
Cr and U stable isotopes as paleo-redox proxies

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1 INTRODUCTION

The steady improvement of mass spectrometry during the last decades, especially the development of thermal ionisation mass spectrometry (TIMS) in the 1980s (Thurber et al., 1965) and later, the introduction of multiple collector inductively coupled mass spectrometry (MC-ICP-MS) (Andersen et al., 2004), measurement of transition metals and other heavy elements was put into practice (Weyer et al., 2008; Bullen and Eisenhauer, 2009). The interest in chromium isotopes initially grew because of its potential as a method to track pollution of the toxic Cr(VI) in groundwater or aqueous systems (see for examples Izbicki et al. (2008); Paulukat et al. (2015)). Attracted by the redox sensitivity and isotope fractionation associated with different oxidation states, extensive research is being conducted to evaluate the potential of chromium and uranium as paleo-redox proxies in seawater, anoxic to oxic sediments, sedimentary rocks and biogenic carbonates (for example Frei et al. (2009, 2011); Johnson (2012); Crowe et al. (2013); Frei et al. (2014); Reinhard et al. (2014); Scheiderich et al. (2015); Pereira et al. (2015); Reeder et al. (2001); Elzinga et al. (2004); Stirling et al. (2007); Andersen et al. (2008); Weyer et al. (2008); Montoya-Pino et al. (2010); Brennecke et al. (2011); Kendall et al. (2013); Romaniello et al. (2013); Stirling et al. (2015)).

2 CR ISOTOPE SYSTEM

Naturally, four different isotopes of chromium exist: ^{50}Cr (4.35%), ^{52}Cr (83.79%), ^{53}Cr (9.50%) and ^{54}Cr (2.36%) (Rotaru et al., 1992; Trinquier et al., 2008). Cr mainly occurs in oxidation states (VI) and (III). The reduced Cr(III), abundant in chromite, is found in igneous terrestrial reservoirs (Frei et al., 2011) as well as in soils and sediments, where it is adsorbed onto mineral surfaces (Oze et al., 2007; Cranston and Murray, 1978). During oxidative weathering, manganese minerals, which coat the surfaces of soil minerals and are found along fractures in rocks enriched in Cr, catalyse the oxidation to Cr(VI) (Eary and Rai, 1988; Oze et al., 2007), which is thermodynamically favoured in today's atmosphere (Frei et al., 2009). The oxidised form, present as chromate (CrO_4^{2-}) and bichromate (HCrO_4^-), is toxic, highly soluble and mobile (Kortenkamp, 1996). Associated with its release from continents and the transport through rivers to the oceans, soluble Cr(VI) is enriched in heavy Cr isotopes (Frei et al., 2009, 2011). The reduction of Cr(VI) to Cr(III) may be influenced by microorganisms or proceed in presence of Fe-bearing minerals (Ellis et al., 2002; Oze et al., 2007; Døssing et al., 2011).¹ Both processes are accompanied by mass-dependent isotope fractionation between ^{53}Cr and ^{52}Cr , the latter up to 7.6‰ (Ellis et al., 2002). This fractionation is caused by the preference of light isotopes to react during reduction, resulting in a lighter isotope signature of the reduced Cr(III) (Ellis et al., 2002; Frei et al., 2009; Bonnand et al., 2011). As an example, the reconstruction by Frei et al. (2009) of small-scale oxygen fluctuations in the Precambrian atmosphere, recorded in oceanic sediments, shall be mentioned. The study of Zink et al. (2010) showed, that the difference in

¹Re-oxidation of Cr(III) was considered insignificant due to the low abundance of MnO_2 in oceans (Frei et al., 2011).

fractionation decreases to +0.04‰ within one day of reaction time due to isotopic exchange approaching equilibrium. Supposedly, the fractionation caused by microbially mediated reduction is significantly larger (4.00 - 4.5 ‰ in ^{53}Cr and ^{52}Cr (Sikora et al. (2008); Zink et al. (2010)).

