



Uranium and molybdenum isotope systematics in modern euxinic basins: Case studies from the central Baltic Sea and the Kyllaren fjord (Norway)



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ABSTRACT

Recent investigations have revealed significant fractionation of $^{238}\text{U}/^{235}\text{U}$ between organic-rich sediments of anoxic marginal seas and seawater, indicating redox-dependent U isotope fractionation. This study explores the conditions controlling U isotope fractionation in selected modern anoxic basins (Baltic Sea: Landsort and Gotland Deeps and the Kyllaren fjord in Norway) and compares U with Mo isotope fractionation. Therefore, the concentrations and isotope compositions of dissolved U and Mo from the water column and organic-rich sediments from three currently anoxic basins have been analysed.

The water column samples from the Kyllaren fjord display a moderate depletion of U and a strong depletion of Mo with increasing depth. These variations are associated with a decrease in $\delta^{238}\text{U}$ and an increase in $\delta^{98}\text{Mo}$ with depth, from -0.35‰ to -0.70‰ and from 2.4‰ to 2.6‰ , respectively. From the U isotope composition of the deep euxinic water column of the Kyllaren fjord, a minimum value of $\Delta^{238}\text{U}_{\text{red}} \approx 0.7\text{‰}$ for the U isotope fractionation during reduction is inferred. Due to the high sedimentation rate in the Kyllaren fjord, surface sediment samples are only moderately enriched in U and Mo ($\sim 4\text{ }\mu\text{g/g}$ and $6\text{ }\mu\text{g/g}$ to $37\text{ }\mu\text{g/g}$, respectively) and display $\delta^{238}\text{U}$ and $\delta^{98}\text{Mo}$ averages of $-0.26\text{‰} \pm 0.10\text{‰}$ and $2.18\text{‰} \pm 0.21\text{‰}$, respectively.

Water column samples from the Baltic Sea display a minor decrease in the U and Mo concentrations and only negligible U and Mo isotope fractionation compared to open seawater. The sediment layers from the Baltic Sea (Landsort Deep), which were deposited under mostly anoxic conditions, are moderately enriched in U (up to $8\text{ }\mu\text{g/g}$) and highly enriched in Mo (up to $222\text{ }\mu\text{g/g}$). However, U and Mo isotopic compositions are significantly lighter (with $\delta^{238}\text{U}$ of $-0.36\text{‰} \pm 0.08\text{‰}$ and $\delta^{98}\text{Mo}$ of $-0.04\text{‰} \pm 0.11\text{‰}$) than those of typical organic-rich sediments from anoxic basins.

These findings reveal that compared to Mo, the U isotopic composition of sediments in restricted and strongly euxinic basins like the Kyllaren fjord is significantly more dependent on (1) the extent of U removal from the water column, which is lower than that of Mo, and on (2) the sedimentation rate (i.e., the fraction of authigenic U relative to detrital U in the sediment), which is also lower compared to that of Mo. In more open and only temporarily euxinic basins such as the investigated basins of the Baltic Sea, strong Mo is coupled with weak U isotope fractionation between water and sediment. These signatures were likely the result of isotope fractionation under weakly sulfidic conditions and the generation of isotopically light Mo during frequently occurring flushing events with oxygen-rich water from the open sea. This implies that Mo and U isotope signatures of sediments only record paleo-water column redox conditions of restricted basins if the water column was permanently stratified.

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1. Introduction

Uranium and Mo are redox-sensitive trace elements with long ocean residence times (0.5 Ma and 0.8 Ma, respectively; Morford and Emerson, 1999; Dunk et al., 2002) and with similar redox behaviour in

