

LIMNOLOGY and OCEANOGRAPHY: METHODS

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Limnol. Oceanogr.: Methods 18, 2020, 8–19
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Wiley Periodicals, Inc. on behalf of Association for the Sciences of
Limnology and Oceanography.
doi: 10.1002/lom3.10342

A Mg(OH)₂ coprecipitation method for determining chromium speciation and isotopic composition in seawater

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Abstract

Chromium (Cr) stable isotopes have emerged as a powerful tool for tracking environmental redox transformations. This is because Cr isotopes are fractionated during redox reactions between Cr(III) and Cr(VI). In order to fully exploit the information recorded within Cr isotope compositions, we must be able to track changes in Cr speciation throughout the environment and, in particular, the changes in speciation between input to the ocean and eventual deposition in sediments. We must also be able to access the isotope compositions of each Cr species, rather than only total dissolved Cr. We have thus developed a magnesium hydroxide coprecipitation method that meets these objectives. This method achieves complete recovery and has a typical precision on concentration measurements of $\pm 8\%$ (1σ). It was tested using seawater collected from Saanich Inlet, a persistently anoxic fjord on the Pacific coast of Canada. Chromium speciation profiles and proof-of-concept isotope ratio measurements on selected samples indicate that isotopically lighter Cr(III) can be isolated from coexisting isotopically heavier Cr(VI), effectively resolving species-specific Cr isotope compositions. While the oxygenated surface waters of Saanich Inlet follow the generally observed correlation between seawater Cr concentration and its isotopic composition, seawater from anoxic depths diverges from this array, indicating that different processes are responsible for setting the isotope composition of these deeper waters. Broader application of Mg(OH)₂ coprecipitation has strong potential to yield new insights into the fractionation of Cr isotopes in the oceans and the pathways that ultimately set the Cr isotopic composition of marine sediments and sedimentary archives.

Chromium is a redox sensitive element observed in two natural valence states at Earth's surface, Cr(III) and Cr(VI). Most Cr in Earth's crust is hosted as Cr(III) in minerals (Alloway 1995). The formation of Cr(VI) from mineral Cr(III) in the environment is generally catalyzed by manganese oxides (Oze et al. 2007), which themselves form due to oxidation of Mn(II) by oxygen (Tipping 1984). Redox reactions involving Cr can induce isotope fractionation, and ultimately lead to the formation of isotopically heavy aqueous Cr(VI) (e.g., Ellis et al. 2002; Schauble et al. 2004; Zink et al. 2010). Subsequent reduction

and removal of this Cr(VI) can leave distinct isotope signals in rocks providing a tracer that records Cr redox cycling, and by extension the presence of oxygen in the geologic past. It was originally proposed (Frei et al. 2009) that Cr isotopes could be used as a paleo-oxygen barometer, based on evidence that Cr isotope fractionation is associated with redox reactions in Earth surface environments that cause Cr(VI)–Cr(III) interconversions, and the fact that the crustal sources of Cr have a very uniform Cr isotope composition. Accordingly, variation in Cr isotopic composition beyond these crustal inventory values could be attributed to oxidative weathering (Frei et al. 2009; Crowe et al. 2013), whereas the absence of Cr isotope fractionation might imply low oxygen weathering (e.g., Planavsky et al. 2014). Viewed through the lens of this framework, previous studies of the Cr isotopic record likely overlooked more nuanced information regarding the biogeochemical cycling of Cr. For example, there is redox cycling of Cr in rivers through to the oceans (Frei et al. 2014; Scheiderich et al. 2015; D'Arcy

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et al. 2016; Paulukat et al. 2016; Goring-Harford et al. 2018; Sun et al. 2019) and this can affect the isotopic signal of oxidative weathering of the continents, with potential to cause local-scale variability in Cr isotope compositions in marine sedimentary rocks that are not directly related to the redox signal of global-scale continental weathering (e.g., Holmden et al. 2016).

