

Silicon isotope variation in the Buck Reef Chert (Barberton Greenstone Belt) records early Archean basin evolution

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Silicon isotopic signatures of chemical sediments receive growing attention, given their applicability in the search for properties of ancient seawater and the understanding of the environment in which the first life evolved. An important target is the reconstruction of secular changes in surface temperature of the Precambrian Earth, however, interpretations are problematic since controls of the isotopic signals are potentially manifold. Here we report the existence of significant silicon isotope variability in, chemically precipitated chert layers covering a continuous stratigraphic section across the ~3.42 Ga Buck Reef Chert (BRC) in the Barberton Greenstone Belt (South Africa). The $\delta^{30}\text{Si}$ values range from +0.36‰ for shallow-marine sediments in the lower part of the section to -1.25‰ for deeper water deposits in the upper part. A total shift of 1.6‰ thus accompanied chert formation in a single Archean basin in the course of deepening. Cherts at the base of the section represent silicified felsic volcanoclastic sediments and have exclusively positive $\delta^{30}\text{Si}$ values between +0.14 and +0.68‰.

Rare earth elements and yttrium patterns confirm the marine origin of the cherts and support the presumed basin evolution, from coastal shallow waters to a deep basin, well-below storm base. From the combined evidence we infer that the $\delta^{30}\text{Si}$ variations in the BRC reflect changes in the predominant origin of the silica, with terrigenous input supplying positive $\delta^{30}\text{Si}$ to shallow waters and seafloor hydrothermal sources negative $\delta^{30}\text{Si}$ to deeper levels. Our findings demonstrate the viability of silicon isotopes of cherts for reconstructing the evolution of ancient marine basins.

Complexation of oxyanions by diatom cells

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Diatoms are unicellular algae located at the base of short, energy-efficient food webs. Since they are widespread and exhibit strong amphoteric properties, they are expected to constitute important environmental sorbants for potential or known toxic trace elements such as Cr(VI), Mo(VI) and W(VI). However, most of the studies devoted to these oxyanions underline the lack of information regarding their mobility or their speciation in natural systems. Particularly, their interaction with microorganisms is poorly documented despite the potential control they can exert on trace elements cycling. The main goal of this study is thus to provide a surface complexation model able to describe the sorption of chromate, molybdate and tungstate ions onto diatom surfaces.

Four diatom species (*Navicula minima*, *Achnantheidium minutissimum*, *Skeletonema costatum*, *Thalassiosira weissflogii*) representative of freshwater, estuarine and marine systems were investigated. Cr(VI), Mo(VI) and W(VI) sorption isotherms as a function of pH and oxyanion concentration were collected. Experimental data were modelled assuming a constant capacitance to account for the coulombic interactions in the EDL. Both molybdate and tungstate exhibit a maximum in sorption at acidic pH, with a sorption edge between pH 4.5 and 6.5 depending on the cell/oxyanion ratio. Sorption onto the cell surface differs for these two elements with a stronger complexation constant for tungstate (logK=12.2 for *Thalassiosira weissflogii*) compared to molybdate (logK=10.5). Interestingly, freshwater species display generally a higher affinity for molybdate compared to the marine and estuarine diatoms. Chromate behaves differently, with a sorption edge around pH 7.5, but also with a strong desorption occurring at low pH (around pH 3). No reduction from Cr(VI) to Cr(III) was necessary to model chromate sorption isotherms. For the three oxyanions, the experimental data were best fitted considering monodentate mononuclear complexes with the positively charged amino groups present in the diatom cell wall structure. Because of the rigorous thermodynamic approach used in this study, this work constitutes an important step for the understanding of oxyanions cycling in natural systems.