The chromium isotopic composition of seawater and marine carbonates

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A B S T R A C T

Chromium isotopes are fractionated during redox reactions and have the potential to provide a record of changes in the oxygenation levels of the oceans in the geological past. However, Cr is a trace metal in seawater and its low concentrations make isotopic measurements challenging. Here we report the first determinations of δ^{53}Cr for seawater from open ocean (Argentine Basin) and coastal (Southampton Water) settings, using a double-spike technique. The total chromium concentration in seawater from Southampton Water is 1.85 nM, whereas the Cr content of Argentine Basin samples is 5.8–6.6 nM. The δ^{53}Cr value of seawater from the Argentine Basin is 0.491–0.556‰ in intermediate and deep waters, and varies between 0.412 and 0.664‰ in surface waters ($<$150 m). The δ^{53}Cr value of Southampton Water seawater is 1.505‰, which may reflect *in situ* reduction of Cr(VI) to Cr(III). All of our seawater samples have higher δ^{53}Cr than crustal and mantle silicates, and mass balance modelling demonstrates that river water must also be enriched in heavy Cr isotopes, indicating that Cr isotopes are fractionated during weathering and/or during transport to the oceans.

We also show that the Cr isotopic composition of modern non-skeletal marine carbonates (0.640–0.745‰) encompasses the range that we measure for Argentine Basin seawater. Thus, fractionation of Cr isotopes during precipitation of these marine carbonates is likely to be small ($<$0.2‰), and they have the potential to provide a record of the Cr isotopic composition of ancient seawater. Phanerozoic carbonates are also characterised by heavy δ^{53}Cr and a correlation between δ^{53}Cr and Ce/Ce* suggests that the Cr and Ce cycles in the ocean are linked.

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1. Introduction

Chromium is one of a number of trace metals, whose isotopic composition may provide important information about redox-controlled element cycling in the oceans (Anbar and Rouxel, 2007; Bullen and Eisenhauer, 2009). Although variations in the chromium concentration of seawater have attracted significant scientific interest for the past 40 years (e.g., Elderfield, 1970; Grimaud and Michard, 1974; Cranston and Murray, 1978; Jeandel and Minster, 1987; Connelly et al., 2006), Cr is present in concentrations of only a few nanomoles per litre (see Table 1 for compilation) so its distribution has been difficult to fully assess. Early research suggested that chromium was depleted in surface seawater, so Cr was assigned to the 'recycled' group of elements whose distribution in the oceans is similar to that of the nutrient elements,

such as nitrate or phosphate (Whitfield and Turner, 1987). However, more recent studies indicate that the surface depletion is modest, and there is no substantial difference between Atlantic and Pacific deep-water concentrations (e.g. Sirinawin et al., 2000). Moreover, there is no correlation between Cr and the nutrient elements at the global scale (Sirinawin et al., 2000). For this reason, Cr is probably best described as intermediate between a 'conservative' and 'recycled' element, consistent with estimates of its residence time (8000–45,000 years: Campbell and Yeats, 1981; Broecker and Peng, 1982; Quinby-Hunt and Turekian, 1983; Whitfield and Turner, 1987).

In oxic seawater, the dominant chromium oxidation state is Cr(VI), which is consistent with thermodynamic calculations (Elderfield, 1970). However, significant amounts of Cr(III) have also been measured. The percentage of Cr(III) is usually $<$5% (e.g. Mugo and Orians, 1993), although some authors have found much higher quantities, sometimes accounting for over 90% of the total dissolved Cr (Connelly et al., 2006; Sander et al., 2003). It is generally accepted that the two Cr species display different behaviour in natural waters, with Cr(VI) being highly soluble in oxic waters, whereas Cr(III) is particle-reactive and forms insoluble chromium

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Table 1

Concentrations of Cr(VI) and total Cr (Cr(VI) + Cr(III)) measured in seawater and relatively pristine river waters.

	Reference	Cr(VI) (nM)	Total Cr (nM)
Ocean area			
NE Pacific Ocean	Cranston and Murray, 1978	1.6–3.5	
NE Pacific Ocean	Cranston, 1983		1.7–4.0
Eastern Pacific Ocean	Murray et al., 1983	1.1–6.0	
East Pacific Rise	Jeandel and Minster, 1984		1.9–15.8[*]
South Pacific Ocean	Golimowski et al., 1985		2.4
South and North Pacific Ocean	Jeandel and Minster, 1987		2.3–6.5
Pacific Ocean	Isshiki et al., 1989	2.1–4.2	2.9–4.6
Pacific Ocean	Sander et al., 2003	0.7–6.8	6.3–19.4[†]
North Pacific Ocean	Mugo and Orians, 1993	2.3–4.3	2.3–4.3
Indian Ocean	Ghaddaf, 1990	0.3–2.4	0.9–2.8
Mediterranean and Alboran Sea	Sherrell and Boyle, 1988		2.5–5.9
NW Mediterranean	Boussemart et al., 1992	4.5–5.8	
Mediterranean and Gibraltar	Achterberg and van den Berg, 1997	1.7–3.5	1.7–4.7
Atlantic Ocean near Gibraltar	Sherrell and Boyle, 1988		2.9–3.5
NW Atlantic Ocean	Campbell and Yeats, 1981		3.2–5.2
North Atlantic Ocean	Jeandel and Minster, 1987		2.0–4.6
North–South Atlantic Ocean	Sirinawin et al., 2000	3.1–7.3	
North Atlantic Ocean	Mugo and Orians, 1993		2.5–4.5
Arctic Ocean	Sirinawin et al., 2000	3.0–6.1	
Caribbean Sea	Sander et al., 2003	1.5-2.5	
Sargasso Sea	Connelly et al., 2006		2.5–6.5
Rivers			
Columbia river	Cranston and Murray, 1980	1.7–3.5	1.8–3.8
Humber estuary	Comber and Gardner, 2003	1.5–6.2	1.2–17.1
Sava river	Dragun et al., 2009		4.8–6.5
Orinoco river	Mora et al., 2009		1.4–11.3
Sacramento River	Taylor et al., 2012		1–7

[*] The sample with 15.8 nM Cr is thought to be affected by release of Cr from sediment pore fluids. All other samples have <3.7 nM Cr.
[†] Samples with high Cr(III) are thought to be affected by hydrothermal inputs.

hydroxide compounds (Cranston and Murray, 1978). While these differences can explain the low concentration and the relative proportions of Cr(VI) and Cr(III) in seawater, most Cr speciation calculations have been performed at Cr concentrations far higher than seawater. Fig. 1 shows the results of speciation calculations for seawater with a Cr concentration of 5 nM, with hydrolysis constants for Cr(III) hydroxides taken from Rai et al. (1987). These calculations confirm that Cr(III) hydroxide species are stable over a wide range of Eh and pH conditions (Fig. 1a), but at typical seawater Eh and pH values, chromate species dominate (Fig. 1b). The presence of dissolved Cr(III) in seawater is therefore inconsistent with speciation calculations, and is most probably due to sluggish oxidation of Cr(III) to Cr(VI) (Schroeder and Lee, 1975).

Isotopes of redox-sensitive metals have provided key information about past redox conditions at the Earth's surface. The most widely used elements are Fe (e.g. Rouxel et al., 2005) and Mo (Siebert et al., 2003; Archer and Vance, 2008; Duan et al., 2010; Voegelin et al., 2009). Cr also has the potential to provide constraints on redox conditions in the oceans and atmosphere because Cr isotopes are fractionated during redox reactions (Ellis et al., 2002), and a number of recent studies have attempted to use this system to trace changes in the level of O_2 in the atmosphere in the Archaean and Neoproterozoic (Frei et al., 2009; Frei et al., 2011; Frei et al., 2013). Nevertheless, before Cr isotope data can be fully interpreted, it is essential to properly ascertain the operation of the Cr cycle in Earth system processes.

