

HELGES: Helmholtz Laboratory for the Geochemistry of the Earth Surface

GFZ German Research Centre for Geosciences *

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Abstract: New developments in Geochemistry during the last two decades have revolutionized our understanding of the processes that shape Earth's surface. Here, complex interactions occur between the tectonic forces acting from within the Earth and the exogenic forces like climate that are strongly modulated by biota and, increasingly today, by human activity. Within the Helmholtz Laboratory for the Geochemistry of the Earth Surface (HELGES) of the Helmholtz Centre Potsdam GFZ German Research Centre for Geosciences, it is our goal to quantify the rates and fluxes of these processes in detail and to develop new techniques to fingerprint them over various temporal and spatial scales. We use mass spectrometry to analyze metal stable isotopes, element concentrations, and cosmogenic nuclides to fingerprint and quantify geomorphological changes driven by erosion and weathering processes. We use these novel geochemical tools, to quantify, for example, the recycling of metals in plants after their release during weathering of rocks and soils, soil formation and its erosion rates, and mechanisms and speed of sediment transport through drainage basins. Our research is thus dedicated towards quantifying material turnover rates at the Earth's surface by using geochemical fingerprints.

1 Introduction

Our goal is to understand in detail the range of processes that shape the Earth's surface. To this end, we employ state-of-the-art analytical tools at the Helmholtz Laboratory for the Geochemistry of the

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Earth Surface (HELGES) that is operated by the Earth Surface Geochemistry group at the GFZ German Research Centre for Geosciences (GFZ). At the heart of the laboratory are analytical instruments such as a multicollector ICP-mass spectrometer, single-collector ICP mass spectrometers, an ICP optical emission spectrometer, for analysis of dissolved samples, an in-house built femtosecond laser ablation system coupled to the ICP-MS or OES for concentration and isotope ratio measurements performed on solid samples, and ultraclean chemical preparation laboratories. To accommodate the HELGES laboratories, an annex to the existing building was constructed between 2011 and 2013. Construction was completed in August 2013 and now more than 200 m² of laboratory space is available for sample preparation of terrestrial and atmospheric cosmogenic nuclides (¹⁰Be and ²⁶Al) and measurement of stable isotopes of metals and metalloids (e.g., Li, Mg, Si, Fe, Sr). We perform these analyses in geological and environmental sample materials, such as sediment, rock, river water, soil, and vegetation. Two clean laboratories, with laminar flow workstations, are available for sample preparation of low concentration samples to avoid contamination in order to obtain accurate measurements. In addition to the clean laboratories, several dry and wet chemistry laboratories provide the necessary equipment for preparation of solid and liquid samples. We maintain dry laboratories for mineral separation such as rock crushing and sieving, wet chemical laboratories for filtration of water samples, microwave assisted sample dissolution and specific methods for the separation of quartz for terrestrial cosmogenic nuclide analysis, as well as laboratories for microscopy and micro-analytical work by femtosecond laser ablation.

2 Methods

2.1 Cosmogenic-nuclide based Geomorphology

The possibility to measure the rates and dates of landscape processes by terrestrial cosmogenic nuclides (e.g., ¹⁰Be and ²⁶Al) is currently leading to an entirely new understanding of the processes that shape the Earth's surface. Cosmogenic nuclides are generated when secondary cosmic rays (mainly neutrons) hit molecules in the atmosphere ("meteoric") or at the Earth's surface ("in situ"). The generated atoms are so rare (only 10⁴ to 10⁸ atoms/g sample) that measurement by a high-sensitivity accelerator mass spectrometer preceded by physical and chemical pre-concentration is required. We routinely use terrestrial cosmogenic nuclides in river sand and rock samples to measure rates of erosion and weathering, from the individual soil profile to a continental drainage basin, and the duration of exposure of portions of the Earth's surface. For example, we use these nuclides to quantify sediment transfer through river floodplains over long time- and large spatial scales, or when glaciers were at their maximum extent. We very recently developed a mass-balance framework in which the ratio of the meteoric cosmogenic nuclide ¹⁰Be to that of stable lithosphere-derived ⁹Be is employed as an innovative tracer of Earth surface processes. We apply this method to small volumes (< 1 g) of fine-grained sediment and water samples.

