



Si and S isotopic ratios in environmental and biological samples using MC-ICP-MS

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Silicon and sulphur are two very important elements. Silicon is the seventh and sulphur is the tenth most abundant elements in the universe. They both are very abundant elements in nature and essential for terrestrial life. For example silicon dioxide is a dietary requirement for various organisms and sulphur is one of the components that make up proteins and vitamins. Sulphur is found in a variety of different forms in nature because it can possess a +6 to -2 oxidation state, while silicon is found in silica form and in uncountable variations from the natural silicates (e.g. talc, mica etc). Sulphur and silicon compounds can be found extensively throughout the hydrosphere. Natural silicon contains 92.23% of Si-28, 4.68% of Si-29 and 3.09% of Si-30, and natural sulphur contains 94.93% of S-32, 0.76% of S-33, 4.29% of S-34 and 0.02% of S-36. Silicon and sulphur isotope variations are important to address different aspects. Sulphur isotopes are used in hydrology to trace natural and anthropogenic sources of sulphur. Sulfur isotope fractionation generally occurs by two processes in nature: 1) equilibrium fractionation during inorganic reactions between sulfur bearing ions, molecules and solids; 2) fractionation due to the reduction of sulphate ions (by either inorganic process or biogenic processes). Silicon isotope variations are important to address different aspects of global aquatic cycles of Si. And fractionation can occur either due to biological processes or due to inorganic processes. ICP-MS technique can be very powerful tool for precise measurement of Si and S isotopic ratios, especially after appearance of high-resolution ICP-MS, multi-collector ICP-MS and desolvating sample introduction systems. To measure isotopic ratios of Si and S, NEPTUNE multicollector

tor ICP-MS instrument was used throughout this work. Cups configuration and instrumental parameters were optimized. For precise measurement of both Si and S isotopes using ICP-MS it is necessary to solve similar issues: solvent-based polyatomic interferences (i.e. CO, NO, O₂, SH etc). To solve this problem instrumental parameters were optimized in medium-resolution mode, and different sample introduction systems (i.e.. Aridus and APEX desolvating units) were compared for reducing oxides and hydrides. Also, for precise measurement bracketing technique, “reference material - sample - reference material”, was applied. NIST-8546 (NBS-28, Silica Sand, SiO₂) and NIST-8554 (NZ1, Silver Sulfide, Ag₂S) were used as isotopic standards for Si and S, respectively. To extract biogenic silica from Lake Baikal sediments for the analysis, original method developed in the Vinogradov Institute of Geochemistry was used. In addition, sample preparation techniques using MW digestion were developed for different environmental samples. The developed and optimized procedures were applied for the measurement of Si and S isotopes in different environmental samples, including water, soil, sediments and some biological samples. Analyzed samples are different standard reference materials and environmental samples from Lake Baikal region (Siberia).