Stable Cr isotope ratios are reported in standard delta notation relative to the SRM 979 Cr isotope standard:

$$\delta^{53}Cr = \left(\frac{\frac{^{53}Cr}{^{52}Cr}\, sample}{\frac{^{53}Cr}{^{52}Cr}\, NBS979} - 1 \right) * 1000 \qquad (1)$$

The Cr isotopic composition of terrestrial silicates is relatively homogenous, with $\delta^{53}Cr$ values for the mantle and the continental crust ranging from −0.26‰ to −0.04‰ (Schoenberg et al., 2008). By contrast, groundwaters have higher $\delta^{53}Cr$ values, that range from 0.3 to 5.9‰ (Ellis et al., 2002; Izbicki et al., 2008). Low values are attributed to input of anthropogenic Cr, while high values appear to be characteristic of groundwater with low levels of oxygen. This is because reduction of Cr(VI) to Cr(III), which is favoured when oxygen levels are low, leaves the remaining Cr(VI) enriched in the heavy isotopes (Ellis et al., 2002; Ellis et al., 2004; Zink et al., 2010). Biotic reduction of Cr(VI) to Cr(III) has the same effect (Sikora et al., 2008). Water samples from fully oxic groundwater recharge areas have $\delta^{53}Cr$ values of 1.2–2.3‰. As oxidation of Cr(III) to Cr(VI) does not appear to fractionate Cr isotopes (Zink et al., 2010), these relatively high $\delta^{53}Cr$ values are attributed to fractionation on mineral surfaces during oxidative weathering (Izbicki et al., 2008). As a result of these groundwater studies, a number of authors have postulated that modern (oxic) seawater should have $\delta^{53}Cr > 0‰$ (Izbicki et al., 2008; Frei et al., 2009), and analyses of seawater precipitates (marine carbonates and BIFs) support this idea (Bonnand et al., 2011; Frei et al., 2009). A recent study of highly weathered carbonates (Frei and Polat, 2013) and our own analyses indicate that weathering residues have low $\delta^{53}Cr$ values, which provides further evidence that weathering will produce isotopically heavy fluids which will ultimately be delivered to the oceans via rivers. Thus, the Cr isotopic composition of modern seawater has the potential to help constrain the sources of Cr to the ocean, provide mechanistic explanations for the distribution of Cr(VI) and Cr(III), and assess the controls on the availability of toxic Cr(VI). Moreover, information about past variations in seawater $\delta^{53}Cr$ could potentially be obtained from analyses of marine carbonates (Bonnand et al., 2011; Frei et al., 2011) but, as yet, little is known about the relationship between the Cr isotopic composition of seawater and carbonates.

To date, however, there have been no direct measurements of the Cr isotope composition of seawater. In order to fill this gap, a number of challenges need to be overcome. These include the
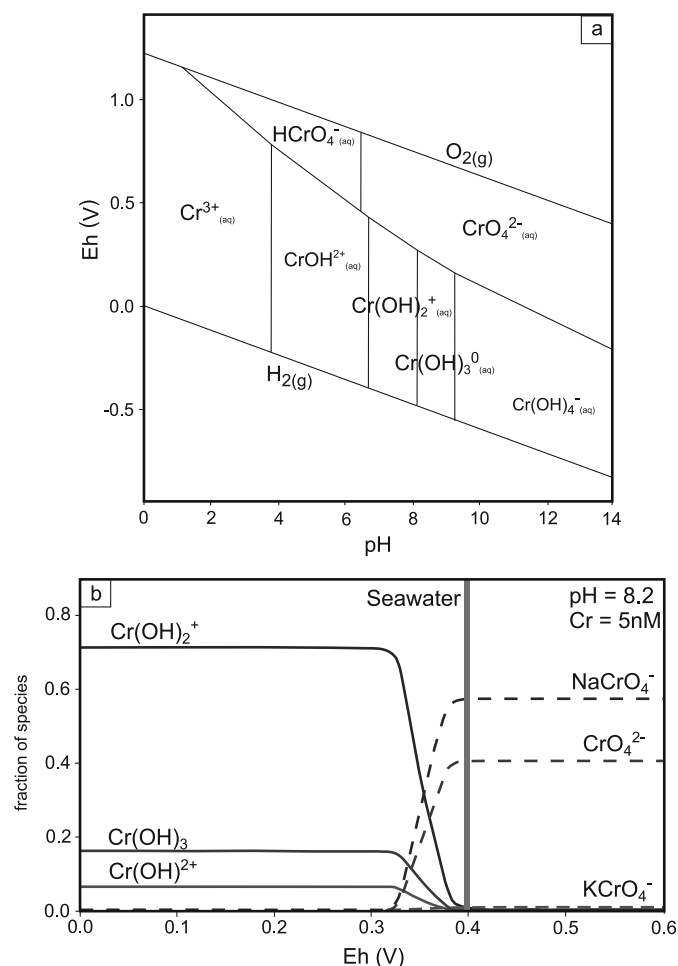
Fig. 1. (a) Speciation of Cr in seawater as a function of Eh and pH. (b) Relative proportion of different Cr species in seawater as a function of Eh, where pH = 8.2. Calculations were undertaken using Geochemists Workbench, for a total Cr concentration of 5 nM.

low concentration of Cr in seawater (usually 1–7 nM; Table 1), which means that large sample volumes are required, the need for low-blank methodologies for the separation of Cr from the sample matrix, and development of mass spectrometric techniques capable of providing Cr isotope data with high accuracy and precision.

Here, we present the first measurements of the Cr isotopic composition of coastal and open ocean seawater. We provide a detailed description of the pre-concentration and chemical separation methods that have enabled us to measure seawater Cr isotopes to high precision. Our data suggest that coastal seawater from Southampton Water has higher $\delta^{53}Cr$ (1.50‰) than open ocean waters collected from the Argentine Basin (0.41 to 0.66‰). We also present new Cr isotope data for modern ooids and Phanerozoic oolitic limestones, which demonstrate that there is a good agreement between seawater $\delta^{53}Cr$ values and those of modern non-skeletal carbonate precipitates. Thus, these initial results indicate that the Cr isotopic composition of marine carbonates may potentially be used to reconstruct past variations in the Cr isotopic composition of seawater.

2. Samples

2.1. Seawater samples

Samples of open ocean seawater were collected from the Argentine Basin in the South Atlantic (40°33.22′S, 51°26.64′W) during

RRS *James Cook* cruise JC42 in February 2010. The sampling site is located within the subtropical gyre at a water depth of 5349 m. Five samples were collected from the upper part of the water column, at 30, 150, 700, 1500 and 2289 m water depth. Water samples were collected using acid-cleaned 10-L Go-Flo bottles, fitted with external springs and modified for trace metal work. The bottles were mounted on a titanium CTD frame, which was deployed from a Kevlar wire. In addition to Cr and Cr isotopes, the water samples were also analysed for their nutrient (nitrate, silicate and phosphate) content (Fig. 2). No nitrite was detectable in any of the water samples. In-situ measurements of conductivity, temperature and dissolved oxygen were made using instruments attached to the CTD frame at the time of water sampling and these data are also shown in Fig. 2. Conductivity data were calibrated against bottle samples measured using a salinometer. As there was no time to analyse the oxygen content of the bottle samples, the calibration from the previous cast (determined four days earlier) was applied. As a result, there may be an offset between the actual and measured values, but this is likely to be small.

