



Uranium isotope fractionation in Saanich Inlet: A modern analog study of a paleoredox tracer

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Abstract

Uranium isotope fractionation was studied in the sediment and water of Saanich Inlet, a seasonally anoxic fjord on the east coast of Vancouver Island. The concentration of dissolved U is the same above and below the redoxcline at ~120 m depth, with an average $\delta^{238}\text{U}$ value of $-0.45 \pm 0.06\text{‰}$ (2 s.e.), which is indistinguishable from seawater values reported in other studies. This finding is consistent with water renewal times for the inlet that are roughly seasonal in frequency, thus hiding the impact of the U losses to the anoxic sediment of the inlet. Complete digests of the anoxic sediment yielded higher $\delta^{238}\text{U}$ values than seawater ($-0.21 \pm 0.11\text{‰}$ (2 s.e.)). By contrast, complete digests of the sediment trap samples yielded lower $\delta^{238}\text{U}$ values than seawater ($-0.52 \pm 0.10\text{‰}$ (2 s.e.)), and marine plankton from the inlet yielded the lowest $\delta^{238}\text{U}$ value of $-1.24 \pm 0.17\text{‰}$ (2 σ). Cross-plots of $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ vs. Th/U reveal strong correlations indicative of two-component mixing when the data from traps and anoxic inlet sediment are combined. One mixing end-member is fractionated uranium of seawater origin, with a $\delta^{238}\text{U}$ value of $0.17 \pm 0.14\text{‰}$ (2 σ). The other is detrital uranium with a $\delta^{238}\text{U}$ value of $-0.83 \pm 0.12\text{‰}$ (2 σ). The detrital end-member is lower than the range of $\delta^{238}\text{U}$ values reported in the literature for granitoid igneous rocks (-0.44‰ to -0.17‰ , 2 σ) (Telus et al., 2012), suggesting that continental weathering fractionates uranium isotopes, with preferential release of ^{238}U . Development and application of U isotopes as a paleoredox proxy has its basis in the nuclear volume fractionation. The data from Saanich Inlet meets this expectation, with a positive fractionation factor ($\Delta_{\text{aq(VI)}^{\text{sed(IV)}}}^{\text{sed(IV)}}$) of $0.62 \pm 0.17\text{‰}$ (2 σ) calculated as the difference in $\delta^{238}\text{U}$ between authigenic U in anoxic sediments and sediment traps ($+0.17\text{‰}$) and U dissolved in seawater (-0.45‰). However, it is widely believed that U(VI) reduction in the marine environment occurs on the surfaces of particles and that the negative isotope effect associated with U(VI) sorption to plankton ($\Delta_{\text{seawater}}^{\text{plankton}} = -0.79 \pm 0.17\text{‰}$ (2 σ)) opens up the possibility that the particulate pool of seawater derived U(VI) is fractionated from the dissolved pool. Accordingly, the reduction of U(VI) in the marine environment might involve two steps: (1) U(VI) sorption to particles with a negative fractionation, and (2) reduction to U(IV) on particles with a positive fractionation. Environmental factors that are not yet well understood may influence the relative reaction rates for the two steps, thus affecting the magnitude and sign of the overall fractionation. This has the potential to explain conflicting results reported for U(VI) reduction experiments in the literature (laboratory and field), where both positive and negative fractionations have been observed, and in some instances, no fractionation at all. Variation in the fractionation factor has the potential to complicate application of U isotopes as a paleoredox proxy, but this study and a study of the Black Sea (Romaniello, 2012) give the same results (within their respective uncertainties) suggesting that $0.62 \pm 0.17\text{‰}$ (2 σ) is a robust assessment of the apparent U isotope fractionation factor associated with reductive deposition of seawater U(VI) in both anoxic and euxinic marine sediments of the present day.

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1. INTRODUCTION

This study explores the redox-controlled fractionation of uranium isotopes ($^{238}\text{U}/^{235}\text{U}$) in the water and sediment of Saanich Inlet, a seasonally anoxic fjord on the east coast of Vancouver Island (Fig. 1). The anoxic central-basin sediment of the fjord is high in redox sensitive trace metals removed from seawater (e.g., Francois, 1988; Crusius et al., 1996; Morford et al., 2001), thus bearing a strong resemblance to metal-rich black shale successions in the sedimentary rock record that are commonly interpreted to reflect deposition beneath anoxic bottom waters (e.g., Algeo and Maynard, 2004). Because U isotope fractionation is linked to changes in the oxidation state of U (Stirling et al., 2007; Weyer et al., 2008), and the main sinks for seawater U are suboxic and anoxic sediment (Dunk et al., 2002), this has prompted development of a U isotope proxy aimed at tracing changing fluctuations in ocean

anoxia in the geological past (Montoya-Pino et al., 2010; Brennecke et al., 2011a; Asael et al., 2013; Kendall et al., 2013) with potential links to changing climate and tectonics. The basis of the proxy is the changing area of the sea floor covered by oxygen starved bottom waters, which has the potential to drive changes in the $^{238}\text{U}/^{235}\text{U}$ ratio of seawater (Weyer et al., 2008).