Motivated by potential for a more nuanced interpretive framework for the application of Cr isotopes to a range of research questions from proxy-based reconstructions of paleoredox conditions to modern elemental cycling in the oceans, we turned our attention to the problem of making Cr isotope ratio measurements on individual Cr(III) and Cr(VI) species in seawater. There exists a wide range of approaches to determining Cr speciation in seawater, and these leverage a suite of analytical techniques that can be broadly classified as: spectrophotometric, electrochemical, resin-based, and coprecipitation. Cr(VI) can be determined spectrophotometrically by selective reaction with diphenylcarbazide (Allen 1958); Cr(III) can also be determined as the difference between total Cr and Cr(VI) following Cr(III) oxidation to Cr(VI) and then treatment with diphenylcarbazide (American Public Health Association 1971). The detection limits with standard equipment (generally μM range), however, are often too high to measure Cr species in seawater, where total Cr concentrations range from 2 to 10 nM with variable Cr(III):Cr(VI) ratios (Elderfield 1970; Cranston and Murray 1978; Pettine et al. 1992; Yao and Byrne 1999). Electrochemical methods such as catalytic adsorptive stripping voltammetry have been used to determine Cr speciation and in addition to discriminating between redox states, also differentiate between organically bound forms of Cr (Sander and Koschinsky 2000). Neither spectrophotometry nor electrochemistry provide a physical separation of Cr species thus leaving subsequent species-specific determinations of Cr isotope ratios by mass spectrometry intractable.

Resin-based methods and coprecipitation reactions are more suited to the task at hand, typically taking advantage of species-selective chemical reactions to separate and concentrate Cr species, overcoming low Cr concentrations, the relatively high salt content of seawater, and dissolved organic carbon (DOC) concentrations that render the precise determination of Cr speciation in seawater a challenge. At the same time, these approaches achieve the physical separation of Cr species needed for isotope ratio analyses. Resin-based methods employ either ion-exchange chromatography or solid-phase extraction. For example, cation- and anion-exchange resins can be used to selectively bind and concentrate Cr(III) or Cr(VI) (e.g., Pankow et al. 1977). Solid-phase extraction has been achieved using alumina, pumice, and iminodiacetate chelating resins (e.g., Uluçinar and Onar 2005; Sumida et al. 2006). Use of resins and solid-phase extractions, however, may be undesirable for application to Cr isotope measurements since several liters of seawater need to be passed through columns to recover sufficient Cr, and if recovery from the column is not 100%, fractionation of Cr isotopes can occur due to successive sorption–desorption reactions

(Ellis et al. 2004). Coprecipitation reactions, on the other hand, achieve both concentration and selective separation of Cr species without repeated sorption–desorption reactions and are readily scaled to large volumes. Coprecipitation methods usually employ two treatments: first, a precipitation step that is specific to particle reactive Cr(III), and a separate precipitation of total Cr (Cr(III) + Cr(VI)) following Cr(VI) reduction to Cr(III). The particles from each treatment can be physically separated from the remaining seawater matrix.

Iron-based coprecipitation is widely used in Cr speciation measurements and to determine the isotope ratios of total dissolved Cr (e.g., Cranston and Murray 1978; Jeandel and Minster 1987; Kaczynski and Kieber 1993; Abu-Saba and Flegal 1995; Connelly et al. 2006; Scheiderich et al. 2015), and more recently in combination with resin-based extractions to yield species-specific Cr isotope compositions (Wang et al. 2019). It may, however, suffer from variable Cr(III)-organic complex recovery affecting both Cr(III) and Cr(tot) fractions (Walsh and O'Halloran 1996). Variations on coprecipitation approaches have been developed to better handle the presence of organic compounds. For example, Nakayama et al. (1981) developed a coprecipitation method using hydrated bismuth oxide, enabling collection of both Cr(III) and Cr(VI) without requiring a reduction step. They then employed a decomposition step with ammonium persulfate to release inorganic Cr(III) and Cr(VI) into solution, which could then be coprecipitated with bismuth oxide. Magnesium hydroxide ($\text{Mg}(\text{OH})_2$) coprecipitation also effectively recovers Cr(III) ($101.6 \pm 1.8\%$, 1SD), from synthetic ocean water (SOW, prepared as per Price et al. 1989), while remaining selective for Cr(III) with $<5\%$ of Cr(VI) recovered from solutions with both species present (Semeniuk et al. 2016). The capacity of $\text{Mg}(\text{OH})_2$ coprecipitates to recover organically bound Cr has not previously been investigated. It has, however, been applied to large volume (1 L) samples for Cr isotope ratio determinations of total Cr, with the addition of a Cr isotope double spike to correct for any loss of Cr (Moos and Boyle 2018). The use of a Cr isotope double spike enables Cr isotope information on the total Cr pool to be recovered from a few of the methods above, regardless of recovery. $\text{Mg}(\text{OH})_2$, iron, and bismuth oxide coprecipitation approaches thus appear to hold the greatest promise for resolving the Cr isotope composition of Cr(III) and Cr(VI) in seawater.

