

The application of natural divalent cation isotope (Ca, Sr, Mg) fractionation (DCIF) in earth system research

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Geochemical records of elemental and isotopic variations in magnesium (Mg), calcium (Ca) and strontium (Sr) provide key information for the chemical history of our planet, its long term climate evolution and the reconstruction of past water temperatures. In particular, the recent progress in instrumentation (e.g., multi-collector ICP-MS applications) and the improvements of isotope measurement techniques (e.g., TIMS double spike technique) showed that the divalent cation isotope ratios like $^{44}\text{Ca}/^{40}\text{Ca}$, $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{26}\text{Mg}/^{24}\text{Mg}$ are spatially and temporarily not constant on Earth, but rather change as a function of the intensity of continental weathering, mineral polymorphism, pH, the precipitation rates and as a function of ambient temperature during inorganic mineral precipitation and biomineralisation. High temperature controlled, Raleigh type DCIF is observed during hydrothermal processes related to rock and mineral differentiation in magma chambers as well as during the precipitation of anhydrites, calcites and aragonites in the hydrothermal plumbing systems of the mid-ocean ridges. However, very large isotope fractionation ($\sim 4\%$) values for Ca isotopes can be observed during physiologically controlled fractionation in the human body related to its trace metal homeostasis. Similar to trace element partitioning, temperature dependent DCIF is different for inorganically and biologically precipitated minerals (e.g. carbonates). In addition, there are species dependent DCIF processes which reflect the strong physiological control of uni- and multi-cellular organisms on their trace element homeostasis while sequestering trace elements in different reservoirs. In this regard the DCIF may contribute to a better understanding of the function of ion selective channels and pumps on the trace element partitioning between biominerals and the bulk solution.

Guided nanoscale remodeling of soluble surfaces using a novel probe-based method

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A methodology for remodeling surfaces at nanometer length scales would enable the mitigation of defect or damage sites in a broad range of technologically relevant materials, such as optics used in high-fluence lasers. Here we describe a novel probe-based method to guide the remodeling of KDP (KH₂PO₄) surfaces that exploits two phenomena occurring at nm lengthscales: 1) the unique physical chemistry that occurs in the region surrounding a nanoscale tip-surface contact, and 2) the natural driving force for elimination of regions of high curvature. This method takes advantage of the meniscus that forms through condensation at a tip-surface contact in a humid environment. Surrounding this meniscus is a naturally occurring ultrathin aqueous film on the crystal surface. Our experimental model consists of two parts: 1) repair of a groove etched into the KDP surface by hard contact with an atomic force microscope (AFM) tip and 2) creation of pillars and beams by tip-induced overgrowth on a smooth KDP surface.

We find that the wet micro-environment formed by the meniscus, combined with tip rastering during AFM scanning over a groove site, results in local surface smoothing and filling-in of the groove such that groove depth decreases with time. We present *in situ* AFM measurements of the kinetics of this surface remodeling process. Starting with the Gibbs-Thompson relation, we present a quantitative physical analysis of damage site remodeling. With the controlling parameters in the model constrained by independent measurements, we find that the predictions are in good agreement with experimental results.