2.2 Metal stable isotopes

We explore the field of metal (e.g., Fe, Li, Mg) and metalloid (Si) stable isotope fractionation. Breaking and binding of chemical bonds leads to minute shifts in the relative isotope ratios of these elements (amounting to less than a permil in an isotope ratio). The analytical challenge posed is enormous, and amounts to measuring the circumference of a football field to the precision of the length of a match-box. These methods are employed to fields such as the budgets of the Earth's principle geochemical reservoirs, experimental calibration of stable isotope fractionation, and evolution of the Earth's hydrosphere's redox-state. The emphasis is on calibrating these new tools in settings in which we understand the underlying geomorphic and weathering processes, including the cycling of these elements through plants.

2.3 Low-level element concentrations in environmental samples

To determine fluxes and processes of cycling of elements through the Earth surface the determination of major and trace element concentrations is required. As these levels are often very low, for example in the dissolved form in river water or as micro-nutrients in organisms, dedicated low-level measurement facilities are required. One challenge is to accommodate the large variety in sample matrices in inorganic and biogenic Earth surface materials. A second challenge is to be able to measure these a) in natural fluids, b) in the dissolved form after sample decomposition, and c) in solids by a micro-analytical.

Applications to Earth Science problems

- Exploring processes that shape Earth's surface on different temporal and spatial scales
- How fast is soil formed and how fast it is eroded? How rapidly are mountains eroded?
- What is the speed of sediment transport? How fast is weathering?
- Biogeochemical transformations in the Earth's "Critical Zone"
- Sediment budgets for large river basins
- Fingerprinting metal uptake and translocation in higher plants
- Tracing chert sediment formation with stable silicon isotopes
- The role of plants in weathering and cycling of mineral nutrients
- Ages of Earth surface deposits
- Transfer of dissolved elements in rivers

3 Laboratory infrastructure and instrumentation

We operate clean laboratories for "non-traditional" (e.g. metal and metalloid) stable isotope and cosmogenic nuclide sample preparation. Sample preparation for stable isotope measurements is performed in a metal-free clean room laboratory supplied with filtered air to avoid addition of environmental contamination to small sample amounts. Critical low-blank applications are performed in metal-free laminar-flow-workstations supplied with filtered air.

Diverse sample preparation methods are available. These include hotplate acid dissolution of rocks, soils, plant and other sample types. Also microwave assisted sample dissolution and alkali-flux fusion at 700°C is available. Furthermore, an iridium strip heater is available to allow flux-free fusion of powder samples (from e.g. rocks, soils) to produce homogenous glasses for laser ablation ICP-MS analyses of element concentrations and isotope ratios.

For the treatment of terrestrial *in situ*-produced cosmogenic nuclides (^{10}Be and ^{26}Al) on river and rock samples, we perform several purification steps. From sieved samples, minerals are separated by magnetic separation and/or heavy liquids, and silicate and oxide minerals are chemically separated from quartz, mainly employing ultrasonic bath treatment and acid treatment as well small- and large-scale feldspar flotation, in order to obtain pure quartz samples. Purity of quartz samples is routinely checked by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Varian 720ES). Pure quartz samples are then treated in the clean laboratory; we use selective enrichment methods that include, after acid dissolution, element separation by ion chromatography and alkaline precipitation. The selective enrichment of meteoric cosmogenic nuclides is performed using similar clean laboratory methods on fine-grained sediment or soil samples by a sequential chemical leaching. The measurement of cosmogenic nuclides using accelerator mass spectrometry (AMS) is performed within a collaboration agreement with the University of Cologne on the German National Science Foundation (DFG)-funded 6MV AMS. During the sample preparation procedure, we add a ^9Be -carrier that was prepared from a phenakite mineral obtained from a deep mine. $^{10}\text{Be}/^9\text{Be}(\text{carrier})$ ratios of the long-term procedural lab blanks are around 10^{-16} , showing the stable low-blank performance of the laboratory. This low laboratory background in ^{10}Be , coupled to the possibility to measure sample ratios $^{10}\text{Be}/^9\text{Be}$ of 10^{-15} at the AMS, allows the routine preparation of samples from rapidly eroding settings (> 2 mm/yr) or having very young (< 100 years) exposure ages.





