



Global variability of chromium isotopes in seawater demonstrated by Pacific, Atlantic, and Arctic Ocean samples



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ARTICLE INFO

Article history:

Received 21 November 2014

Received in revised form 24 April 2015

Accepted 27 April 2015

Available online 13 May 2015

Editor: G.M. Henderson

Keywords:

chromium isotopes
seawater
chromium speciation
chromium cycling

ABSTRACT

Seawater chromium (Cr) isotope and concentration data are presented from multiple sites in the Arctic Ocean, and three locations in the Atlantic and Pacific Oceans. A 2400-m profile illustrates the heterogeneity of $\delta^{53}\text{Cr}$ in the Arctic Ocean with depth and water-mass source (Pacific vs. Atlantic). The highest $\delta^{53}\text{Cr}$ values occur in Pacific-sourced waters, which also have the lowest Cr concentration. Chromium concentration and $\delta^{53}\text{Cr}$ data from these locations, in conjunction with published data for the South Atlantic Ocean, yield a simple logarithmic function, as predicted by Rayleigh fractionation in a closed system. The observed Cr isotope signature is hypothesized to arise from fractionation during the reduction of Cr(VI) in surface waters and oxygen minimum zones, scavenging of isotopically light Cr(III) to deeper water and sediment, and subsequent release of this seawater-derived Cr(III) back into seawater, either as organic complexes with Cr(III) or after oxidation to Cr(VI). The isotopic fractionation factor (ϵ) associated with Cr cycling in seawater is estimated to be $-0.80 \pm 0.03\%$ (2σ). Samples from the sea-ice affected Surface Mixed Layer of the Arctic Ocean (~ 10 m depth) deviate from the general trend, and samples proximal to rivers illustrate geographic variation in $\delta^{53}\text{Cr}$ values for continental runoff, but prompt loss of this signature away from the source.

Published by Elsevier B.V.

1. Introduction

Chromium is a trace element in seawater whose concentration (~ 90 – 340 ng/kg) (Cranston and Murray, 1978) and distribution is strongly controlled by its oxidation state. Cr(VI) is soluble in oxygenated seawater in the form of the thermodynamically stable chromate (CrO_4^{2-}) and bichromate (HCrO_4^-) oxyanions, and is generally $>70\%$ of total Cr (e.g., Achterberg and van den Berg, 1997; Sirinawin et al., 2000). Reduction to reactive Cr(III) species, such as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, causes Cr removal from seawater (likely as $\text{Cr}(\text{OH})_3$), although Cr(III) can occasionally constitute up to 50% of total dissolved Cr (Connelly et al., 2006), made soluble through complexation with organic ligands (e.g., Yamazaki et al., 1980; Sander and Koschinsky, 2000, 2011). Field and laboratory experiments have shown that the isotopes of Cr are fractionated during Cr(VI) reduction, with the light isotopes partitioning into the product Cr(III) (Table 1). Thus, the isotopes of Cr may be used to study the ocean

Cr cycle, which is poorly understood. The low abundance of Cr in seawater, however, presents a major challenge for obtaining precise and routine isotopic analyses. In this paper, we use a TIMS technique for measurement of total Cr (VI + III) $^{53}\text{Cr}/^{52}\text{Cr}$ ratios in seawater (reported as $\delta^{53}\text{Cr}$ values), representing some of the ocean's major water masses. We find that Cr isotopes correlate strongly with Cr concentration ($[\text{Cr}]$), revealing a strong internal cycling of Cr and its isotopes in the ocean.

2. Background

The residence time of Cr in the ocean has been estimated at ~ 9000 – $40,000$ y (Campbell and Yeats, 1984; Reinhard et al., 2013). Rivers are the main source of dissolved Cr to the ocean ($\sim 7 \times 10^8$ mol y^{-1}) and “suboxic” and anoxic marine sediment are the main Cr sinks (Jeandel and Minster, 1987). Weathering reactions driven by Mn-oxhydroxides rapidly oxidize Cr(III) (Nakayama et al., 1981c; Eary and Rai, 1987) that is released from silicate rocks with high [Cr] (average bulk continental crust ~ 138 $\mu\text{g/g}$, Rudnick and Gao, 2003). Thus, river input is mainly Cr(VI) as chromate (CrO_4^{2-}) (e.g., Cranston and Murray, 1980). In oxygenated seawater, oxyanions of Cr(VI) may be reduced to Cr(III) by electron donors such as organic matter and Fe(II), where