The hydrographic data presented in Fig. 2 indicate that the water column consists of four different water masses. Water in the upper part of the water column (0 to ∼300 m) is relatively warm and saline, with intermediate levels of dissolved oxygen. This is referred to as 'surface water' (Heywood and King, 2002). This water is underlain by fresher, highly oxygenated Antarctic Intermediate Water (AAIW), which reaches to depths of ∼1000 m. Upper Circumpolar Deep Water (UCDW) lies beneath AAIW and is identified by its low oxygen and high phosphate signature (Fig. 2; Heywood and King, 2002). UCDW extends to a depth of ∼2200 m, and is underlain by colder, more saline North Atlantic Deep Water (NADW). The core of the NADW is located at ∼2500 m according to Heywood and King (2002), but no hydrographic measurements were made below 2295 m on this occasion.

Samples of coastal seawater were collected at four depths (surface, 3, 5 and 11.5 m) from Southampton Water (50°46.75′N, 001°20.53′W) in July 2010, using acid-cleaned 5 L Niskin bottles, adapted for trace metal use and deployed on a Kevlar wire from RV *Callista*. Samples were collected from the outer part of the estuary (water depth 12 m). At the time of sampling, there was no variation in temperature (19 °C) or salinity (34) with depth, indicating that the water column was well-mixed. Nutrient concentrations of the seawater samples were also invariant with depth, with nitrate = 1.58 μmol L⁻¹, nitrite = 0.21 μmol L⁻¹, silicate = 3.59 μmol L⁻¹ and phosphate = 0.16 μmol L⁻¹. Thus, all four samples come from the same water mass, and can be considered replicates.

2.2. Carbonate samples

Oolitic carbonates were chosen to represent the composition of shallow surface sea water free of terrigenous impurities. Samples of non-skeletal modern marine carbonates (ooids) were obtained from the Bahama Bank (B08, NPCOScem and NPCOSunc) and Yucatan (C48). Phanerozoic oolitic limestone material is represented by a middle Jurassic oolite from the Cotswolds, UK (C17), an oolitic limestone from the Carboniferous Caswell Bay oolite, UK (C171) and a Cretaceous oolitic limestone from Spain (C443). The Cr isotopic composition of a series of certified carbonate standard reference materials, all of which are from the Phanerozoic, has been previously reported in Bonnand et al. (2011). These include JDo-1 (Permian dolomite), BCS-CRM 513 (limestone), BCS-CRM 512 (dolomite), JLs-1 (Triassic limestone) and Cal-S (Miocene limestone).
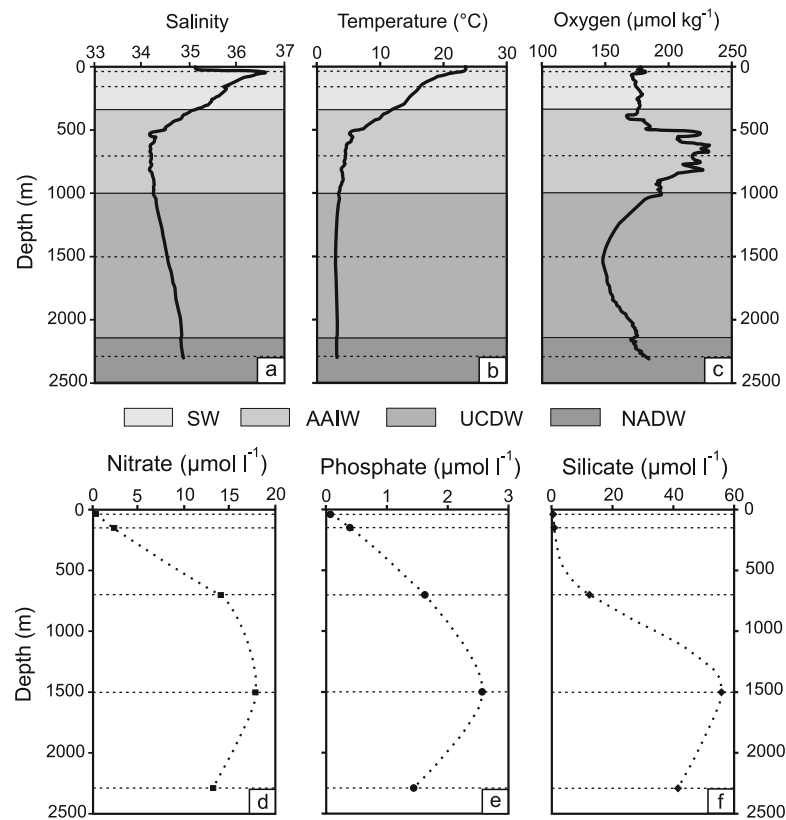
Fig. 2. Profiles of (a) salinity, (b) temperature, (c) dissolved oxygen, (d) nitrate, (e) phosphate and (f) silicate in upper part of the water column in the Argentine Basin. Note that the measured values for dissolved oxygen concentrations may show a small offset from the true values as no measurements were made on bottle samples from this cast (see text for details). The dashed horizontal lines show the depths from which the samples were collected. The solid horizontal lines show the position of the different water masses: SW = surface water, AAIW = Antarctic Intermediate Water; UCDW = Upper Circumpolar Deep Water; NADW = North Atlantic Deep Water.

3. Methods

Cr isotope measurements were made using a double-spike technique that allows us to correct for isotope fractionation during sample processing and for instrumental mass bias effects (Dodson, 1963). Full details of our techniques for the analysis of Cr isotopes in carbonates by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) can be found in Bonnand et al. (2011). In this study, we utilise the same mass spectrometry techniques, but new pre-concentration and chemical separation procedures were developed for the analysis of seawater samples. Full details of these procedures are provided in the Supplementary Information. Briefly, seawater samples were spiked with an appropriate amount of our ^{50}Cr–^{54}Cr double spike, and the Cr was co-precipitated with Fe (derived from ammonium Fe(II) sulphate hexahydrate) (Connelly et al., 2006; Cranston and Murray, 1978). Cr was separated from the Fe by anion exchange chromatography (Grimaud and Michard, 1974). As the Cr fraction also contains small quantities of residual salts that adhere to the Fe precipitate, it is also processed through a cation exchange column as described in Bonnand et al. (2011). The purified sample is then evaporated to dryness and re-dissolved in 0.6M HNO_3 for MC-ICP-MS analysis.

4. Results

4.1. Evaluation of the co-precipitation and chemical purification procedures

In order to evaluate the efficiency of the column separation procedure, a mixed solution of the ^{50}Cr–^{54}Cr double-spike and the NBS979 Cr isotope reference material, containing 100–500 ng of Cr, was processed through both anion and cation column chemistry procedures. The Cr isotopic composition measured for this solution is $\delta^{53}Cr = -0.056 \pm 0.028‰$ (2σ, where σ is the standard deviation; $n = 3$). To test for any potential effects of the Fe co-precipitation procedure, four aliquots of the same mixed standard-spike solution were co-precipitated with Fe(II) hydroxide, and then passed through both steps of the chemical purification procedure. The Cr isotopic composition derived for the standard is $-0.042 \pm 0.029‰$ (2σ, $n = 4$), which is within error of the mixed standard-spike solution that had only passed through column chemistry.

