Chemical Geology 444 (2016) 101–109

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

The Cr-isotope signature of surface seawater — A global perspective

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ARTICLE INFO

Article history:
Received 20 March 2016
Received in revised form 2 October 2016
Accepted 4 October 2016
Available online 5 October 2016

Keywords:
Chromium isotopes
Chromium cycling
Global distribution
Seawater
Redox proxies

ABSTRACT

This study presents chromium-isotope data (expressed as $\delta^{53}Cr$) and chromium concentrations (Cr) of surface seawater (0–2 m depth) from a variety of locations worldwide. In addition to samples from the open ocean (Arctic, Southern, Pacific, and Atlantic Oceans), samples were analysed from areas with more restricted water exchange rates (the Mediterranean Sea, Øresund, and Baltic Sea). The data indicate a heterogeneous distribution of $\delta^{53}Cr$ in seawater with a total range from +0.13‰ to +1.24‰. The data are in agreement with a previous study, which focused on depth profiles, suggesting that seawater heterogeneity in $\delta^{53}Cr$ and Cr concentration can be explained using a single fractionation factor for Cr-reduction ($\varepsilon = -0.79 \pm 0.06$‰ 2SD). In basins with limited water exchange with the open ocean, however, local factors seem to control the Cr-isotope composition.

1. Introduction

Chromium (Cr) is a transition metal that exists as a trace element in seawater with concentrations ranging from ~80 to 550 ng/kg (Bonnand et al., 2013; Cranston and Murray, 1978; Economou-Eliopoulos et al., 2016; Jeandel and Minster, 1987; Pereira et al., 2015; Scheiderich et al., 2015). In oxygenated seawater, generally >70% of total Cr occurs as soluble Cr(VI) in the form of thermodynamically stable chromate (CrO_4^{2-}) (Achterberg and Van Den Berg, 1997; Elderfield, 1970). Reduction to Cr(III) species (e.g., $Cr(H_2O)_6^{3+}$) is typically accompanied by Cr removal from seawater; however, Cr(III) can contribute up to 50% of total dissolved Cr in some natural settings (Connelly et al., 2006). High Cr(III) concentrations are probably attributable to photo- and biochemical processes in surface waters, such as organic complexation (Achterberg and Van Den Berg, 1997). Isotopic fractionation of Cr is also controlled by redox reactions, where isotopically light ^{52}Cr (compared to the narrow range of igneous rock values, $\delta^{53}Cr = -0.124 \pm 0.101$‰; Scheiderich et al. (2015)) is favoured by the reduced Cr(III) species during both Cr oxidation and reduction. As a result, Cr(III) oxidation produces mobile Cr(VI) that is generally ^{53}Cr-enriched, and partial Cr(VI) reduction further enriches residual Cr(VI) in ^{53}Cr (Døssing et al., 2011; Frei et al., 2009; Frei and Polat, 2013; Scheiderich et al., 2015).

Because of the redox-sensitivity of Cr isotopes and their potential as a paleo-redox proxy, there has been recent interest in quantifying the concentration and isotopic composition of Cr in modern seawater.

Bonnand et al. (2013) were the first to measure seawater $\delta^{53}Cr$ values, and the relatively small amount of variation in Cr concentration with depth in the Argentine Basin down to ~2500 m suggested that Cr behaves as a conservative element at this site. Furthermore, these authors used an average $\delta^{53}Cr$ value of +0.53‰ calculated for the Argentine Basin water profile—which they assumed to be equal to global average seawater—in their Cr budget calculations. Coastal seawater from Southampton was significantly ^{53}Cr-enriched compared to the Argentine Basin (+1.51‰ compared to +0.41–0.66‰, respectively), which the authors attributed to fractionation processes during weathering/transport or redox reactions in estuaries that preferentially affected coastal environments.

With their global survey of seawater $\delta^{53}Cr$ values, Scheiderich et al. (2015) presented clear evidence that the Cr-isotope composition of the open oceans is substantially heterogeneous, ranging between +0.41‰ and +1.53‰. Heterogeneity was present across ocean basins (Arctic, Pacific, and Atlantic) and $\delta^{53}Cr$ varied systematically with depth in an Arctic Ocean profile. Remarkably, a strong inverse correlation ($R^2 = 0.95$) was reported between $\delta^{53}Cr$ and ln[Cr] for globally distributed samples, with the exception of Arctic samples from the surface mixed layer. The authors hypothesized that this relationship was driven by Cr(VI) reduction in surface waters and the oxygen minimum zone, removal of particle-reactive Cr(III) to deep water and sediment, and subsequent release of Cr(III) back to seawater, with associated redox-

