Fe isotope fractionation during phyllosilicate dissolution: Effect of protons, ligands and K concentration

M. KICZKA[1,2], J.G. WIEDERHOLD[1,2], S.M. KRAEMER[3], B. BOURDON[2] AND R. KRETZSCHMAR[1]

[1]Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, Switzerland (mirjam.kiczka@env.ethz.ch)
[2]Institute of Isotope Geochemistry and Mineral Resources, ETH Zurich, Switzerland
[3]Department of Environmental Geosciences, University of Vienna, Austria

Chemical weathering of primary phyllosilicates is a major soil-forming process in young granitic soils and an important nutrient source for plants. We investigated Fe isotope fractionation during proton- and ligand-controlled dissolution of biotite and chlorite to develop Fe isotopes as a tracer for the biogeochemical Fe cycle. The effect of potassium (K) was studied since it prevents the expansion and exfoliation of biotite, possibly influencing the accessibility of Fe sites and hence Fe isotope fractionation during dissolution.

Dissolution of a biotite/chlorite-enriched mineral fraction of the Aare granite (Central Alps, CH) in HCl or 5mM oxalic acid was followed from 2h to 100d. Initial pH was 4 and 4.5, respectively and drifted up to 5.5. The initial K concentration in solution was 0, 0.5, or 5mM. Experiments were performed under anoxic conditions to avoid instantaneous precipitation of Fe-hydroxides. Filtrates were analyzed for major cations and Fe^{2+}/Fe^{3+}. Fe isotope ratios were measured by HR-MC-ICP-MS (Nu1700, Nu Plasma).

The dissolution rate in oxalic acid was ~15 times higher than in HCl. Addition of 5mM K decreased the dissolution rate by 60 and 35% in HCl and oxalic acid, respectively. The early dissolved fractions were always enriched in light Fe isotopes (up to 1.4‰ lighter in δ^{56}Fe), indicating a kinetic isotope fractionation effect. K had no significant influence on Fe isotope fractionation during ligand-promoted dissolution, but had a major effect in proton-promoted dissolution. At comparable fractions of total Fe dissolved, samples with K addition exhibited δ^{56}Fe values ~0.7‰ lighter than in the K-free treatments. In the late stages (~20% of Fe dissolved), Fe isotope composition during proton-promoted dissolution reached bulk composition (additional experiment at pH 2, no K) while solutions in oxalic acid systems remained ~0.12‰ lighter in δ^{56}Fe. Our results indicate that Fe weathering fluxes should be enriched in light isotopes, whereby the extent of fractionation is controlled by i) the relative importance of dissolution mechanisms, and ii) pore water chemistry influencing the degree of mineral exfoliation.

Challenges in modeling warm Cenozoic climates

JEFFREY T. KIEHL

National Center for Atmospheric Research, Climate Change Research Section, 1850 Table Mesa Drive, Boulder, CO 80305 USA (jtkon@ucar.edu)

The current and future rate of carbon dioxide emissions due to human activity is unprecedented. The estimated range of radiative forcing for the end of this century is around 5 to 10 Wm^{-2} depending on assumed energy use strategies. This change in forcing will take place on the order of a century. The last time Earth experienced this level of radiative forcing was during the early to mid Cenozoic, in which the rate of increase in forcing took place on much longer time scales (millennia to millions of years). Thus, understanding warm Cenozoic climates provides unique insight into important climate processes operative in warm climate regimes. One of the greatest challenges to climate modeling is the realistic representation of warm climates of deep time. The equable climate of the early Cenozoic is representative of a time when polar regions experienced extreme warmth (of around 20°C), while the tropics were also warm (perhaps close to 40°C). This presentation will provide an analysis of the temporal evolution of radiative forcing for the Cenozoic and how this relates to future climate forcing. Simulations of warm Eocene climates will be presented to explore possible physical mechanisms for maintaining the observed pole-to-equator temperature gradient. Implications of these model simulations for warm Eocene ocean circulations will also be discussed. Finally, the importance of these results to climate sensitivity in warm climate regimes will be explored.