Up to 50 mL of 2mM ammonium Fe(II) sulphate hexahydrate was added to each sample, but this solution contains non-negligible Cr. To correct for this, it was necessary to determine the Cr concentration and Cr isotopic composition of the Fe solution. The Cr concentration was 0.97 ± 0.03 ng mL^{-1} (2σ, $n = 3$), and the $\delta^{53}Cr$ value was $0.34 \pm 0.11‰$ (2σ, $n = 3$). Chromium concentrations and the Cr isotopic composition of the samples reported in Table 2 are corrected for this contribution, and the uncertainties associated with this correction are propagated into the uncertainty of the final isotope composition. For the Argentine Basin samples, the correction reduces Cr concentrations by ~3%, and increases $\delta^{53}Cr$ by 0.021–0.031‰. For the Southampton Water samples, the correction reduces Cr concentrations by ~9%, and increases $\delta^{53}Cr$ by 0.177–0.191‰.

4.2. Cr concentration and Cr isotope composition of seawater

The Cr concentration and the Cr isotopic composition of seawater collected from the Argentine Basin and Southampton Water are presented in Table 2 and Fig. 3. As expected for a well-mixed water column (see Section 2.1), all of the samples col-

Table 2
Concentration of total Cr (Cr(III) + Cr(VI)) and Cr isotopic composition of seawater in the Argentine Basin and Southampton Water. As the Fe(II) salt used in the pre-concentration procedure contains non-negligible Cr, its contribution has be subtracted from the measured (uncorrected) data (see text for details). s.d. is the external reproducibility (standard deviation) of the sample measurements, with error propagation (see text for details).

Sampling site	Depth (m)	Uncorrected			Corrected		
		Cr_{TOT} (nM)	$\delta^{53}Cr_{TOT}$ (‰)	2 s.d. (‰)	Cr_{TOT} (nM)	$\delta^{53}Cr_{TOT}$ (‰)	2 s.d. (‰)
Argentine Basin	30	6.55	0.388	0.030	6.36	0.412	0.036
	150	6.43	0.633	0.031	6.24	0.664	0.036
	700	6.69	0.529	0.031	6.50	0.556	0.036
	1500	5.99	0.489	0.030	5.80	0.518	0.036
	2289	6.27	0.464	0.030	6.08	0.491	0.036
Southampton Water	surf.	2.05	1.332	0.032	1.86	1.509	0.047
	3	2.04	1.321	0.032	1.85	1.498	0.047
	5	2.02	1.331	0.032	1.83	1.512	0.047
	11.5	2.04	1.321	0.032	1.85	1.499	0.047

Table 3
Cr concentration and Cr isotopic composition of oolitic limestones and Phanerozoic carbonates, together with other key geochemical data.

Sample	Cr ($\mu g\,g^{-1}$)	$\delta^{53}Cr$ (‰)	Ce/Ce[*]	Eu/Eu[*]	Er/Yb	Zr ($ng\,g^{-1}$)	Th ($ng\,g^{-1}$)
Modern ooids							
C48	2.6	0.765	0.52	1.24	1.43	27	9
NPCOS cem	2.4	0.651	0.71	1.19	1.37	54	8
NPCOS unc	2.3	0.663	0.64	1.16	1.34	50	10
B08	4.0	0.640	0.70	1.24	1.40	18	41
Phanerozoic oolitic limestones							
C17	3.6	0.848	0.98	1.15	1.07	95	163
C171	6.5	1.939	0.31	1.15	1.29	47	70
C443	4.4	0.931	0.85	1.25	1.21	219	1390
Carbonate standards							
BCS-CRM 512[*]	0.8	0.737	0.88	1.25	1.15	915	21
BCS-CRM 513[*]	4.0	1.329	0.63	1.35	1.22	53	2
Cal-S[*]	2.5	1.819	0.39	1.20	1.18	14	19
JDo-1[*]	7.2	1.719	0.23	1.11	1.52	111	42
JLs-1[*]	1.1	1.994	n.d.	n.d.	n.d.	n.d.	n.d.

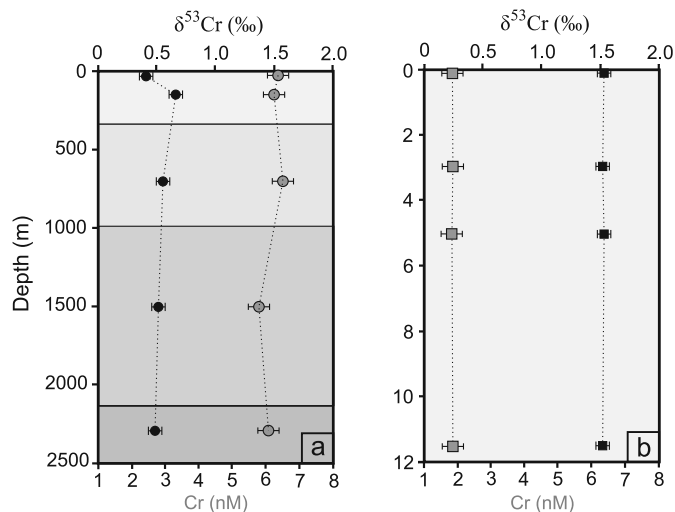[*] Data from Bonnand et al. (2011). n.d. – not determined.

Fig. 3. Profiles of the Cr concentration (Cr(III) + Cr(VI)) (grey symbols) and $\delta^{53}Cr$ (black symbols) in seawater samples from (a) the Argentine Basin and (b) Southampton Water. Error bars show the external reproducibility (± 0.047‰ for $\delta^{53}Cr$, $\pm 4\%$ for Cr concentration, see text for details). Key for different water masses in the Argentine Basin is given in Fig. 2.

lected from Southampton Water have the same Cr concentration (1.85 ± 0.01 nM; 2σ) and $\delta^{53}Cr$ value (1.505 ± 0.007‰; 2σ). Concentrations of Cr in seawater from the Argentine Basin range from 5.80 to 6.50 nM, with no systematic variation with depth. $\delta^{53}Cr$

values are lower than measured in Southampton Water, ranging from 0.491 to 0.556‰ in intermediate and deep waters, and from 0.412 to 0.664‰ in surface waters (<150 m). The sample collected from closest to the sea surface has the lowest $\delta^{53}Cr$ value. There is no obvious relationship between Cr or $\delta^{53}Cr$ and the nutrient elements, dissolved oxygen, salinity or temperature in the Argentine Basin (Figs. 2 and 3).

4.3. Chemical composition and Cr isotope composition of carbonates

The Cr isotopic composition of the carbonates is reported in Table 3, together with other relevant data. Our analyses of the trace element concentration of the carbonate leachates reveals that they contain very little Th and Zr, which are strongly enriched in detrital phases (Taylor and McLennan, 1985), and the lack of any correlation between the REEs and Zr and Th suggests that they are not contaminated by incorporation and/or leaching of detrital material (Frimmel, 2009). The REE patterns of the carbonates are similar to modern seawater, with a negative Ce anomaly and a positive Y anomaly (Fig. 4). It is however important to note that there are large variations in the size of these anomalies, for example JDo-1 has the biggest Ce anomaly, whereas modern ooids are characterized by small negative Ce anomalies.