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http://dx.doi.org/10.1016/j.chemgeo.2016.10.004
0009-2541/

related isotopic fractionation. Furthermore, strong correlation between δ^{53}Cr and ln[Cr] may indicate that the Cr isotope composition of the world's oceans is driven by a single fractionation factor ($\varepsilon = -0.80 \pm 0.03$‰) for Cr reduction. Additional seawater Cr isotope data were recently contributed by Pereira et al. (2015) (Rocas Atoll, Brazil), Paulukat et al. (2015) (Bay of Bengal, India), and Economou-Eliopoulos et al. (2016) (eastern Mediterranean Sea), each of which provide further evidence for seawater δ^{53}Cr heterogeneity.

In this study, we expand on the work of Scheiderich et al. (2015) and present Cr-isotope data for surface seawater globally, as well as seasonal data and data from restricted basins with limited open ocean exchange. We focused on surface seawater across a range of environments to test the impact of local factors on Cr reduction processes. Our sample suite includes surface samples from the Atlantic, Pacific, Southern, and Arctic Oceans. Additionally, we explore the potential effect of limited water exchange on Cr cycling using samples from the Mediterranean Sea, the Baltic Sea, and the connection between the Baltic Sea and the Atlantic Ocean (Danish straits: the Kattegat and Skagerrak). Results are discussed in the context of previous hypotheses regarding seawater Cr-isotope values, including the fractionation factor (ε) associated with Cr reduction and its control on the Cr isotope distribution of the global oceans. Furthermore, other parameters, such as riverine Cr influx and seasonal effects, are discussed. This study provides critical information on modern Cr cycling that informs the use of Cr isotopes as a redox proxy in ancient strata.

2. Materials and methods

2.1. Seawater samples

All samples are listed in Table 1 and shown in Fig. 1. For sampling, acid cleaned Nalgene bottles were used. All samples, except Helgoland 2, are surface-water samples from a maximum depth of 2 m. Arctic seawater originates from approximately 20 km northwest of Spitsbergen (Svalbard). Antarctic seawater was collected during the ANT-27/2 expedition 2011 (Alfred-Wegener-Institute) approximately 200 km northwest of the South Shetland Islands. North Pacific coastal seawater samples were collected in Santa Barbara and Cambria (California, USA). A seawater sample from the South Pacific was collected close to the island Mo'orea (French Polynesia) and from the northwest coast of Lady Eliot Island (Australia). Two samples of North Sea water were sampled approximately 2 km (deep trench) and 9.5 km south of the coast of Helgoland. Furthermore, two coastal North Sea water samples were collected at the Danish west (Thorsminde) and northwest coast (Skagerrak). Seawater from the North Atlantic is represented by a sample from the southern coast of Disko Island (W′ Greenland; Baffin Bay)

Table 1
Sample list with Cr-isotope values and Cr concentrations.