We therefore compared the $\text{Mg}(\text{OH})_2$, bismuth oxide, and iron coprecipitation techniques for the recovery of Cr(III) and Cr(VI), and determination of their respective isotopic compositions in seawater. Our tests showed that the recovery and specificity achieved using $\text{Mg}(\text{OH})_2$ was superior to both iron and bismuth, and we thus performed a series of experiments with the $\text{Mg}(\text{OH})_2$ method to ensure optimal Cr recovery from natural seawater, and to evaluate the recovery of organically-bound Cr. We then conducted proof-of-concept experiments to determine the isotopic composition of Cr(III) and Cr(VI) in seawater from Saanich Inlet, a persistently anoxic fjord on the east coast of Vancouver Island.

Materials and procedures

Reagents

The majority of chemicals used in this study were reagent grade, including ammonium hydroxide (NH_4OH ; ACS) and hydrogen peroxide (H_2O_2 ; 30%, Sigma Aldrich) used for precipitations, magnesium chloride hexahydrate ($\text{MgCl}_2 \times 6\text{H}_2\text{O}$; Sigma Aldrich) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$; Sigma Aldrich) used for recovery experiments, and nitrilotriacetic acid (NTA; $\text{N}(\text{CH}_2\text{CO}_2\text{H})_3$), desferrioxamine B (DFB; $\text{C}_{25}\text{H}_{48}\text{N}_6\text{O}_8$), ethylenediaminetetraacetic acid (EDTA; $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$), and citrate (from sodium citrate dihydrate, $\text{HOC}(\text{COONa})(\text{CH}_2\text{COONa})_2 \cdot 2\text{H}_2\text{O}$; all from Sigma Aldrich), used for organically bound Cr recovery experiments. All reagent dilutions were made using 18 Ω MQ water (Millipore). Hydrochloric (HCl) and nitric (HNO_3) acids were ultrapure and quartz-distilled. High-purity, concentrated stock solutions of 1000 ppm Cr(III) (Delta Scientific) and Sc (Inorganic Ventures) were diluted and used for recovery experiments and as an ICP-MS internal standard, respectively. Ultrapure ammonium hydroxide and ferrous ammonium sulfate were used during preparation for Cr isotope ratio determinations.

Mg(OH)₂ coprecipitation methodology

Mg(OH)₂ coprecipitation collects Cr(III) from solution after the addition of a base, in this case ammonium hydroxide, which causes Mg(OH)₂ to precipitate out of solution, removing Cr from in the process. The Cr can then be collected as a precipitate and dissolved in dilute acid for Cr determination, or further purified using cation and anion exchange resins for isotope ratio determination. Optimal coprecipitation parameters were identified and tested, and the recommended protocol is detailed later. We opted to use two separate samples: a 14 mL sample for Cr species determination and large 2–4 L samples for species-specific Cr isotope ratio determination. If all samples are intended for isotope ratio determination, this twofold sampling and analysis can be negated by double-spiking samples before precipitation, allowing both Cr species concentrations and isotopic compositions to be determined from the same sample. While less efficient, we opted for the two-sample approach so we could rapidly test and analyze larger numbers of small volume samples for species concentrations alone.