Uranium occurs in two oxidation states, U(IV) and U(VI), in rocks and minerals. In oxidative weathering environments U(IV) is converted to U(VI), which combines with oxygen to create the stable uranyl cation (UO_2^{+2}), which is soluble in water. At neutral to slightly alkaline pH, dissolved carbonate ion combines with the uranyl cation to form $\text{UO}_2(\text{CO}_3^{-2})_3^{-4}$, which is the dominant U species in seawater (Ku et al., 1977; Ivanovich and Harmon, 1992). The U isotope composition of seawater (reported as $\delta^{238}\text{U}$ values) is $-0.44 \pm 0.07\text{‰}$ (2σ) (Stirling et al., 2007; Weyer et al., 2008). Seawater is uniform in $\delta^{238}\text{U}$ due to the long residence time of U in the oceans of about 0.5 Ma (Dunk et al., 2002). The use of $\delta^{238}\text{U}$ as a paleoredox proxy is supported by evidence for fractionation of U isotopes in recently deposited suboxic sediments of the Peru Margin upwelling zone, yielding an average $\delta^{238}\text{U}$ value of $-0.29 \pm 0.18\text{‰}$ (2σ , $n = 8$), which is on average higher than seawater (-0.44‰) (Weyer et al., 2008). Recently deposited anoxic sediment from the Black Sea is even higher at -0.06‰ .

The positive sense of fractionation of U isotopes observed between seawater and its main oceanic sinks (suboxic and anoxic marine sediment) is opposite to the negative sense of (kinetic isotope) fractionation that is common among low mass elements, where the products of irreversible reactions are typically enriched in the light isotopes. The positive sense of fractionation is a hallmark of a nuclear volume dependent isotope effect between reactant U(VI) and product U(IV) species (Bigeleisen, 1996; Schauble, 2007; Abe et al., 2008), and the basis for applications of U isotopes as a paleoredox proxy. A few studies have measured U isotope fractionation during U(VI) reduction experiments ($\Delta_{\text{aq}}^{\text{sed(IV)}}$), but the nuclear volume effect is not always apparent. For example, U(VI) reduction experiments utilizing metal reducing bacteria in laboratory culture experiments caused enrichment in the light isotopes of uranium in the product U(IV) ($\Delta_{\text{aq}}^{\text{bacteria}} \approx -0.33\text{‰}$) (Rademacher et al., 2006), which is opposite to the sense of U isotope fractionation observed between seawater and suboxic and anoxic marine sediment (Weyer et al., 2008). Another experiment by the same authors involving U(VI) reduction using zero-valent iron particles resulted in no fractionation between U(VI) and U(IV). Stirling et al. (2007) also reported no fractionation of U isotopes in laboratory reduction experiments with zero-valent zinc particles. Bopp et al. (2010) reported a positive isotope fractionation accompanying U(VI) reduction in a bioremediation field experiment by native bacteria, yielding $\Delta_{\text{aq}}^{\text{bacteria}} = 0.46 \pm 0.13\text{‰}$ (2σ), which is evidence for a nuclear volume isotope effect. Roll front U deposits (believed to form by reductive scavenging of U(VI) from formation waters flowing through sedimentary basins at

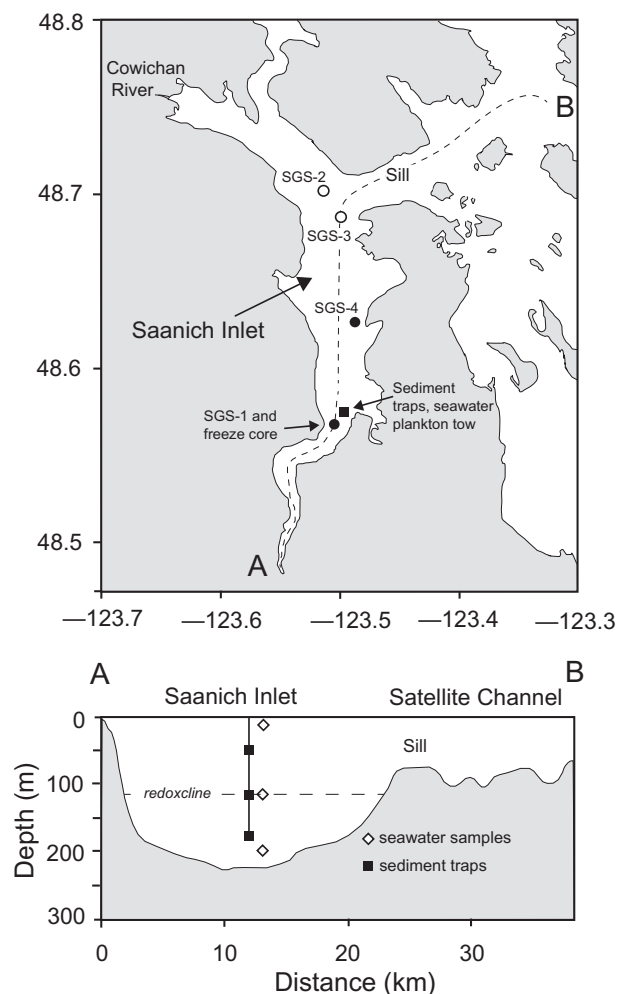


Fig. 1. (A) Map of Saanich Inlet showing the locations of the sampling stations. Open symbols = Sill samples. Closed symbols = Inlet samples. (B) Cross section showing bathymetry of Saanich Inlet. Seawater sampling depths are shown as well as the deployment depths of the sediment traps.

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