Cr(VI) may be removed from solution to ocean sediments by adsorption onto Al and Fe hydrous oxides (Ellis et al., 2004; Frei et al., 2009; Reinhard et al., 2014). Furthermore, during crystal growth of CaCO_3 , chromate (Cr(VI)O_4^{2-}) may co-precipitate and incorporate into the crystal structure (Tang et al., 2007; Sanchez-Pastor et al., 2011; Rodler et al., 2015). Thereby, the crystal structure is disturbed due to the larger size of chromate anions relative to carbonate ions (CO_3^{2-}). The oxidation state does not change (Tang et al., 2007), but Cr isotope fractionation is observed. In experiments of co-precipitation of Cr(VI) and calcite, Rodler et al. (2015) found a preferential incorporation of heavier Cr isotopes into calcite. With increasing concentration of Cr(VI), the growth of aragonite and vaterite were found to be favoured over calcite (Sanchez-Pastor et al., 2011). Biogenic carbonates as corals were studied by Pereira et al. (2015). According to their model, toxic Cr(VI) is photo-reduced in the endodermal layer of corals, whereafter re-oxidation of isotopically light Cr(III) takes place, resulting in isotopically light Cr(VI) being incorporated into the growing skeleton. As Pereira et al. (2015) measured a fractionation towards light Cr(VI) in coral skeletons, it is crucial to notice the dis-equilibrium of certain biogenic carbonates to seawater (0.9‰). Additionally, they detected variations of global seawater samples in $\delta^{53}\text{Cr}$ of $+0.92 \pm 0.2\text{‰}$ (see also Bonnand et al. (2013); Scheiderich et al. (2015)).

Measurement of chromium and its stable isotopes follows a chemical separation of Cr and is conducted by thermal ionisation mass spectrometry (TIMS) or by multi collector inductively coupled mass spectrometry (MC-ICP-MS) (e.g. Frei et al. (2009); Bonnand et al. (2011)). To avoid and correct for fractionation during sample preparation or isobaric interferences, a double-spike technique (^{54}Cr - ^{50}Cr) is applied (e.g. Schoenberg et al. (2008); Frei et al. (2009); Rodler et al. (2015)), as these isotopes have a very low abundance (Bonnand et al., 2011).

3 U ISOTOPE SYSTEM

Uranium as the heaviest naturally occurring element (Stirling et al., 2007) has a variety of isotopes. Here, ^{238}U (99.28%) and ^{235}U (0.72%) are of main interest.² They are primordial and their half-lives exceed 10^9 years (Weyer et al., 2008). Hence, these isotopes are considered as stable, despite the significant change the $^{238}\text{U}/^{235}\text{U}$ isotope ratio has undergone since early Earth (Cowan and Adler, 1976). However, the variation observed in today's environments is supposed to be due to chemical reactions fractionating these isotopes (Weyer et al., 2008). Processes thought to be sensitive to U isotope fractionation are adsorption, changes in U speciation or redox chemistry (Weyer et al., 2008).

Two different oxidation states of U occur, U(IV) being rather insoluble, and the oxidised and soluble U(VI) (Andersen et al., 2014). In oxygenated aqueous systems, U occurs as soluble U(VI) in uranyl bi-carbonate complexes (Langmuir, 1978), which are transported by rivers into oceans, where the main output is allocated in suboxic to anoxic sediments (Klinkhammer and Palmer, 1991).

In solution, U(VI) preferentially incorporates into aragonite rather than into calcite (usually less than 10ppm), where it co-precipitates, forming a solid solution with stable complexes with CO_3^{2-} (e.g. Reeder et al. (2001); Elzinga et al. (2004)). In a variety of biogenic and inorganic modern carbonates, only a small offset in $\delta^{238}\text{U}$ was observed relative to seawater (Romaniello et al., 2013). Fractionation occurred neither during the growth of Ca-aragonitic corals, nor due to general diagenetic alteration (Stirling et al., 2007). However, Romaniello et al. (2013) measured an offset of the sediment relative to seawater towards heavier U isotopes in Bahamian shallow water precipitates, caused by decaying organic matter leading to reducing conditions in pore water.

