Advances in Stable Isotope Measurements With High Mass Resolution MC-ICPMS

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The interest in stable isotope fractionation of metals has increased within the last few years in geo- and cosmochemistry. Using MC-ICPMS the study of natural mass dependent isotope fractionation increased to heavier elements including the transition metals (e.g. Fe, Cu, Mo) and even heavy metals, such as Hg, Tl. However, many elements, particularly in the mass range of < 80 amu suffer from polyatomic interferences: Ar-oxides, -nitrides, -hydroxides, -carbides, combinations of C, N, O, H and from interferences coming from the sample itself, in particular for the Laser technique. All these interferences can reduce the analytical accuracy and precision.

We present a general approach to eliminate the polyatomic interferences using the **Thermo**Finnigan NEPTUNE MC-ICPMS in high mass resolution mode. All polyatomic interferences up to ca. mass 90 are heavier as the respective elemental species of the same nominal mass. Therefore, high mass resolution isotope measurements can be performed by closing down the entrance slit of the analyser, but leaving the collector slits of the detectors in low resolution mode. The interferences are clipped at the high mass side of the detector slit, while the elemental peak enters the detector. This technique offers the possibility to measure e.g. Si, Ca, Cr, Fe without any limitation in the sample introduction setup in order to suppress interferences. Measurements of Si, Ca, Cr and Fe were performed using Laser ablation or running them from solutions on standards and spiked samples. Wet plasma and dry plasma techniques (using the Cetac ARIDUS) were used over a wide range of sample concentrations to demonstrate the robustness and flexibility of the technique. All results agreed within analytical uncertainties (of ca 0.05-0.1‰) irrespective of sample inlet system. For the elements up to iron NEPTUNE's medium resolution mode is sufficient to perform all measurements with flat top peaks.

Due to NEPTUNE's high sensitivity concentration levels as low as 100ppb for Cr or Fe could be measured precisely in medium mass resolution mode.

As sample concentrations decrease the plasma related interferences become more and more dominant. Because of NEPTUNE's high abundance sensitivity elemental isotope ratios can be measured with no loss pf accuracy even with polyatomic peaks at similar intensities present.

If interferences levels increase too much higher values (x 20 higher than elemental intensities), an analytical blank correction maybe adequate.

Hydrologic and thermodynamic controls on chemical weathering

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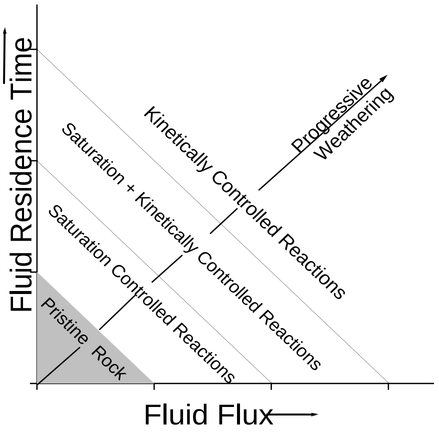
Introduction

The extent to which chemical weathering is coupled to changes in atmospheric CO_2 and long-global climate was been a matter of considerable recent debate. While the linkage between precipitation and natural silicate weathering is established [1] the exact chemical mechanisms that control this relationship is not well documented. Although kinetics have been the primary focus in experimental studies, this paper argues that most natural weathering occurs in water/rock systems that are in near-thermodynamic saturation with respect to primary silicate phases. Therefore, much weathering is transport-limited and that small changes in magnitude of fluid fluxes produced by differences in precipitation have large impacts on the respective dissolution rates

Results

Data from several soil environments demonstrate that natural weathering of feldspars is both much slower and more selective than predicted based on experimental kinetic studies. Calculations involving detailed determin-ations of solute compositions, including dissolved Al speciation and soil gas CO2, indicate near-thermodynamic saturation, which based on transition state theory, strongly retards weathering. Concurrent hydrologic char-acterization shows that fluid fluxes, which control solute and gas compositions, are exponentially dependent on moisture content and that solutes are recharge only under relatively wet conditions. A simple spread sheet model coupling these relationships show that weathering is strongly dependent on solute transport and on the magnitude of the fluid flux, which in many weathering environments correlates directly with precipitation. The progressive evolution of transported to kinetically limited weathering is shown in the schematic below.



[1]White A. F. and Blum A. E. (1995). *Geochimica et Cosmochimica Acta* **59**, 1729-1747.