



Behaviour of chromium isotopes in the eastern sub-tropical Atlantic Oxygen Minimum Zone

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Abstract

Constraints on the variability of chromium (Cr) isotopic compositions in the modern ocean are required to validate the use of Cr isotopic signatures in ancient authigenic marine sediments for reconstructing past levels of atmospheric and ocean oxygenation. This study presents dissolved Cr concentrations (Cr_T , where $Cr_T = Cr(VI) + Cr(III)$) and Cr isotope data ($\delta^{53}Cr$) for shelf, slope and open ocean waters within the oxygen minimum zone (OMZ) of the eastern sub-tropical Atlantic Ocean. Although dissolved oxygen concentrations were as low as $44\text{--}90\ \mu\text{mol kg}^{-1}$ in the core of the OMZ, there was no evidence for removal of Cr(VI). Nonetheless, there was significant variability in seawater $\delta^{53}Cr$, with values ranging from 1.08 to 1.72‰. Shelf Cr_T concentrations were slightly lower ($2.21 \pm 0.07\ \text{nmol kg}^{-1}$) than in open ocean waters at the same water depth (between 0 and 160 m, $2.48 \pm 0.07\ \text{nmol kg}^{-1}$). The shelf waters also had higher $\delta^{53}Cr$ values ($1.41 \pm 0.14\text{‰}$ compared to $1.18 \pm 0.05\text{‰}$ for open ocean waters shallower than 160 m). This is consistent with partial reduction of Cr(VI) to Cr(III), with subsequent removal of isotopically light Cr(III) onto biogenic particles. We also provide evidence for input of relatively isotopically heavy Cr from sediments on the shelf. Intermediate and deep water masses (AAIW and NADW) show a rather limited range of $\delta^{53}Cr$ values ($1.19 \pm 0.09\text{‰}$) and inputs of Cr from remineralisation of organic material or re-oxidation of Cr(III) appear to be minimal. Authigenic marine precipitates deposited in deep water in the open ocean therefore have the potential to faithfully record seawater $\delta^{53}Cr$, whereas archives of seawater $\delta^{53}Cr$ derived from shelf sediments must be interpreted with caution.

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1. INTRODUCTION

Analyses of the chromium (Cr) isotopic composition of authigenic marine sediments are being used to reconstruct the Cr isotopic composition of ancient seawater and, in

turn, to provide constraints on the evolution of atmospheric oxygen and the redox history of the oceans (Crowe et al., 2013; Frei et al., 2009; Planavsky et al., 2014). This is because Cr has two stable valence states at Earth surface conditions, Cr(III) and Cr(VI), and mass dependent fractionation of the four stable Cr isotopes (^{50}Cr , ^{52}Cr , ^{53}Cr and ^{54}Cr) occurs during oxidation and reduction reactions (Ellis et al., 2002; Schauble et al., 2004; Zink et al., 2010; Døssing et al., 2011; Kitchen

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et al., 2012). Moreover, these valence states have different solubilities; Cr(VI) is relatively soluble whereas Cr(III) is not. Chromium isotope ratios are expressed in delta notation relative to the international reference material NBS979 as follows (Eq. (1)):

$$\delta^{53}\text{Cr} (\text{‰}) = \left[\frac{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}}}{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{NBS979}}} - 1 \right] \times 1000 \quad (1)$$

Application of the Cr isotope proxy requires a detailed process-based understanding of the behaviour of Cr and its isotopes in the modern ocean.

1.1. Distribution of Cr in seawater

Chromium (Cr) is a trace element in seawater and, although it has a relatively long residence time of ~9500 years (Reinhard et al., 2013), its concentration is variable and usually within the range 0.9–6.5 nM (Campbell and Yeats, 1981; Cranston, 1983; Jeandel and Minster, 1984; Achterberg and Berg, 1997; Sirinawin et al., 2000; Connelly et al., 2006; Bonnand et al., 2013; Scheiderich et al., 2015). In oxygenated seawater, Cr is present primarily as Cr(VI) in the chromate oxyanion, CrO_4^{2-} and, to a lesser extent as Cr(III) in aquahydroxyl or hydroxyl ions (Elderfield, 1970). Chromium changes valence state from Cr(VI) to Cr(III) under mildly reducing conditions and, while Cr(VI) is not significantly particle reactive and is only weakly held on most mineral surfaces (Zachara et al., 1988; Gaillardet et al., 2003), Cr(III) species readily adsorb to biogenic particles (Semeniuk et al., 2016), authigenic precipitates (Crawford et al., 1993) and sediments (Schroeder and Lee, 1975; Richard and Bourg, 1991).

