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Ultra-trace determination of Ga/Al in continental waters using offline extraction and quadrupole ICP-MS

DR. QUENTIN DUBOIS-DAUPHIN[1], LOUIS A DERRY[2] AND PIERRE BÜRCKEL[3]

[1]Institut de Physique du Globe de Paris
[2]Institut de Physique du Globe de Paris, Université Paris Cité, CNRS
[3]Institut de physique du globe de Paris
Presenting Author: duboisdauphin@ipgp.fr

Flow paths and chemical reactions vary with time and hydrological conditions in the Critical Zone. To elucidate the complex relationships between stream discharge and solute concentrations, high frequency time series measurements of reactive and non-reactive tracers are needed. Here, we have developed a standardized method for successful determination of the (bio)geochemically important ultra-trace metals in stream water. This method relies on the commercially available automatized preconcentration system, SeaFAST-Litre (Elemental Scientific, Omaha, NE, USA). Stream waters are less saline but more variable than seawater and can have higher DOC. Prior to separation stream waters are filtered, acidified and subject to UV oxidation to eliminate organics that could interfere with column chelation. Twenty milliliters of a spiked sample are loaded on the line where it mixes with buffer. The buffered sample is then pushed across the analytical column containing Nobias PA-1 resin to selectively bind trace metals from water. Unchelated matrix ions are washed away with a mixed buffer and MQ water. Trace metals are eluted with nitric acid and collected in pre-cleaned, metal-free centrifuge tubes. The resulting solution is then analyzed using Agilent 7900 ICPMS. Measured blanks and detection limits were < 0.050 nmol/L levels with yields of more than 80%. The addition of an enriched isotopic tracer prior to separation allows for isotope dilution determination of selected metals at low levels. We also report results for the certified reference material SLRS-6, collected in the St. Lawrence River. In addition, we have focused on Ga/Al in continental water as a tracer of the aluminum cycle. Ga and Al have similar chemical properties and are often found together in natural systems. While Ga and Al undergo similar aqueous reactions in the environment, hydrolysis and ligand stability constants for the two metals differ. Ga/Al ratio in water samples can yield insight into the sources and fate of Al in aquatic ecosystems as well as better understand the impacts of human activities on water quality and aquatic life. Here, we report preliminary results in water from different locations in France.