In order to measure Cr speciation with the Mg(OH)₂ coprecipitation, we use two separate steps. In the first, a coprecipitation of naturally occurring seawater Mg was directly induced by the addition of concentrated (14.8 M) ammonium hydroxide (NH_4OH) to collect Cr(III). In the second, a reduction step was used to convert all Cr(VI) to Cr(III), followed by coprecipitation induced by NH_4OH to collect total Cr. Our choice of concentrated NH_4OH addition volumes and reaction times was guided by prior use of Mg(OH)₂ coprecipitation for the collection of diverse metals (Wu and Boyle 1997, 1998; Saito and Schneider 2006) and limited to the salinity range 29–35 ppt (details in supplementary material). We, however, also conducted additional

experiments to determine the optimal pellet size, the range in [Mg] and salinity that supports full recovery of Cr, the stability of Cr species in unfiltered seawater samples over 12 h, and the precipitation mechanism, which are further described in the supplementary material.

To determine Cr(III) concentrations, Cr(III) was recovered from a 14 mL filtered seawater sample by the addition of 35 μL NH_4OH . The sample was allowed to react for 3 min, inverted, and allowed to sit for an additional 3 min, then centrifuged (4500 $\times g$) to a pellet, and the supernatant decanted (Wu and Boyle 1998). The pellet was then centrifuged and decanted for a second time to remove as much remaining seawater as possible before dissolving the final pellet in 1% HNO_3 . To determine Cr(tot) concentration, Cr(VI) was first reduced by acidifying a 14 mL sample to pH 1.8 with HNO_3 , and treating with hydrogen peroxide at a final H_2O_2 concentration of 100 μM . The sample was allowed to react for at least 3 h (Pettine et al. 2002) before coprecipitation was induced by adding 100 μL NH_4OH . The larger volume of NH_4OH , compared to the coprecipitation of Cr(III) alone, was required to offset the acid added to facilitate reduction of Cr(VI). Details regarding the optimization of the reaction time for the reduction step are provided in the Supplemental Information. Samples were centrifuged to generate a pellet as described earlier. Pellets were then dissolved in 3 mL of 1% HNO_3 and Cr determined by ICP-MS. To determine Cr isotope ratios, sample volumes were scaled up to 2.0–4.0 L in order to recover at least 100 ng of Cr per sample. Reagent volumes were thus scaled up proportionally.

Measurement of Cr(III) and Cr(VI) concentrations

Mg(OH)₂ pellets were dissolved in 1% HNO_3 and spiked with Sc to attain a concentration of 100 ppb before Cr determination on either a NexION 300D (PerkinElmer) or an Agilent 7700 series quadrupole inductively coupled plasma-mass spectrometer (ICP-MS). Blanks (1% HNO_3 + 100 ppb Sc) were run after every five samples. A certified seawater standard, North Atlantic Standard Seawater 6 (NASS-6; NRC) and our in-house seawater standard were coprecipitated following the same protocol as seawater samples and run during each analytical session. Counts on mass 52 were normalized to the internal standard (Sc) to correct for matrix effects and drift. As an additional precaution, a ^{50}Cr isotope spike was added to seawater before coprecipitation in order to correct for any sample loss during sample processing. Isotope dilution calculations were not applied during any tests of method recovery, but were used in the calculation of Cr concentrations from the January 2018 speciation profile.

Cr isotope ratio determinations

The Mg(OH)₂ pellets from the large volume samples were dissolved in 5% HNO_3 to a volume of ~45 mL in 50 mL centrifuge tubes. A weighed aliquot of ^{50}Cr - ^{54}Cr double-spike was added to each sample to correct for any isotopic fractionation