All of the carbonates have Cr concentrations between 0.8 and 7.2 $\mu g\,g^{-1}$. Modern carbonates contain 2.3–4.0 $\mu g\,g^{-1}$, suggesting that Cr is enriched in carbonates by a factor of $\sim 10^4$ relative to seawater. The modern carbonates all have positive $\delta^{53}Cr$ values (0.640–0.745‰), and are therefore isotopically heavy compared to the continental crust and mantle (-0.26 to -0.04‰; Schoenberg
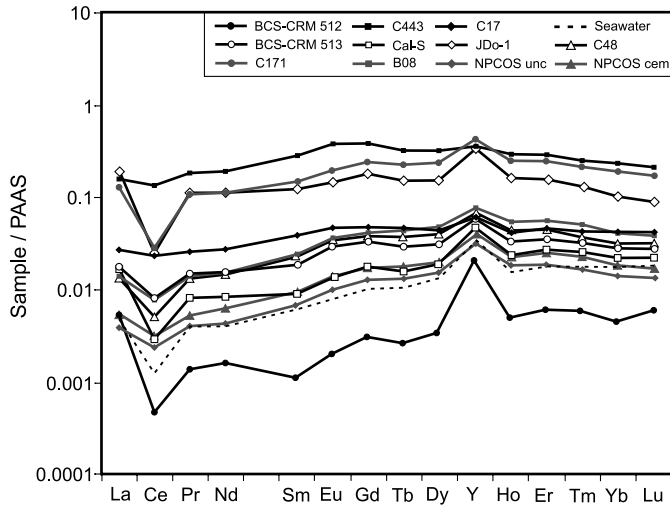
Fig. 4. Shale-normalised REE-Y patterns of modern-day (B08, NPCOS cem, NPCOS unc, C48) and Phanerozoic carbonates. Seawater is shown for comparison, although the concentrations have been multiplied by 10 000. Shale values from Taylor and McLennan (1985).
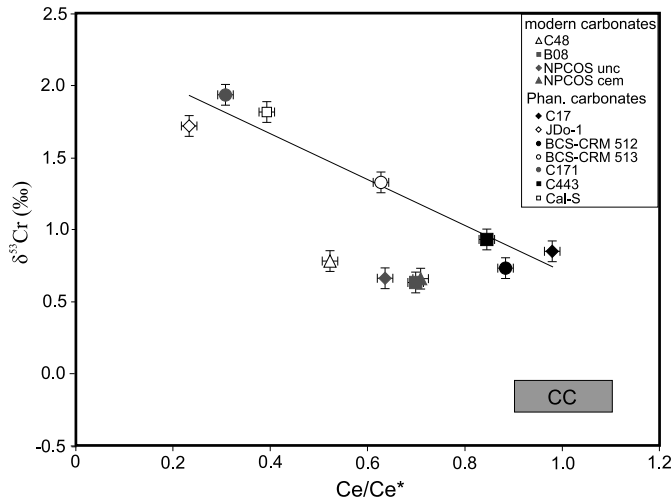

Fig. 5. δ^{53}Cr versus Ce/Ce* (Ce anomaly) for modern ooids and Phanerozoic carbonates. Solid line shows correlation between δ^{53}Cr and Ce/Ce* for Phanerozoic carbonates. CC = continental crust.

et al., 2008). The three Bahama ooid samples have similar δ^{53}Cr values, 0.65 ± 0.02‰, whereas the sample from Yucatan has a slightly higher value (δ^{53}Cr = 0.765‰). There is no correlation between δ^{53}Cr and Cr concentration for any of these ooid samples. By contrast, the Phanerozoic carbonates have δ^{53}Cr values ranging from 0.737 to 1.994‰, with the four oolitic limestones ranging from 0.848 to 1.939‰ and the carbonate standards (both calcites and dolomites), ranging from 0.737 to 1.994‰. Although δ^{53}Cr does not correlate with the Cr concentration or Eu anomaly, in the Phanerozoic carbonates, there is a strong negative correlation ($r^2 = 0.88$) between δ^{53}Cr and the Ce anomaly (Fig. 5).

5. Discussion

5.1. Accuracy and reproducibility of Cr isotope measurements

Assessment of the external reproducibility of our Cr isotope analyses of carbonates is described in detail in Bonnand et al. (2011). Briefly, the JDo-1 dolomite standard reference material was subject to the leaching and column chemistry procedures multiple times, and its Cr isotopic composition was determined. The aver-

age δ^{53}Cr value we obtain for this standard is 1.719 ± 0.059‰ (2σ, $n = 10$). The reproducibility of the δ^{53}Cr value is slightly worse than the external reproducibility of the NBS 979 solution (± 0.031‰, 2σ, $n = 147$), which might be due to small amounts of matrix in the Cr fraction, or the heterogeneity of JDo-1.

The accuracy of our isotope measurements was assessed by analysis of a synthetic carbonate sample, that consists of the NBS 979 standard doped with a carbonate matrix (Ca, Mg, Na, Fe, Ti and V) in the same proportions as found in natural carbonate samples. This solution was then spiked and treated as a sample. The Cr isotopic composition of this synthetic carbonate sample is indistinguishable from that of the NBS 979 standard, with δ^{53}Cr = 0.011 ± 0.008‰ (2σ, $n = 4$), given the external reproducibility of the analyses.

The external reproducibility of our Cr isotope measurements of seawater can be estimated from our analyses of the four Southampton Water samples, which are identical (Section 2.1). The average δ^{53}Cr value for Southampton Water seawater is 1.505 ± 0.007‰ (2σ, $n = 4$), which suggests that the reproducibility of our analyses is excellent, and better than it is for carbonates. However, it is important to note that the δ^{53}Cr value we obtain for a standard-spike mixture that has been through the column chemistry for seawater samples is slightly lower (-0.056‰) than expected (0‰). This may be because the Cr forms a complex with the 7M HCl before it passes through the anion exchange column, whereas our double spike calculation models mass fractionation in terms of elemental Cr. Furthermore, we need to consider the effect of correcting for the blank from the coprecipitation procedure, as well as the effect of assuming that our samples are fractionated by kinetic (rather than equilibrium) fractionation. In the case of the latter, the difference produces an inaccuracy of -0.009‰ per 1‰ difference in the true δ^{53}Cr (Schoenberg et al., 2008; Bonnand et al., 2011). Propagation of all of these uncertainties, together with the analytical uncertainty, indicates that the external reproducibility of our seawater Cr isotope analyses is ± 0.047‰ (2σ). This value is slightly better than we obtain for carbonates (± 0.059‰).

Although we have not assessed the accuracy of our seawater technique by analysis of synthetic seawater (or other methods, e.g. Takano et al., 2013), we have: (i) demonstrated that our pre-concentration procedure does not result in fractionation (Section 4.1), and (ii) fully corrected for the (small) isotope fractionation that occurs during sample purification that cannot be accommodated using our double spike technique. It is important to note that the pre-concentration procedure excludes the seawater matrix, with the exception of tiny quantities of residual salts that adhere to the Fe precipitate, such that the solution that passes through the Cr separation procedure contains significantly fewer impurities than the carbonate leachates. As described above, analysis of NBS 979 (i) with and (ii) without (carbonate) matrix produces identical δ^{53}Cr values. Thus, we are confident that the pre-concentration procedure, the chemical separation techniques, and the mass spectrometry procedures that we have adopted for the analysis of seawater, give reliable data for the Cr concentration and Cr isotopic composition of seawater. Crucially, the reproducibility of the replicate analyses of the samples from Southampton Water, is excellent.

5.2. Cr isotopic composition of seawater

The concentration of total Cr in the Southampton Water samples (1.85 nM) is within the range reported for other samples of coastal water from this area (3.39 ± 2.42 nM; Auger et al., 1999; Dolamore-Frank, 1984). Similarly, the concentration of Cr in the Argentine Basin samples is within the range reported for open ocean seawater (Table 1). The concentration–depth profile of Cr in the

Argentine Basin (Fig. 3) shows no evidence for depletion of Cr in surface waters, hence Cr appears to behave as a conservative, rather than a recycled, element at this location.

