Rates of silicate dissolution in deep-sea sediments

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Ocean Drilling Project Site 984 in the North Atlantic is composed of high-porosity, uncemented, silicate-rich sediment derived primarily from Iceland. Geochemical profiles from Site 984, spanning approximately 2 million years of sediment accumulation, are modeled using a multi-component reactive transport model (Crunch) to determine in-situ rates of plagioclase dissolution and other diagenetic processes, including sulfate reduction and anaerobic methane oxidation. The dominant transport mechanisms in this system are molecular diffusion and burial. Thus many of the proposed mechanisms for the inhibition of dissolution in natural systems, such as hydrologic limitation of reactive surface area or variable fluid flow, are not present. The model also includes formulations for modeling the $^{234}U/^{238}U$ isotopic system. The $^{234}U/^{238}U$ in the pore water, sediment, and bulk calcite offers an additional constraint on the rate of plagioclase dissolution, and the rate and magnitude of calcite recrystallization. Many other factors that have been discussed as possible explanations for the discrepancy between laboratory and field rates, including the effect of solution saturation state (reaction affinity), Al-inhibition and the rates of transport relative to reaction, are also explicitly considered in the reactive transport formulation.

Plagioclase surface area was estimated at 3.0 ± 0.6 m^2/g based on geometric arguments and the depletion of $^{234}U/^{238}U$ in the solid sediment as a result of α-recoil of ^{234}Th. Using this surface area value for the reactive surface area, the modeling predicts a dissolution rate constant that is about 10^4 to 10^5 times smaller than the laboratory-measured value when a linear dependence of the rate on the reaction affinity is assumed. Alternative rate law formulations, including Al-inhibition and a nonlinear dependence on the undersaturation of the pore water with respect to plagioclase do not account for the slow rate because the pore fluid-plagioclase system is maintained strongly out of equilibrium by microbial processes and clay precipitation. The major element and isotopic models predict similar dissolution rate constants if additional lowering of the $^{234}U/^{238}U$ ratio is attributed to isotopic exchange via recrystallization of marine calcite. The results also highlight the important link between the biogeochemical and inorganic reaction pathways.

Length and time dependent properties at mineral-water interfaces

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Experimental observation of elementary step edge motion on mineral surfaces using *in-situ* Scanning Probe Microscopy (SPM) in aqueous solutions has enabled the calculation of specific properties relating to growth and dissolution at the atomic scale. In particular, the length dependent behavior of elementary steps may be directly linked to the dynamics of ion attachment and detachment from surface sites. Step speeds at very short step lengths (< 300 nm) are generally found to increase with step length, but the observations are dependent on the experimental parameters chosen and thus, potentially biased. When these parameters were optimized, data scatter precluded quantitative comparison of different theoretical models in light of the experimental data. Analysis of experimental errors revealed that significant experimental bias in the determination of step edge properties such as the edge free energy and kinetics of kink propagation and nucleation are introduced if the instrument bandwidth is not appropriate for the specific dynamics of the step edge. In light of step growth models based on either equilibrium assumptions or non-equilibrium assumptions, these biases tend to favor one model over the other.

The time dependence of surface properties, characterized with SPM, reveals the response of surfaces to changing of solution variables such as pH and saturation state. These two variables, which probably are the most geochemically significant in terms of determining the kinetics of mineralization and dissolution in natural waters, influence both the kinetics at elementary step edges as well as mineral surface morphology. While step edges may respond relatively quickly to changes in conditions, the surface morphology often exhibits a history-dependence that may prevail for significantly longer time periods. This hysteresis has important implications in the modelling of mineral-water reactions.