During periods of high biological productivity, Cr(III) can constitute up to ~50% of the dissolved Cr inventory in the upper water column (Achterberg and Berg, 1997; Connelly et al., 2006). Chromium is not thought to be a nutrient for marine bacteria and phytoplankton, but inadvertent biological uptake is well documented (Wang and Dei, 2001; Sikora et al., 2008; Li et al., 2009; Basu et al., 2014) and may be responsible for reduction of Cr(VI) in surface waters. High concentrations of Fe(II) and organic material in surface waters can also facilitate reduction of Cr(VI) (Døssing et al., 2011; Kitchen et al., 2012). Organic molecules can reduce Cr(VI) in their own right or support reduction by other mechanisms (Jamieson-Hanes et al., 2012; Kitchen et al., 2012), and they can also act to solubilise Cr(III) (Kaczynski and Kieber, 1994).

Reduction of Cr(VI) may also occur in those parts of the ocean that have relatively low concentrations of dissolved oxygen. Low-oxygen waters (<5 $\mu\text{mol kg}^{-1}$ of dissolved O_2) from within the ‘oxygen minimum zone’ (OMZ) in the tropical East Pacific were found to be depleted in Cr (VI) relative to adjacent oxygenated waters, and concentrations of dissolved Cr(III) and particulate Cr were highest at the top of the OMZ (Murray et al., 1983; Rue et al., 1997). In the Saanich Inlet, an intermittently anoxic fjord, Cr(III) concentrations were close to zero in the upper oxygenated waters whereas Cr(III) constituted >70% of total dissolved Cr in deep anoxic waters (Emerson et al., 1979).

Reduction of Cr(VI) in surface waters and uptake of Cr (III) on particles means that total dissolved Cr concentrations (Cr_T , where $\text{Cr}_T = \text{Cr(VI)} + \text{Cr(III)}$) in the surface ocean are typically slightly lower than they are at depth (Campbell and Yeats, 1981; Cranston, 1983; Dauby et al., 1994; Achterberg and Berg, 1997; Connelly et al., 2006). However, in some parts of the ocean, concentrations of Cr_T in surface waters may be relatively high due to atmospheric inputs (Achterberg and Berg, 1997), and inputs of Cr from marine sediments and hydrothermal vents can result in relatively high concentrations close to the seabed at some locations (up to 20 nmol kg^{-1} ; Jeandel and Minster, 1984; Sander and Koschinsky, 2000). If there are no external inputs of Cr and rates of biological activity are low, then Cr_T concentrations may simply reflect those of newly formed water masses that are subducted into the interior ocean (Sirinawin et al., 2000), or mixing between different water masses (Scheiderich et al., 2015).

1.2. Cr isotope composition of seawater

To date there are only a handful of studies of the isotopic composition of Cr_T in seawater, and $\delta^{53}\text{Cr}$ values reported for seawater range between 0.13 and 1.55‰ (Bonnand et al., 2013; Paulukat et al., 2015; Pereira et al., 2015; Scheiderich et al., 2015; Economou-Eliopoulos et al., 2016; Holmden et al., 2016; Paulukat et al., 2016). Most of these seawater samples have $\delta^{53}\text{Cr}$ values that are higher than those for crustal rocks ($-0.12 \pm 0.10\text{‰}$; Schoenberg et al., 2008). As rivers are the main source of Cr to the oceans (90–98%; Chester and Murphy, 1990; Bonnand et al., 2013; McClain and Maher, 2016), this suggests either that (i) isotopically heavy Cr is preferentially released during weathering processes, (ii) the weathering signal is modified during transport to the oceans (e.g. during estuarine mixing), or (iii) Cr isotopes are fractionated by Cr cycling within the oceans.

There is a growing body of evidence that indicates that oxidative weathering preferentially retains light Cr isotopes in the solid phase (Frei et al., 2009; Crowe et al., 2013; Frei and Polat, 2013; Berger and Frei, 2014; Frei et al., 2014; Planavsky et al., 2014; D’Arcy et al., 2016). Water samples from fully oxic groundwater recharge regions are reported to have $\delta^{53}\text{Cr}$ values of 1.2–2.3‰ (Izbicki et al., 2008), and most river waters that drain into the sea that have been analysed to date are enriched in heavy Cr isotopes ($\delta^{53}\text{Cr} = 0.43 \pm 0.38\text{‰}$ 1SD, $n = 46$; D’Arcy et al., 2016; Frei et al., 2014; Paulukat et al., 2015; Wu et al., 2017) relative to crustal rocks. On the other hand, paleosols weathered under oxic conditions (Crowe et al., 2013; Frei and Polat, 2013) and modern soils are enriched in light Cr isotopes (modern soil $\delta^{53}\text{Cr} = -0.21 \pm 0.11\text{‰}$ 1SD, $n = 74$; Frei et al., 2014; D’Arcy et al., 2016; Wu et al., 2017). The exact mechanisms that lead to fractionation of Cr isotopes during oxidation reactions are, however, unclear, and laboratory experiments indicate that under some circumstances, oxidation of Cr(III) to Cr(VI) could alternatively lead to retention of heavy Cr isotopes in the residual solid phase (Bain and Bullen, 2005; Zink et al., 2010; Joshi et al., 2011).

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