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the ocean. Under oxidising conditions (e.g. $\geq 10^{-4}$ mol O₂ L⁻¹), they occur in a valence state of + VI and as soluble uranyl complexes (e.g. UO₂(CO₃)₃⁴⁻) and soluble molybdate (MoO₄²⁻; Morford and Emerson, 1999). Under these conditions, both Mo and U are assumed to typically display conservative behaviour in the water column, with only a few exceptions (e.g., observed for Mo in coastal waters in the Wadden Sea of NW Germany; Dellwig et al. (2007) and Kowalski et al. (2009)). Under suboxic (e.g. 10^{-5} to 10^{-4} mol O₂ L⁻¹) to anoxic ($< 10^{-6}$ mol H₂S L⁻¹, $< 10^{-5}$ mol O₂ L⁻¹) conditions (e.g., at continental margins), both Mo and U become non-conservative and enriched in the sediments (McManus et al., 2006). Under highly euxinic conditions (H₂S > 11 μM; 0 mol O₂ L⁻¹, Erickson and Helz, 2000), which occur in the deep water columns of some stratified isolated basins (e.g., Black Sea), Mo is quantitatively transformed to particle-reactive thiomolybdate (MoS₄²⁻) and therefore, almost quantitatively removed from the water column into organic-rich sediments (Helz et al., 1996; Erickson and Helz, 2000; Neubert et al., 2008). In such cases, sediments can essentially record the original seawater Mo isotopic composition due to a closed-system reservoir effect (Barling et al., 2001; Nägler et al., 2005; Neubert et al., 2008; Nägler et al., 2011); however, the overall transformation to thiomolybdate is associated with Mo isotope fractionation between seawater and sediment (on the order of $\Delta^{98}\text{Mo}_{\text{sed-water}} = -0.5\%$; Nägler et al., 2011). In contrast to Mo, U is assumed to occur as soluble and chemically labile U(VI), even under highly euxinic conditions such as the deep water column of the Black Sea (Anderson et al., 1989). Reduction and removal of U in such environments is assumed to occur in the sediment or within the pore water rather than by scavenging from the water column. This process appears to be associated with significant U isotope fractionation of approximately 0.4‰ to 0.7‰ relative to seawater (Weyer et al., 2008), resulting in sediments with a high $\delta^{238}\text{U}$ of up to 0.4‰ (Weyer et al., 2008; Bopp et al., 2010; Montoya-Pino et al., 2010; Andersen et al., 2014). Under such conditions, the direction of U isotope fractionation during reduction appears to be opposite that of Mo, probably due to volume-dependent isotope effects (i.e. “nuclear field shift”, Bigeleisen, 1996; Schauble, 2007; Abe et al., 2008) dominating U isotope fractionation.

Adsorption of Mo to pelagic clays, ferromanganese oxides or Mo removal to reducing sediments (e.g., at continental margins) results in significant isotope fractionation (on the order of 1‰ to 3‰; Goldberg et al., 2009; Poulson et al., 2009; Goldberg et al., 2012) towards a light Mo isotopic composition compared to the mean ocean water value ($\delta^{98}\text{Mo} = 2.3\%$; Siebert et al., 2003; Barling and Anbar, 2004; Siebert et al., 2006). Uranium displays only minor U isotope fractionation under oxic conditions towards lower $\delta^{238}\text{U}$, relative to the mean ocean water value of -0.4% (e.g., that occurs during adsorption to ferromanganese oxides) (Stirling et al., 2007; Weyer et al., 2008; Brennecke et al., 2011a).

Although modern anoxic basins (e.g. the Black Sea, deeps in the Baltic Sea, and Cariaco Basin) account for only 0.3% of the modern oceans (Bertine and Turekian, 1973), they play a significant role as a sink for Mo and U from ocean water. This results from the low solubility behaviour of Mo and U in the water column under anoxic conditions and their high enrichment in the organic-rich sediments of such basins. As Mo and U display significant isotope fractionation between oxic and anoxic sinks, both isotope systems have the potential to record the redox evolution of the oceans (e.g., Arnold et al., 2004; Wille et al., 2007; Pearce et al., 2008; Wille et al., 2008; Kendall et al., 2009; Dahl et al., 2010; Montoya-Pino et al., 2010; Brennecke et al., 2011b; Nägler et al., 2011; Asael et al., 2013; Dahl et al., 2014). However, sedimentary records of ancient seawater Mo and U isotopic compositions, such as black shales, should be used with caution as variable isotope fractionation may occur depending on the local redox conditions during their deposition (Nägler et al., 2005; Poulson et al., 2006; Neubert et al., 2008; Gordon et al., 2009; Dahl et al., 2010; Montoya-Pino et al., 2010; Nägler et al., 2011; Goldberg et al., 2012). In contrast to Mo, whose isotopic composition in seawater may be directly reflected by black shales