At the sediment-water interface, U is removed from seawater due to diffusion into anoxic sediment pore-waters, where soluble U(VI) carbonate complexes are reduced to precipitate uraninite (UO_2) in pore-waters, accumulating U(IV) in sediments (Klinkhammer and Palmer, 1991; Andersen et al., 2014). This reaction requires microbially mediated reduction of sulphate, as well as a decrease in Fe concentration (Klinkhammer and Palmer, 1991; Romaniello et al., 2013). As microbes prefer light isotopes, ^{235}U is preferentially removed from solution, resulting in U(IV) with an isotopically negative composition (Rademacher et al., 2006; Klinkhammer and Palmer, 1991). This was observed in Ca-dolomitic chimneys, where microbially mediated reduction of U(VI) to U(IV) was

²Another common U isotope used in earth sciences is a decay-product of ^{238}U , ^{234}U , with an abundance of ca. 0.0054% and a half-life of ca. 10^5y (Weyer et al., 2008). Alpha-recoil creates large variations between ^{234}U and ^{238}U , making it a valuable tool for U series dating (Andersen et al., 2004).

accompanied by crystals preferentially incorporating light U isotopes (Stirling et al., 2007). Additionally, dolomitisation, supposedly microbially influenced, was found to cause negative U isotope compositions (Romaniello et al., 2013).

In contrast, Weyer et al. (2008) measured the opposite fractionation associated with U reduction in anoxic to euxinic environments, resulting in U(IV) with heavy isotopes. These findings exclude fractionation caused by microbes. Instead, they support the theory of the nuclear volume effects (Bigeleisen, 1996; Schauble et al., 2004; Schauble, 2007). This theory predicts larger volume- than mass-dependent fractionation at equilibrium and thus results in the opposite of what is expected. Accordingly, changes of the oxidation state cause shifts in nuclear volumes and electron density distribution. Thereby, oxidised species preferably enrich in heavy isotopes (Schauble, 2007; Stirling et al., 2007).

The measurement of U isotopes closely follows the Cr isotope measurement, besides the favoured measurement by MC-ICP-MS because of the simpler ionisation with a plasma source (Andersen et al., 2004). Furthermore, MC-ICP-MS is an excellent tool to measure the low U concentrations of especially non-aragonitic carbonates.

4 OUTLOOK

The findings of Frei et al. (2011) of the isotopic signals of modern seawater and shallow water carbonates or BIF's hardly deviating from each other, approve the Cr isotope system as a paleo-proxy for redox changes. Still, one has to pay attention as the Cr oxidation during oxidative weathering depends on the stability of MnO₂, facilitated by elevated oxygen fugacities (Frei et al., 2009), and thus, the atmosphere's oxygenation state (Frei et al., 2011). Furthermore, fractionation processes caused by subsequent redox changes and possibly during the incorporation of Cr(VI) into carbonates have to be taken into account (e.g. Rodler et al. (2015)).

Various authors (e.g. Weyer et al. (2008); Romaniello et al. (2013)) consider the uranium isotope system as a valuable tool to reconstruct oceanic redox conditions, as the isotopic fractionation of seawater and primary precipitates as well as biogenic carbonaceous precipitates generally is very small. Considering redox changes as cause of U isotope fractionation, distinct variations in the U isotope composition (²³⁸U/²³⁵U) were observed. In sedimentary rocks and sediments, U isotopes were found to fractionate in opposite directions from oxic to anoxic/euxinic depositional settings (e.g. Weyer et al. (2008); Brennecka et al. (2011); Montoya-Pino et al. (2010)). Despite the low concentration of Cr and U in brachiopods, the widespread abundance of brachiopods during the Phanerozoic (Brand et al., 2003) render them a powerful tool in reconstructing past oceanic redox conditions. The combination of the two non-traditional isotope systems of Cr and U will reveal important data about the past of the Earth. Possible fractionation processes during the uptake of U and Cr from seawater into the carbonaceous shells is of high interest to establish a future paleo-redox proxy.

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