There has been considerable speculation about the Cr isotopic composition of seawater, with most workers assuming a heavy value relative to silicate Earth (Ellis et al., 2002; Izbicki et al., 2008). Our new isotope data confirm that seawater does indeed have a heavy δ^{53}Cr value for total Cr. As ∼90% of seawater Cr comes from rivers (Chester and Murphy, 1990), and oxidation of Cr(III) (the dominant Cr species in silicate rocks; Rai et al., 1989) does not appear to result in significant isotope fractionation (Zink et al., 2010), then this implies that fractionation of Cr isotopes must occur during the weathering process, and/or during transport to the oceans (Frei et al., 2009; Frei and Polat, 2013; Izbicki et al., 2008).

The δ^{53}Cr value that we have measured for coastal seawater (1.505‰) is close to that reported for groundwater recharge areas that are fully oxic and have low Cr concentrations (1.2 to 2.3‰; Izbicki et al., 2008). Assuming that river waters have similar δ^{53}Cr values (there are no direct measurements of the Cr isotopic composition of river waters to date), then a first-order observation is that the δ^{53}Cr value of coastal seawater is identical to the (local) riverine input. However, as the Cr concentration of seawater is not uniform throughout the world's oceans (Table 1), some variation in seawater δ^{53}Cr can be expected. Our samples from the Argentine Basin have lower δ^{53}Cr (and higher Cr) than Southampton Water, varying between 0.412 and 0.664‰. This difference may imply that the δ^{53}Cr value of the riverine input to this region is different, but there are a number of alternative explanations, which we explore below.

Firstly, the Argentine Basin is more likely to receive a higher proportion of its Cr from atmospheric sources. If addition of Cr from the dissolution of atmospheric dust is accompanied by significantly less isotope fractionation than terrestrial weathering processes then, to a first approximation, this could explain the lower δ^{53}Cr values. In this connection, the seawater sample taken from closest to the sea surface (∼30 m water depth) has the lowest δ^{53}Cr value (0.412‰). The average annual dust flux to the Argentine Basin is 0.02–0.05 mg cm^{-2} a^{-1} (Schulz et al., 2012). Assuming that dust has a Cr concentration equal to that of average continental crust (100 ppm), then 2–5 ng Cr cm^{-2} are delivered to the region each year. Approximately 10% of this Cr is soluble (Chester and Murphy, 1990), so, assuming that dissolution occurs in the upper 100 m of the water column, the input of dissolved Cr from the atmosphere is equivalent to an increase of <0.1 pM per year to the surface. Thus, the difference in seawater δ^{53}Cr between the Argentine Basin and Southampton Water sites is extremely unlikely to be caused by dissolution of aeolian material. In support of this, the Cr concentration in surface seawater is within error of all of the other samples from this depth profile. Secondly, the seawater samples from the Argentine Basin were not filtered. This means that the pre-concentration method will measure dissolved plus any particulate Cr, which is trapped in the iron precipitate and potentially released upon re-dissolution in 7M HCl. However, the concentration of suspended particulate material at this site, determined from measurements of light scattering from a sensor mounted on the CTD frame, is very low (∼ 10 g L^{-1}), as expected for an oligotrophic gyre (e.g. Connelly et al., 2006). This would make an insignificant contribution (<2%) to the total amount of Cr in the seawater sample. Thirdly, there is the possibility that Southampton Water receives anthropogenic inputs of Cr. It has been argued that effluent from Fawley oil refinery is responsible for high levels of hydrocarbons (e.g. Dicks and Levell, 1989), copper and possibly lead (Croudace and Cundy, 1995) in Southampton Water, and Cr is one of the most abundant heavy metals in oil waste (Adesodun and Mbagwu, 2008). However, in recent years,

improvements in effluent quality have led to a marked reduction in the level of contaminants (Cundy et al., 2003), and most Cr isotope studies indicate that anthropogenic sources have δ^{53}Cr values that are close to zero (e.g. Izbicki et al., 2008). The relatively low concentration of Cr in Southampton Water, as well as high seawater δ^{53}Cr, suggests that the anthropogenic contribution to the Cr inventory at this site is minimal.

Assuming that the global variation in the δ^{53}Cr value of river water is small, then the difference in seawater δ^{53}Cr that we observe between Southampton Water and the Argentine Basin is most likely due to chemical and possibly biological processes occurring in the estuarine mixing zone, and possibly further modification of the Cr and Cr isotopic signatures of coastal water during transport to the open ocean. While some studies (e.g. Cranston and Murray, 1980) indicate that most Cr is present as Cr(VI) in rivers and the estuarine environment, others suggest that Cr(III) is the dominant Cr species in uncontaminated river waters (e.g. Shuman and Dempsey, 1977; Pankow et al., 1977; Comber and Gardner, 2003) and coastal waters (Chuecas and Riley, 1966; Elderfield, 1970). Cr speciation was not determined in this study, but analyses of dissolved Cr species in the Beaulieu River estuary, which enters Southampton Water ∼5 km to the west of our sampling site, indicate that while the concentration of total Cr increases from ∼1.6 nM at low salinities ($S = 6.4$) to ∼5.7 nM at high salinity ($S = 31.5$), the proportion of Cr(VI) to Cr(III) also increases, from 11 to 68% (Dolamore-Frank, 1984). Removal of Cr, usually Cr(VI) (i.e. from the seawater end-member), in the low- to mid-salinity zone is reported for a number of estuaries (e.g. Cranston et al., 1975; Campbell and Yeats, 1984; Cranston and Murray, 1980), and has been attributed to adsorption onto suspended particulate material via reduction to Cr(III) by organic rich floccules (Cranston and Murray, 1980). More recent studies have shown that reduction of Cr(VI) to Cr(III) can also occur in the presence of Fe(II) (Kitchen et al., 2012) or via photoreduction (Kieber and Helz, 1992; Li et al., 2009). Crucially, reduction of Cr(VI) to Cr(III) in the estuarine environment will increase the δ^{53}Cr value of the remaining Cr. Reduction of ∼25% of Cr(VI) that has δ^{53}Cr = 0.53‰ (i.e. the average of our Argentine Basin seawater samples), to Cr(III), is sufficient to shift the δ^{53}Cr value of seawater by +1‰ (where α, the fractionation factor between the ^{53}Cr/^{52}Cr ratio of the Cr(III) and the Cr(VI), = 0.9967; Ellis et al., 2002), i.e. the value that we measure in Southampton Water.

5.3. Chromium isotope budget of seawater

Our new Cr isotope data for open ocean and coastal waters provides useful information for understanding the Cr and Cr isotope budget of seawater. To this end, the isotopic composition of the Cr inputs to seawater, δ^{53}Cr$_{IN}$, is given by:

$$\delta^{53}\text{Cr}_{IN} = \frac{f_{riv}\delta^{53}\text{Cr}_{riv} + f_{hyd}\delta^{53}\text{Cr}_{hyd} + f_{gw}\delta^{53}\text{Cr}_{gw}}{f_{riv} + f_{hyd} + f_{gw} + f_{dust} + f_{benth}}$$
$$+ \frac{f_{dust}\delta^{53}\text{Cr}_{dust} + f_{benth}\delta^{53}\text{Cr}_{benth}}{f_{riv} + f_{hyd} + f_{gw} + f_{dust} + f_{benth}} \qquad (2)$$

where f_{riv}, f_{hyd}, f_{gw}, f_{dust} and f_{benth} are the riverine, hydrothermal, groundwater, dust and benthic fluxes respectively. At steady state,

$$\delta^{53}\text{Cr}_{SW} = \delta^{53}\text{Cr}_{IN} - \Delta^{53}\text{Cr} \qquad (3)$$

where Δ^{53}Cr is the difference between the δ^{53}Cr value of the Cr outputs (δ^{53}Cr$_{OUT}$), and the δ^{53}Cr value of seawater (δ^{53}Cr$_{SW}$). If there is no fractionation of Cr isotopes during removal of Cr from seawater, then δ^{53}Cr$_{IN}$ = δ^{53}Cr$_{OUT}$. Estimates of the values of these variables are presented in Table 4. The riverine flux is calculated using the modern-day discharge rate reported by Vance

Table 4

Cr concentration, Cr isotopic composition and annual flux of Cr inputs to, and outputs from, the ocean used in seawater modelling (see text for details). The δ^{53}Cr value of global average seawater is assumed to be equal to the average value of seawater from the Argentine Basin.