accumulated under strong euxinic conditions with concentrations of total dissolved sulphide > 100 μmol/L (Barling et al., 2001; Neubert et al., 2008; Nägler et al., 2011), U isotopes generally display large fractionation between organic-rich sediments and seawater (Weyer et al., 2008; Montoya-Pino et al., 2010). However, little is currently known about the parameters and environmental conditions that control the extent of U isotope fractionation.

In this study, U and Mo concentrations and isotope compositions of the water columns and the sediments of recent anoxic basins (including the Kyllaren fjord and the Landsort and Gotland Deeps of the Baltic Sea) are presented. The findings for U isotopes have been compared with the better understood Mo isotope systematics. A particular focus of the study was on the effect of the degree and persistence of water column stratification on the U and Mo isotope signatures observed in the sediments and on their liability to be affected by detrital components.

2. Sampling locations

2.1. Kyllaren fjord

The Kyllaren fjord is a 29 m deep basin that is located on the west coast of Norway (Fig. 1a, 61°25'N, 5°10'E) and connected to the Norwegian Sea by a narrow 5 km long and 1–2 m deep tidal channel. The water column of the Kyllaren fjord is strongly stratified. The salinity increases with depth from 14 g/kg to 25 g/kg, which is similar to the Black Sea. The oxygen concentration decreases to undetectable levels at approximately 4 m depth, while the H₂S concentration increases to ~4000 μmol/L at a depth of approximately 6 m, which is an order of magnitude higher than H₂S_{total} in the Black Sea water column (Neretin et al., 2001; Fig. 1b; Smittenberg et al., 2004; van Breugel et al., 2005a,b). The chemocline (the area with the strongest increase in salinity and the strongest decrease in oxygen concentration) in the Kyllaren fjord is usually located at a depth of approximately 3.5 m (van Breugel et al., 2005a). In 1954 and 1988, dams were built in Straume and Askvika (Fig. 1a), which reduced the connection to the open sea from 400 m to two connections of 15 m width each (Smittenberg et al., 2004). In 1993, another 2 m wide opening was built into the dam at Straume (Smittenberg et al., 2004; van Breugel et al., 2005a). As a result of the anthropogenic restriction, anoxic degassing events have frequently occurred since 1993.

The water samples for this study were collected using a tube, a winch and a vacuum pump; all parts are composed of plastic components, which were intensively cleaned with 2% HNO₃ and Milli-Q® H₂O. The two 40 cm deep sediment cores (KY09-1 und KY09-3) were collected from two different stations in the fjord (at 28 m below sea level and 10 m below sea level, respectively) using a gravity corer deployed from a raft in May 2009.

2.2. The Baltic Sea

The Baltic Sea is the largest brackish water basin worldwide (Fig. 2a), displaying a salinity increase with depth from 7 g/kg to 13 g/kg (Jost et al., 2008). The average depth is approximately 50 m, while several deeper basins, such as the Gotland Deep and Landsort Deep, reach maximum depths of 249 m and 459 m, respectively. These basins differ in their spatial extent with the Landsort Deep being much smaller but deeper than the Gotland basin. Both basins are affected by temporary redox stratification and currently have a euxinic deep water column due to limited water exchange between the deeper and shallower parts of the water column resulting from density stratification (Matthäus and Franck, 1992). This water column stratification results in a shuttling of Fe and Mn into the Gotland- and Landsort Deep (Huckriede and Meischner, 1996; Dellwig et al., 2010; Scholz et al., 2013). The chemocline is positioned at an approximate water depth of 90 m in the Landsort Deep and 120 m in the Gotland Deep (Fig. 2b

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