

Chromium isotopes in the marine environment through time – A suitable paleoredox tracer?

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Stable chromium isotopes have the potential to trace redox processes in seawater and during sedimentary processes. We are potentially interested to obtain a picture of chromium isotopes in ancient seawater with the idea that fluctuations (due to Cr(III)-Cr(VI) speciation changes) might be directly correlated with climatic (atmospheric) oxygen fluctuations through time. In a first attempt we applied the chromium stable isotope system to banded iron formations (BIF) as type sediments representing chemical precipitates from ancient seawater. Our present NIST 3112a Cr standard (to which we report Cr isotope ratios of our samples) reproducibility over the last 4 months amounts to $\delta(^{53}\text{Cr}/^{52}\text{Cr}) = \pm 0.04$ (2 σ) permil. Eoarchean (~3.8 Ga) oxide-facies BIFs from Isua (W Greenland) show minimal enrichment of the light Cr isotopes [$\delta(^{53}\text{Cr}/^{52}\text{Cr}) = \sim -0.15$ permil]. Similarly, Neoproterozoic (~2.9 Ga?) oxide-facies BIF from the Black Hills (South Dakota) have $\delta(^{53}\text{Cr}/^{52}\text{Cr})$ values of ~ -0.02 permil and ~2.7 Ga oxide-facies BIFs from within the Botswana-Zimbabwe craton (Phithsane; Matsilodge) yielded $\delta(^{53}\text{Cr}/^{52}\text{Cr}) = -0.11$ to -0.50 permil. These slightly negative Cr isotope compositions of pre-Great Oxygenation Event BIFs can tentatively be explained by resulting from adsorptive processes of Cr to iron oxyhydroxides, preferring the lighter Cr to be adsorbed and therefore to be enriched in the iron-rich sediments. A different mechanism has to be assumed to be responsible for highly positively fractionated Cr isotopes in Fe-rich Neoproterozoic cherts from the late Ediacaran (ca. 580-560 Ma) Yerbal Fm. of the Arroyo del Soldado Group (Uruguay). There, $\delta(^{53}\text{Cr}/^{52}\text{Cr})$ values of up to +4.5 permil have been measured. The tight association of these Fe-rich cherts with organic-rich sediments (graphite-schists) suggests, in accordance with preliminary laboratory experiments, that Cr adsorption on organic material prefers the heavy isotopes. From our preliminary data it becomes clear that the understanding of adsorptive processes with respect to Cr is an absolute necessity before stable Cr isotopes can be used as a proxy for the level of oxygen in seawater through time.

Influence of ionic strength, pH, and cation valence on aggregation kinetics of TiO₂ nanoparticles

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Aggregate formation affects the mobility of nanoparticles and therefore has broad implications for understanding the environmental impact of engineered nanomaterials such as titanium dioxide (nano-TiO₂). While current surface science theory predicts that individual nanoparticles will be highly unstable in aqueous solutions, there have been few systematic investigations of nanoparticle aggregation in dilute electrolytic solutions typical of environmental soil and surface-water conditions. The current study examines the morphology and rate of formation of nano-TiO₂ aggregations in aqueous solutions of varying pH and ionic strength. Dynamic light scattering shows that 4-5 nm titanium dioxide particles form stable aggregates with an average diameter of 50 to 60 nm at pH 4.5 in a NaCl solution with an ionic strength of 0.0045 M. Holding the pH constant, but increasing the ionic strength to 0.0165 M, leads to the formation of micron-sized aggregates within 15 minutes. At all other pH values tested (5.8-8.2) micron-sized aggregates form in less than 5 min, even at low ionic strength (0.0084-0.0099 M with NaCl). In contrast, micron-sized aggregates formed within 5 min in an aqueous solution of CaCl₂ at an ionic strength of 0.0128 M and pH of 4.8, which is significantly faster than observed for NaCl solutions with similar ionic strength and pH. This result may indicate that divalent cations enhance aggregation of nano-TiO₂ in soils and surface waters. *In situ* optical micrographs of nano-TiO₂ showed branching aggregate morphology with sizes ranging from the 1 μm optical limit of the microscope to tens of micrometers in diameter.