarometry to interpret vent chemistry data from seafloor systems is model dependent. Isoleths of vapor salinity and quartz solubility intersect at low angles in P-T space. As a result, slight variations in the slopes of either isopleth cause large differences in estimated P-T conditions. Thus, there is significant uncertainty in P-T estimates made using this method because the P-T conditions vary widely depending on the H<sub>2</sub>O-NaCl equation of state (EOS) and quartz solubility model used. In many cases, the P-T conditions predicted by Si-Cl geothermometry of seafloor vent chemistry data are significantly higher than conditions generally expected in these systems based on other data. An assessment of the errors associated with different EOS and quartz solubility models will be presented along with improvements based on results of two-phase flow modeling and quartz-fluid reaction kinetics.

[1] Von Damm (2004) *Geophys. Monograph* **148**, 285–304.

[2] Fontaine *et al.* (2009) *Geochem. Geophys. Geosyst.* **10**.