Sample	Location nr.	Sample	Coordinates	δ^{53}Cr [‰] ± 2SD*	Conc. [ng/kg]	n	Litre
Arctic	1	Arctic (N' Spitsbergen)	N79° 53.589′ E10° 25.277	1.24 ± 0.05	230	1	0.5
Antarctica	2	Antarctica (1)	S61° 31.11 W64° 30.42	0.54 ± 0.05	374	1	0.2
(Southern Ocean)	2	Antarctica (2)	S61° 31.11 W64° 30.42	0.53 ± 0.05	262	2	0.5
	2	Antarctica (3)	S61° 31.11 W64° 30.42	0.58 ± 0.05	232	1	0.5
North Pacific	3	St. Barbara (California)	N34°24′ W119°41′	0.77 ± 0.01	385	2	0.5
	4	Cambria (California)	N35°33.5′ W121°6.5′	0.96 ± 0.02	166	1	0.5
South Pacific	5	Mer Mo'orea (French Polynesia) (1)	S17°33′ W149°54′	0.53 ± 0.11	340	4	0.5
	5	Mer Mo'orea (French Polynesia) (2)	S17°33′ W149°54′	0.65 ± 0.10	330	4	0.5
	5	Mer Mo'orea (French Polynesia) (3)	S17°33′ W149°54′	0.67 ± 0.18	368	4	0.5
	6	Lady Eliot Island	S24° 6′38.30″ E152°42′45.38″	0.75 ± 0.03	193	1	1
North Atlantic	7	Disko Island (1)	N 69°12′ W 53°31′	0.74 ± 0.04	165	1	0.82
+ North Sea	7	Disko Island (2)	N 69°12′ W 53°31′	0.70 ± 0.03	185	1	0.8
	7	Disko Island (3)	N 69°12′ W 53°31′	0.75 ± 0.10	179	2	0.69
	8	Helgoland 1 (1)	N54° 06′ E008° 00′	0.98 ± 0.01	116	1	0.5
	8	Helgoland 1 (2)	N54° 06′ E008° 00′	0.89 ± 0.13	157	2	0.7
	9	Helgoland 2 (deep trench) (1)	N54°08.50′ E007°54.00′	0.33 ± 0.16	491	5	0.5
	9	Helgoland 2 (deep trench) (2)	N54°08.50′ E007°54.00′	0.31 ± 0.11	492	3	0.5
	9	Helgoland 2 (deep trench) (3)	N54°08.50′ E007°54.00′	0.46 ± 0.06	443	2	0.5
	10	Thorsminde July 2014	N56°22′22.45″ E8° 6′53.28″	1.02 ± 0.04	184	2	0.7
	11	Grenen (Skagerrak) July 2014 (1)	N57°44′50.75″ E10°38′46.36″	1.05 ± 0.02	115	2	0.7
	11	Grenen (Skagerrak) July 2014 (2)	N57°44′50.75″ E10°38′46.36″	0.94 ± 0.02	117	1	0.85
	12	Atlantic (OSIL) (1)	N35° to 40°, W42° to 49°	0.70 ± 0.03	255	1	0.5
	12	Atlantic (OSIL) (2)	N35° to 40°, W42° to 49°	0.81 ± 0.03	228	1	0.8
	12	Atlantic (OSIL) (3)	N35° to 40°, W42° to 49°	0.75 ± 0.04	216	3	0.8
	13	Patos Summer 2015	N42° 9′24.61″ W8°49′27.13″	0.98 ± 0.03	169	1	1
Mediterranean Sea	14	Playa Poniente Summer 2014	N38°32′4.20″ W0°8′57.30″	0.86 ± 0.07	280	4	0.5
	15	Playa Albir Summer 2013	N38°34′36.72″ W0° 3′46.56″	0.90 ± 0.17	239	3	0.5
	15	Playa Albir Summer 2014	N38°34′36.72″ W0° 3′46.56″	0.81 ± 0.03	306	1	0.5
	15	Playa Albir Summer 2015	N38°34′36.72″ W0° 3′46.56″	0.96 ± 0.02	301	1	0.5
Baltic Sea, Øresund	16	Grenen (Kattegat) July 2014	N57°44′34.26″ E10°38′47.04″	0.80 ± 0.07	192	2	0.79
and Kattegat	17	Bellevue Strand November 2013	N55°46′40.28″ E12°35′36.12″	0.31 ± 0.10	153	1	1
	17	Bellevue Strand November 2014	N55°46′40.28″ E12°35′36.12″	0.34 ± 0.06	120	2	1
	18	Hellerup June 2014	N55°43′58.84″ E12°34′58.54″	0.35 ± 0.11	119	1	1
	18	Hellerup October 2013	N55°43′58.84″ E12°34′58.54″	0.63 ± 0.13	120	1	1
	19	Køge bugt June 2013	N55°31′11.28″ E12°23′18.52″	0.24 ± 0.11	391	1	1
	19	Køge bugt June 2014	N55°31′11.28″ E12°23′18.52″	0.20 ± 0.12	258	3	1
	19	Køge bugt October 2014	N55°31′11.28″ E12°23′18.52″	0.56 ± 0.10	104	2	1
	19	Køge bugt April 2015	N55°31′11.28″ E12°23′18.52″	0.61 ± 0.12	80	1	1.5
	20	Feddet-Faxe bugt April 2014	N55°9′11.23″ E12° 6′34.81″	0.50 ± 0.03	83	1	1.35
	21	Storebælt June 2015	N55°30′ E10°52′	0.40 ± 0.02	112	1	1
	22	Bornholm	N55°7′ E14°37′	0.13 ± 0.06	254	1	1
	23	Degerhamn (Öland) Summer 2014	N56°21′23.8″ E016°24′29.0″	n.d.	123	n.d.	1.5
	24	Halltorp (Öland) Summer 2014	N56°48′17.6″ E016°34′23.7″	n.d.	136	n.d.	0.66

n = Number of repeated analyses of the same sample load; *For multiple measurements of the same sample load errors are reported as 2SD, for single measurements of one sample (n = 1) errors are reported as 2SE; Numbers in brackets: Replicates gone through the separation procedure; n.d. = Not determined.