Reservoir	Cr (nM)	Cr (μg g^{-1})	δ^{53}Cr (‰)	Δ^{53}Cr$_{OUT-SW}$ (‰)	Flux Cr (mol a^{-1})
Inputs					
Seawater	6	–	0.53	–	–
Rivers[*]	2–15	–	?	–	0.8–5.6×10^8
Hydrothermal	50	–	−0.15	–	1.5×10^5
Groundwater	6	–	1.2–4.0	–	0.1×10^8
Dust	–	100	−0.13	–	8.7×10^6
Benthic	–	2	0.6	–	6.8×10^6
Outputs					
Carbonate sink	–	2	–	0–0.3	–
Reduced sink	–	100	–	−5–−1.8	–

[*] See Table 1.

Table 5

Results of mass balance modelling, for variable Cr river fluxes and ground water (GW) δ^{53}Cr values. See text for details.

Scenario	River flux (mol a^{-1})	δ^{53}Cr$_{GW} = 1.2$‰	δ^{53}Cr$_{GW} = 4$‰
Fractionation between Cr outputs and seawater (Δ^{53}Cr), assuming δ^{53}Cr$_{RIVER} = 1.50$‰	0.8×10^8	Δ^{53}Cr $= 0.75$	Δ^{53}Cr $= 1.01$
	5.6×10^8	Δ^{53}Cr $= 0.93$	Δ^{53}Cr $= 0.98$
δ^{53}Cr value of the river flux, assuming Δ^{53}Cr $= 0$	0.8×10^8	δ^{53}Cr$_{RIVER} = 0.51$‰	δ^{53}Cr$_{RIVER} = 0.16$‰
	5.6×10^8	δ^{53}Cr$_{RIVER} = 0.53$‰	δ^{53}Cr$_{RIVER} = 0.48$‰
δ^{53}Cr value of the river flux, assuming Δ^{53}Cr $= 0.35$	0.8×10^8	δ^{53}Cr$_{RIVER} = 0.98$‰	δ^{53}Cr$_{RIVER} = 0.63$‰
	5.6×10^8	δ^{53}Cr$_{RIVER} = 0.89$‰	δ^{53}Cr$_{RIVER} = 0.84$‰
δ^{53}Cr value of the river flux, assuming Δ^{53}Cr $= -0.4$	0.8×10^8	δ^{53}Cr$_{RIVER} = -0.01$‰	δ^{53}Cr$_{RIVER} = -0.36$‰
	5.6×10^8	δ^{53}Cr$_{RIVER} = 0.11$‰	δ^{53}Cr$_{RIVER} = 0.06$‰

et al. (2009), assuming an upper limit of 15 nM Cr for river water. Although this value is lower than has been commonly used in the literature in the past (26 nM; Martin and Meybeck, 1979; Broecker and Peng, 1982; Jeandel and Minster, 1984), these studies include rivers that may contain significant anthropogenic Cr. Thus, we only consider measurements of riverine Cr for relatively pristine rivers, which are shown in Table 1. The ground water discharge is assumed to be 5% of the river discharge (Zektser et al., 2007), with a δ^{53}Cr value of between 1.2 and 4‰. Dust will have the same Cr concentration (100 ppm) and δ^{53}Cr value (−0.15‰) as the continental crust. The dust flux is taken from Boyle et al. (2005), which is similar to the value reported in an earlier study (Duce et al., 1991). The hydrothermal flux assumes a value based on geochemical mass balance and thermal considerations for the water discharge at ridge crests (Vance et al., 2009), and a Cr concentration extrapolated from analysis of low-temperature hydrothermal fluids (Sander and Koschinsky, 2000). Our measurements of the Cr isotope composition of hydrothermal fluids indicate that δ^{53}Cr is close to the mantle value, which is consistent with analyses of hydrothermally altered carbonates (Bonnand, 2011). However, it is important to note that because Cr is scavenged by Fe–Mn oxides in the hydrothermal plume, hydrothermal activity most likely results in an overall loss of Cr from seawater (German et al., 1991). The benthic flux of Cr from the diagenesis of carbonates is minor and is derived from analyses of Sr (Palmer and Edmond, 1992), assuming a Cr/Sr ratio of 0.002 with δ^{53}Cr equal to modern carbonates. Finally, Cr is thought to be removed from seawater by reduction processes (Murray, et al., 1983), and by incorporation into marine carbonates (this study). Isotope fractionation during uptake of Cr into carbonates appears to be minimal (Δ^{53}Cr $= 0$ to 0.35‰; see Section 5.4), but laboratory experiments suggest that reduction of Cr(VI) to Cr(III), which is insoluble and subsequently removed from seawater, appears to result in greater fractionation of Cr isotopes (Δ^{53}Cr $= -1.8$ to −5‰; Kitchen et al., 2012 and references therein), with preferential removal of light Cr.

However, the relative importance of these two removal processes is poorly quantified.

Although many of the Cr fluxes and δ^{53}Cr values shown in Table 4 are uncertain, we can make some first-order observations about the Cr isotope budget of the oceans, and the operation of the Cr cycle. To this end, we assume that the average δ^{53}Cr value of seawater is the same as the average value we measure in the Argentine Basin (0.53‰). Firstly, we assess the extent of fractionation between Cr in seawater and Cr outputs, assuming that the δ^{53}Cr value of the river flux is the same as the value for Southampton Water (1.50‰). Depending on the Cr concentration of river water (2–15 nM), and the δ^{53}Cr value of groundwater (1.2–4‰), then the average value of Δ^{53}Cr varies between 0.75 and 1.01 (Table 5). This value implies that heavy Cr isotopes are preferentially removed from seawater. This is inconsistent with removal of Cr via reduction, yet the calculated Δ^{53}Cr values are far higher than the difference that we observe between modern ooids and Argentine Basin seawater (0–0.35‰). Thus, it seems likely that the δ^{53}Cr value of seawater from Southampton Water is higher than the average δ^{53}Cr value of the global river flux. It is also possible, although unlikely, that the δ^{53}Cr value of seawater from the Argentine Basin is significantly lower than the global average. Secondly, we assess the potential δ^{53}Cr value of river water, assuming that carbonates are the main Cr sink, such that the value of Δ^{53}Cr lies within the range that we observe between modern ooids and Argentine Basin seawater (0–0.35‰). Again, depending on the Cr concentration of river water and the δ^{53}Cr value of groundwater, our model predicts that the δ^{53}Cr value of river water is in the range 0.16–0.98‰ (Table 5). This is lower than the value we measure in coastal seawater from Southampton Water (1.50‰), and also lower than the values reported for fully oxic groundwaters from recharge areas (1.2 to 2.3‰; Izbicki et al., 2008). Crucially, the model indicates that the δ^{53}Cr value of the river flux would be lower than the δ^{53}Cr value of continental rocks if Δ^{53}Cr is less than ∼−0.4‰ (Table 5). This implies that reduction of Cr(VI) to

Cr(III) is likely to be a relatively minor Cr sink, comprising $< \sim 20\%$ of the Cr output flux.