that might occur during purification on the ion exchange columns, as well as during isotope ratio measurement in the mass spectrometer. The double-spike was allowed to equilibrate with samples for >24 h. The preparation and composition of the double spike used in this study is described in Scheiderich et al. (2015). Cr(III) was separated from the Mg matrix by coprecipitation with Fe in order to use a well-developed column chemistry protocol (Yamakawa et al. 2009) rather than developing a protocol for Mg(OH)₂ pellets de novo. Briefly, each dissolved Mg(OH)₂ pellet received 3.0 mL of a 0.01 M (NH₄)₂(SO₄)₂Fe solution. The pH was adjusted to 8.2 using ultrapure ammonium hydroxide, at which point flocculates of Fe(II)-Fe(III) hydroxide formed. The resulting coprecipitate bearing solutions were agitated on a shaker table for an hour. The dissolved oxygen in the sample converted any Fe(II) present to Fe(III). The Fe coprecipitates were centrifuged and the supernatant decanted. The Fe pellet containing the Cr(III) was redissolved in dilute HCl and the coprecipitation was repeated to ensure effective separation of Mg prior to further purification using anion and cation exchange columns. After the second Fe coprecipitation, the sample was dissolved in 7 M HCl and loaded onto a column containing Bio-Rad AG[®]1-X8, 200–400 mesh anion exchange resin in the chloride form to separate anionic Fe(III), which strongly adheres to the resin, from cationic Cr(III), which passes through the column for collection. The solution was then dried down and brought up in dilute HCl and passed through a column containing cation exchange resin (Bio-Rad AG[®]50 W-X8, 100–200 mesh) to remove Na, Mg, and other trace cations, including any residual Fe that may have passed through the anion column. Cr was then loaded onto single Re filaments in preparation for mass spectrometry using a boric acid silica gel mixture. Cr isotope ratios were determined using a thermal ionization mass spectrometer (a Thermo Elemental Triton instrument) at the University of Saskatchewan using a peak-hopping procedure described in Scheiderich et al. (2015). Instrumental mass bias corrections were performed offline, and small amounts of ⁵²Cr and ⁵³Cr contributed by the double-spike were numerically unmixed from the sample ⁵³Cr/⁵²Cr ratio. The sample ⁵³Cr/⁵²Cr ratios are reported in delta (δ) notation: $\delta^{53}\text{Cr} = ((^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}} / (^{53}\text{Cr}/^{52}\text{Cr})_{\text{standard}} - 1) * 1000$; relative to the standard SRM 979 (NIST). The external precision of seawater ⁵³Cr/⁵²Cr using a similar technique in the same laboratory published by Scheiderich et al. (2015) was ±0.06‰ (2σ), utilizing sample loads of ~100 ng or larger. However, due to the low Cr content of some of the samples measured in this study (50–160 ng Cr), this level of precision was not achieved for all measurements.

Recovery experiment methods

A comparison of recovery and specificity of other coprecipitation methods (Fe and Bi coprecipitation; Cranston and Murray 1978; Nakayama et al. 1981) was tested with the radioisotope ⁵¹Cr (t_{1/2} = 27.7 d; sodium chromate in saline solution, pH 8; specific activity ~500 TBq mol⁻¹; Perkin Elmer). Fe

and Bi precipitates were allowed to react with 5 nM of either ⁵¹Cr (VI) or ⁵¹Cr(III) added to 40 mL of SOW. At different time intervals, 5 mL of the labeled SOW was filtered onto 0.22 μm pore size (25 mm diameter) polycarbonate filters (AMD). Total ⁵¹Cr activity in the SOW was measured to monitor loss of ⁵¹Cr to the falcon tube walls. Seawater samples, Mg(OH)₂ pellets, and filters were mixed with Scintisafe 50% scintillation cocktail (Fisher) for 24 h before the ⁵¹Cr activity was determined using a Beckman LS65005514 scintillation counter with an internal ⁵¹Cr quench curve. ⁵¹Cr extraction yields were calculated by dividing the Cr removed by the total added ⁵¹Cr activity.

To determine whether the Mg(OH)₂ coprecipitation captures organically bound Cr, Cr concentrations measured before and after UV digestion were compared. Seawater was digested in acid cleaned, quartz UV digestion tubes with PTFE closures. UV irradiation was achieved using a high-pressure mercury vapor lamp, peaking at ~250 nm, with a power output of 125 W. Exposure times of 45 and 130 min were tested, but exposure was limited to 45 min intervals to prevent sample boiling (Achterberg and Van Den Berg 1994).