Figure 1: HELGES clean laboratory facilities showing metal-free laminar workstations.

3.1 Mass spectrometry

We operate five spectrometers with an inductively coupled plasma source (ICP) for element concentration and isotope ratio analyses of liquid and solid samples with liquid sample introduction systems and laser ablation sampling for micro scale measurements, respectively. A Thermo Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) is used for isotope measurements (Li, Mg, Si, Fe, Sr). Concentration measurements are done by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 720ES), quadrupole ICP-MS (Thermo iCAP-Qc), and sector field ICP-MS (Thermo Element2). All ICP instruments can be coupled to an in-house built femtosecond laser ablation system (fsLA-MC-ICP-MS or fsLA-ICP-OES) for *in-situ* elemental concentration and isotope ratio measurements at the micrometer scale.

MC-ICP-MS is a versatile method for high precision isotopic analyses. In an inductively coupled plasma (ICP) elements in a sample are atomized and ionized. The plasma ion source of the mass spectrometer allow ionization and analyses of almost all elements in the periodic table – except gases, as the plasma is operates in ambient atmosphere. A variety of sample introduction systems is available, including solution aspiration and laser ablation. Our Thermo Neptune is a high-resolution multicollector inductively-coupled plasma mass spectrometer with a NeptunePlus upgrade, consisting of a large interface pump and a Jet-cone interface for increased sensitivity. The instrument is equipped with nine Faraday cup detectors (eight are moveable), an axial discrete dynode secondary electron multiplier (SEM) with RPQ for high abundance-sensitivity measurements. In addition, we have a multiple-ion counting system consisting of two discrete-dynodes SEM ion counter, mounted at the outermost positions in the multicollector array (L4 and H4). For liquid sample introduction into the mass spectrometer a quartz glass double Scott/Cyclon spray chamber, a PFA double Scott/Cyclon spray chamber, or an ESI Apex IR + Spiro membrane desolvator is available. For solid sampling a UV femtosecond laser ablation system can be coupled with the Neptune. Our Neptune is currently used for isotope measurements of Li, Mg, Si, Fe, Rb and Sr (stable and radiogenic).

A novel UV femtosecond laser ablation system was custom-build in our lab as a micro-analytical tool for elemental and isotopic analysis of solid materials. Most commercial laser ablation systems employing excimer or Nd:YAG lasers have pulse lengths > 5 nanoseconds (ns). For ns laser ablation, there is enough time for photon energy to disperse in the material as heat during the laser pulse. The ns ablation process is characterized by melting, boiling, and vaporization, affecting the accuracy and precision of concentration and isotope measurements. Femtosecond lasers ablate with minimal thermal

heating to the surrounding area of the crater due to the short laser pulse length compared to the photon relaxation time, i.e., the laser energy can be deposited into the material before it can thermally equilibrate. This predominantly non-thermal ablation offers the potential to eliminate fractionation and matrix dependence. Femtosecond laser ablation provides less sample heating, no laser–plasma interaction and smaller aerosol particle sizes. These characteristics of the laser ablation process facilitate *in situ* measurements of stable isotope ratios on solid samples at the micrometer scale.



Figure 2: Mass spectrometry facilities at HELGES. Shown is the Inductively Coupled Plasma Multi-collector Mass Spectrometer (Thermo Neptune MC-ICP-MS) and the in-house built femtosecond laser ablation system (GFZ fem2).

We analyze a wide range of environmental samples for element concentrations, such as rocks, soils, water, and plants. The Varian 720-ES axial ICP-OES is an optical emission spectrometer that allows simultaneous detection and quantification of most elements in solutions at concentrations ranging from a few ppb to hundreds of ppm. ICP-OES analyses can be done on solutions or by coupling with our femtosecond laser ablation system on solids for *in-situ* microanalyses. Moreover, we operate two Quadrupole ICP-MS (Thermo iCAP-Qc) and a sector field ICP-MS (Thermo Element2) for trace element analyses within the framework of a “low-level” element analytics facility for environmental (water, plants, etc.) samples.

Scientists can apply for access to all HELGES facilities (laboratories and mass spectrometers) by directly contacting the authors.

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