Thus, our modelling suggests that the δ^{53}Cr value of the continental flux that makes it to the open ocean is likely to be higher than the continental crust value (-0.26 to $-0.04‰$; Schoenberg et al., 2008), but it is probably not as high as the value we have measured in seawater from Southampton Water. This indicates that Cr isotopes must be fractionated, with the heavier isotopes going preferentially into solution, either during oxidative weathering, or during transport to the oceans. This behaviour is reminiscent of other transition metal stable isotope systems, including Zn (Vance et al., 2008) and Mo (Archer and Vance, 2008), as well as Li (e.g. Kisakurek et al., 2005). Nevertheless, it is important to note that the Cr and Cr isotope budget of the oceans cannot be fully resolved until a full inventory of all of the marine Cr sinks, and their fractionation factors, is derived and a representative global mean δ^{53}Cr value river water is determined by direct measurements.

5.4. Cr isotopic composition of modern carbonates

To test whether modern non-skeletal marine carbonates record the δ^{53}Cr value of seawater, we have determined the Cr isotopic composition of oolitic sands from Yucatan and the Bahama Banks. Trace element analyses indicate that these ooids are extremely pure and devoid of contaminant detrital material (Table 3). Molybdenum isotope studies of modern ooids and skeletal carbonates such as corals have demonstrated that ooids record seawater Mo isotopic compositions, whereas skeletal carbonates have significantly lower δ^{98}Mo values, which strongly suggests that Mo isotopes are fractionated by biological processes (Voegelin et al., 2009). Similarly, the Bahamian and Yucatan ooid samples have δ^{53}Cr $= 0.65$–$0.76‰$, which is within the range that we have measured for seawater in the Argentine Basin (0.412–0.664‰). Although we have not measured the Cr isotopic composition of seawater from Yucatan or the Bahama Banks, our data nevertheless indicate that any fractionation between seawater and (putatively) inorganically precipitated carbonate is likely to be small ($<0.2‰$). Moreover, the ooids have Cr concentrations of 2–4 $\mu g\,g^{-1}$, some 2–3×10^4 times greater than the concentration of Cr in modern seawater. The Cr concentrations in the ooids are consistent with other pure carbonates which have 1–7 $\mu g\,g^{-1}$ (Bonnand et al., 2011; Frei et al., 2011) and with experimental studies which indicate that significant Cr can be incorporated into the carbonate lattice as a CrO_4^{2-} ion (Tang et al., 2007). These data are consistent with Cr(VI) being the dominant species in seawater and therefore the isotopic composition of Cr is recorded by the ooids. Additionally, the Cr concentration in the carbonates should scale with the Cr(VI) content of seawater, such that carbonate Cr is lower if Cr(III) is the dominant species, or if Cr(VI) is reduced to Cr(III) and removed from seawater, such as might occur if the oceans have reduced levels of oxygen. Low Cr concentrations ($<1\ \mu g\,g^{-1}$) have been observed in Neoproterozoic carbonates, and are thought to reflect low oxygen and Cr(VI) levels in seawater at this time (Bonnand, 2011).

The δ^{53}Cr values of Phanerozoic carbonates (0.737–1.994‰) extend to higher values than we have measured in modern seawater which, providing our assertion that carbonates are likely to preserve the Cr isotopic composition of seawater is correct, implies that the Cr isotopic composition of seawater has either changed through time and/or varies locally.

5.5. Cr isotopes as a tracer of ocean redox

The REE contents of carbonates are a useful guide to interpreting their origin because REE concentrations and ratios vary with depth in seawater due to their short residence times and differential behaviour of the REE with atomic mass (Elderfield, 1988). The carbonates analysed in this study have REE patterns that reflect precipitation from seawater with a negative Ce anomaly, positive Y anomaly and high Er/Yb (Table 3 and Fig. 4), consistent with a shallow water environment (e.g. Zhang and Nozaki 1996, 1998). Phanerozoic carbonates define negative trends between δ^{53}Cr and Ce/Ce* (Fig. 5). Although we have only analyzed a limited number of Phanerozoic carbonates, the trends that we observe suggest that there may be a link between the redox chemistry of Cr and Ce. In oxic seawater Ce mainly exists as Ce(IV) which is taken up in preference to the trivalent rare earth elements onto the surface of manganese oxides, thus producing negative Ce anomalies (Elderfield, 1988; De Baar et al., 1988). Cr(VI) may also be scavenged by redox reactions that involve cycling of $Mn(II)O$–$Mn(IV)O_2$ (Ellis et al., 2002; Izbicki et al., 2008) (as well as ferromanganese (hydr)oxides, Frei et al., 2009), with reduction of seawater Cr(VI) to Cr(III), which is ultimately scavenged. This possibility is borne out by our Cr isotope data, since such a process will produce seawater with higher δ^{53}Cr and lower Ce/Ce*. Mass-balance of the modern and Phanerozoic carbonate data, using published isotope fractionation factors ($\alpha = 0.9967$, Ellis et al., 2002), indicates that, respectively, only 9% and 30% of seawater Cr(VI) is required to be reduced to produce the spread that we observe in δ^{53}Cr in the carbonates. This is within the range of Cr concentrations reported for modern-day seawater (Table 1). Furthermore, the data in Fig. 5 can also be used as an alternative method to estimate the Cr isotopic composition of river water. Surface seawater that is dominated by river inputs has a small negative Ce anomaly (Elderfield, 1988), and extrapolation of the data shown in Fig. 5 to a Ce/Ce* value of 0.9–1.0 would suggest that river water has a δ^{53}Cr value of 0.5–0.8‰, which is compatible with our mass balance calculations.

6. Conclusions

The chromium concentration and Cr isotopic composition of seawater has been determined for samples collected from open ocean (Argentine Basin) and coastal environments (Southampton Water). Concentrations of total Cr are 1.85 nM in Southampton Water, and between 5.80 and 6.50 nM in the Argentine Basin, comparable to previously published data for coastal and open ocean settings. There is little variation in the Cr concentration with depth in the Argentine Basin, and Cr does not vary as a function of nutrient and oxygen concentrations, suggesting that Cr behaves as a conservative element at this site. The δ^{53}Cr value of seawater from Southampton Water is 1.505‰, and in the Argentine Basin δ^{53}Cr values are between 0.412 and 0.664‰. These values are higher than average continental crust ($-0.124‰$). Modelling of the Cr and Cr isotope budget of the oceans indicates that Cr isotopes are likely to be fractionated during the weathering process and/or during transport to the oceans, and possibly as a result of redox reactions in the estuarine environment.

The Cr isotopic composition of non-skeletal marine carbonates overlaps with the range that we have measured in seawater, which suggests that there is likely to be limited isotopic fractionation during carbonate precipitation. If this is confirmed, then the Cr isotopic composition of ancient marine carbonates has the potential to reveal unique information about past variations in the δ^{53}Cr value of seawater. In order to fully interpret changes in seawater δ^{53}Cr, however, it is clear that we need to improve our understanding of the Cr and Cr isotope balance of the oceans, through analyses of seawater from a variety of settings (oxic, anoxic and euxinic), and better quantification of Cr sinks.

Acknowledgements

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2013.09.001.

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