Seawater sampling

Seawater samples were collected from Station S3 (123 30.300 W, 48 35.500 N; Torres-Beltrán et al. 2017) in Saanich Inlet, British Columbia, with 8 or 12 L Niskin bottles at depths ranging from 10 to 200 m. Saanich Inlet is a persistently anoxic basin and through most of the year, depths from 120 to 200 m are both anoxic and sulfidic. Volumes of 4 to 8 L were collected in January 2018 to measure Cr(III) and Cr(VI) concentration profiles. Cr(III) and Cr(tot) isotopic compositions were determined on samples from 90, 135, and 200 m depth, with additional Cr(tot) isotopic compositions at 10 and 40 m depth. Samples were also collected in May 2018 following the same procedure; the analysis of these samples is not discussed in detail, except to constrain potential sampling blanks discussed later. Samples were collected directly into 4 L cubitainers, which were rinsed three times with seawater before filling. Back in the laboratory, samples were filtered into new, rinsed (with filtered seawater) cubitainers through a 0.3 μm pore size glass fiber filter (GF-75, 47 mm diameter, Advantec) within 12 h of collection. Subsamples (14 mL for Cr speciation, 2–4 L for isotopic measurements) were treated by magnesium hydroxide coprecipitation within 24 h of collection. In March 2016 a 10 L sample was acquired from 40 m depth for an in-house seawater standard in order to track long term accuracy and precision of Cr(tot) concentrations; it was filtered in the lab in the same manner as the other samples and then acidified to pH 1.8 with HNO₃.

Ancillary seawater analyses

Supporting geochemical samples were collected on each cruise to provide data for dissolved oxygen (O₂), nitrate (NO₃⁻), and sulfide (H₂S, HS⁻, and S²⁻), as described by Torres-Beltrán et al. (2017). Briefly, dissolved oxygen concentrations were

determined with a Sea-Bird SBE 43 dissolved O₂ sensor attached to a Sea-Bird SBE 25 CTD (conductivity, temperature, and depth). Oxygen data were calibrated using discrete Winkler titrations on depths spanning the water column. Seawater was filtered through a 0.2 µm acrodisc (Pall) and analyzed by the spectrophotometric method of García-Robledo et al. (2014) for nitrate determination. Seawater was preserved with 20% zinc acetate immediately upon sampling and stored at -20°C until sulfide was determined by the spectrophotometric method of Cline (1969).

Assessment and discussion

Chromium blanks

Chromium is a trace element in seawater, and thus methods designed to determine Cr concentrations, speciation and isotopic composition, need to carefully consider reagent contributions to method blanks. As described earlier, the Mg(OH)₂ method uses two reagents, NH₄OH and H₂O₂, with Cr concentrations of 0.1 nM and 0.8 nM in each reagent, respectively. These Cr concentrations in the reagents result in a Cr contribution of 0.001 nM for Cr(tot) and 0.0003 nM for Cr(III) treatment for a 14 mL sample. Given that Cr concentrations in seawater range from 2 to 10 nM (Cranston and Murray 1978), the reagents chosen here made a maximum contribution of 0.15% of the measured values, which is negligible.

Plasticware is sometimes seen as a source of contamination for a number of trace metals. As our samples were collected and subsequently stored in different plastic containers, it was important that we consider the potential contribution of Cr from these containers. As noted earlier, seawater was collected into acid cleaned cubitainers, the seawater was then filtered and portioned into separated speciation and isotope samples. Speciation samples were aliquoted into 15 mL centrifuge tubes that were not acid cleaned. Whenever samples were collected and aliquoted into centrifuge tubes, 3–5 replicates of NASS-6 were prepared at the same time. Irrespective of storage time (2 weeks to a year), [Cr] determined in NASS-6 were within the certified range, suggesting that any Cr leached from the centrifuge tube was negligible relative to the [Cr] concentration in NASS-6, and given that NASS-6 has [Cr] similar to our samples, we also conclude negligible contributions of leaching from plasticware to seawater measurements.

Collection itself may also contribute Cr to seawater samples. Without Cr-free seawater to run through the sampling process, we cannot define a precise sampling blank. However, we can constrain the potential Cr contribution from sampling with our lowest measured concentrations of Cr(III) and Cr(VI). The lowest [Cr(III)] was measured in January 2018 (at 40 m), presented in detail later, at 0.09 ± 0.03 nM. The [Cr(VI)] concentration, determined as the [Cr(tot)] - [Cr(III)] at a given depth, was determined to be within error of 0 nM at seven discrete depths (130–185 m) sampled in May 2018, with the exact concentration and error varying by depth. These results

constrain the maximum potential Cr sampling blank to be 0.09 ± 0.03 nM of Cr(III), and not different than 0 nM for Cr(VI).