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Table 1

Summary of empirically-determined Cr isotope fractionation factors for reduction of Cr(VI) to Cr(III) by various reductants. For convenience, all fractionation factors have been converted to ϵ (equivalent to the usage of $\Delta^{53}\text{Cr}$), defined as $\delta^{53}\text{Cr}_{(\text{III})} - \delta^{53}\text{Cr}_{(\text{VI})}$. ϵ values are related to conventional α values by $\epsilon = (\alpha - 1) \times 1000$ or, similarly, $\epsilon = 1000 \times \ln \alpha$. These reactions all result in Cr(VI) that is enriched in ^{53}Cr (heavy $\delta^{53}\text{Cr}$) and Cr(III) that is depleted in ^{53}Cr (light $\delta^{53}\text{Cr}$), relative to a standard (NBS 979).

Reference	Fractionation factor, as ϵ reductant
Basu and Johnson (2012)	−3.91; −2.67; −2.65; −2.11
Berna et al. (2009)	Goethite, siderite, green rust, FeS −3.07; −2.38
Døssing et al. (2011)	Incubated contaminated sediment −3.60; −1.50
Ellis et al. (2002)	Ferrous Fe; 'Green rust' −3.51
Han et al. (2012)	Magnetite −1.95; −0.38
Jamieson-Hanes et al. (2012)	<i>Pseudomonas</i> : aerobic; denitrifying −2.10; −3.51
Kitchen et al. (2012)	Organic carbon: continuous flow; batch exposure −4.20; −3.11
Sikora et al. (2008)	Low-pH Fe(II); organic reductants −4.11; −1.75
Zink et al. (2010)	<i>Shewanella oneidensis</i> bacteria −3.54; −5.0
	Acidic H_2O_2 ; pH-neutral H_2O_2 (kinetic)

Fe(II) can be generated in surface waters by photochemically produced H_2O_2 in conjunction with organic matter (Zika et al., 1985; Kieber and Helz, 1992; Barbeau et al., 2001). H_2O_2 has also been shown to oxidize Cr(III) in seawater solutions in the laboratory (Pettine and Millero, 1990). Concentrations of Cr(III) correlate with biological activity and bacterial biomass (Connelly et al., 2006), and the solubility of reduced Cr is increased by complexation with dissolved organics (Yamazaki et al., 1980; Nakayama et al., 1981b; Sander and Koschinsky, 2000, 2011). Thus, Cr(III) is likely an important component of total dissolved Cr in several marine regimes, including coastal waters, deep waters (where it may be released from particles in oxygen minimum zones or near the sediment-water interface; e.g., Achterberg and van den Berg, 1997), and near hydrothermal vent systems (e.g., Sander and Koschinsky, 2000; Sander et al., 2003).

Silicate rocks cluster within $\delta^{53}\text{Cr} = -0.124 \pm 0.101\text{‰}$ (Schoenberg et al., 2008). However, a wider range in Cr isotopic signatures ($\delta^{53}\text{Cr} -1.0$ to $+4.9\text{‰}$) is found in the environment, which can be attributed largely to speciation-driven solubility changes (e.g., Ellis et al., 2002; Berna et al., 2009). A compendium of empirical data shows that the reduction of soluble Cr(VI) to insoluble Cr(III) results in an isotopically heavy Cr(VI) pool in solution, and isotopically lighter Cr(III) in precipitates; the direction of fractionation holds regardless of reducing agent, although the magnitude of the isotopic fractionation is variable (Table 1). Additionally, oxidation of Cr(III) appears to preferentially leach/mobilize the heavy isotopes of Cr (Døssing et al., 2011).

Recent studies of Cr isotopes in the alteration products of ultramafic rocks ($+0.9$ to $+1.2\text{‰}$, Farkaš et al., 2013), in paleosols (-1.0 to $+0.13\text{‰}$, Frei and Polat, 2013; Crowe et al., 2013), and tropical soils (-0.4 to $+0.2\text{‰}$, Frei et al., 2014) concur that Cr(III) released from parent rock material is later subjected to redox cycling and its attendant isotopic fractionation. Thus far, it appears that ^{53}Cr -enriched chromate is responsible for the high $\delta^{53}\text{Cr}$ of rivers, and possibly influences seawater $\delta^{53}\text{Cr}$ (Frei et al., 2014). In light of these and other studies highlighting oxidative weathering-driven Cr isotope variations, use of Cr as a tracer for the paleoredox state of seawater is being explored (Frei et al., 2011). The $\delta^{53}\text{Cr}$ values for sedimentary iron formations and shale were used to trace the oxygenation history of Earth, based on the relationship between terrestrial oxidative weathering and Cr isotope fractionation (Frei et al., 2009, 2013; Crowe et al., 2013). Simply described,

iron formation values falling within the range of silicate $\delta^{53}\text{Cr}$ values ($-0.124 \pm 0.1\text{‰}$) imply the absence of free O_2 in earth surface environments, while fractionated values (up to $+4.9\text{‰}$) imply levels of O_2 high enough to allow formation of Mn-oxyhydroxides in soils, which are thought necessary to convert Cr(III) to Cr(VI) in continental weathering environments.

The isotopic composition of Cr in seawater has previously been evaluated in two locations: $+0.41$ to $+0.66\text{‰}$ in the open-ocean Argentine Basin, with small non-systematic variations with depth; and $+1.5\text{‰}$ between the surface and 12 m depth at an outer-estuarine location in Southampton Water, UK (Bonnand et al., 2013). Both locations record seawater $\delta^{53}\text{Cr}$ values higher than igneous rocks, consistent with an isotopically heavy riverine flux of weathered Cr (relative to the continental crust). These authors suggested that the high $\delta^{53}\text{Cr}$ ($+1.5\text{‰}$) and low Cr concentration (~ 100 ng/kg) of Southampton Water reflected localized reduction of riverine-sourced Cr(VI) in estuaries, while also speculating that the lower $\delta^{53}\text{Cr}$ ($\sim +0.5\text{‰}$) and higher Cr concentration (~ 320 ng/kg) in Argentine Basin seawater is more representative of the oceanic average. Here, we present Cr isotope and Cr concentration data from three depth profiles and a shelf-to-basin transect in the Arctic Ocean, as well as data for seawater samples from the Pacific and Atlantic oceans. Together, these data forecast the range of variability in seawater $\delta^{53}\text{Cr}$ values, and begin to address the processes responsible for these variations.

3. Materials and methods

3.1. Atlantic and Pacific seawater samples

The North Atlantic water (OSIL) studied is commercially available from <http://www.osil.co.uk>. It was collected from the surface of the open ocean North Atlantic, near the Sargasso Sea, has a salinity of 35, and is not acidified. North Pacific water was sampled at two locations. At station PAPA (~ 1500 km northwest of Vancouver, BC), seawater was collected with 20 L Niskin bottles at 10 m and 1000 m depth, and acidified shortly after collection. Fifteen liters were also collected at 10 m near the Oregon coast (USA) with an 8 L Niskin water sampler. This batch was spiked with the Cr double-spike and acidified to pH 2 at the time of collection.

It has been shown that seawater Cr does not readily adhere to the walls of polypropylene or Pyrex containers (Fukai and Vas, 1969; Yamazaki et al., 1980). However, as a further precaution, acidification or freezing of samples was carried out soon after collection and filtration, with the exception of OSIL seawater.

3.2. Arctic seawater samples

3.2.1. Sample collection

Seawater was collected during the Canadian IPY-GEOTRACES program as part of the 2009 CCGS *Amundsen* Arctic Expedition (ArcticNet 0903), between August 27 and September 12, 2009, in the Beaufort Sea. Sampling started on the continental shelf and then moved to the deep waters of the Canada Basin (Fig. 1). Samples were collected for Cr isotope measurements at seven of the ten stations sampled (Fig. 2; Table 2). Stations S1, S1.1, S1.2, S2, and L1 were collected using the ship rosette, while L1.1 and L2 were collected with a trace-metal clean rosette. The ship rosette was equipped with a trace-metal clean rosette. The trace-metal rosette had 12 Go-Flo bottles. Samples were passed through $0.45 \mu\text{m}$ Supor-Filters into 20 L acid-cleaned cubitainers (for the shallow samples, 1 L cubitainers were used). A small aliquot of the seawater was used to rinse each cubitainer prior to filling. Samples were frozen, stored, and transported at temperatures $< -10^\circ\text{C}$. The cruise data set, including CTD (conductivity-temperature-depth) and nutrient data is available from <http://www.bodc.ac.uk/geotraces/data/>.

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