Recovery of Cr

Mg(OH)₂ coprecipitation exhibits high selectivity for Cr(III) in the presence of Cr(VI), and achieves full recovery of Cr(III) from SOW (Semeniuk et al. 2016). Before moving forward with the Mg(OH)₂, we compared its selectivity and recovery to other modes of coprecipitation (Fe and Bi coprecipitation; Cranston and Murray 1978; Nakayama et al. 1981) using radioactive ⁵¹Cr. While prior studies detailing these methods report near complete recovery, our tests yield comparably lower recovery. The results for Fe and Bi coprecipitation are given for comparison to coprecipitation with Mg(OH)₂ (Semeniuk et al. 2016) in Table 1. Both the Fe and Bi methods exhibit specificity toward Cr(III), but only achieve ~75% recovery with greater variability than Mg(OH)₂. A comparison of remaining activity, and therefore remaining dissolved Cr, in the control, Fe, and Bi coprecipitation experiments is shown in Table S1 in the supplementary material.

In addition to the radiotracer experiments, we also tested recovery using standard additions of Cr(III) made directly to seawater and to the Mg(OH)₂ pellet solutions. If recovery was less than 100%, the measurements of the standard additions made directly to seawater would yield lower concentrations than those made to the pellet solutions. Agreement between both sets of measurements (slope of 1.02 ± 0.06 , data not shown; Fig. 1) indicates complete recovery of inorganic Cr(III). This agreement also implies lack of matrix effects during the determination of [Cr] that could have arisen from the relatively high Mg concentrations in the final pellet solution. If there were matrix effects, the standard additions to seawater and pellet solution would yield slopes less than 1 vs. acid standards. Measured sensitivities in both Mg-rich and Mg-free solutions were the same within the 99% confidence interval and thus demonstrate limited matrix effects under these conditions. The Mg(OH)₂ coprecipitation method thus offers specificity and more complete recovery as well as more reproducible results than either the Fe or Bi methods.

Precision, accuracy, and detection limit

Given the apparently greater recovery of Cr using Mg(OH)₂ coprecipitation, we further tested its accuracy, precision, and limits of detection. Chromium recovery in natural seawater was verified by the measurement of a certified reference material (CRM), NASS-6 (NRC), during each analytical session. NASS-6 is an acidified (2% HNO₃) seawater standard; due to the acidification, all Cr was expected to be Cr(III) (Rai et al. 1989) and the CRM was treated with the same volume of NH₄OH as the Cr(tot) protocol as both had the same acid concentrations. Using the Mg(OH)₂ method, we determined Cr(tot) concentrations in NASS-6 of $2.30 \text{ nM} \pm 0.18 \text{ nM}$ (1σ ; $n = 25$), within error of the certified concentrations ($2.28 \text{ nM} \pm 0.15 \text{ nM}$, 1σ).

Table 1. Recovery of Cr through of $\text{Mg}(\text{OH})_2$, Fe, and Bi speciation methods using radiolabelled Cr. Treatment refers to the method used to collect Cr, and time is the reaction time between treating the sample and pelleting the solution. Method blanks refer to filters exposed to the same ^{51}Cr solution and rinsed as samples, but without any coprecipitate.

Oxidation state	Treatment	Time	% Recovery (minus method blanks)		References
			Mean	1 s	
Cr(VI)	$\text{Mg}(\text{OH})_2$	1 min	5.0	1.3	Semeniuk et al. (2016)
		3 min	4.9	1.0	
		5 min	4.9	1.1	
Cr(III)	$\text{Mg}(\text{OH})_2$	1 min	99.8	1.8	
		3 min	101.6	1.8	
		5 min	103.1	2.4	
Cr(VI)	$\text{Fe}(\text{OH})_3$	15 min	2.8	1.1	This study
		60 min	1.9	1.0	
		3 h	3.3	0.7	
Cr(III)	$\text{Fe}(\text{OH})_3$	15 min	54.8	5.0	
		60 min	58.8	3.7	
		3 h	74.1	4.0	
Cr(VI)	Bi	3 h	8.1	1.5	This study
Cr(III)	Bi	3 h	77.5	6.2	

Our in-house seawater standard was also coprecipitated and run during each analytical session alongside NASS-6 in order to calibrate it for use as a long-term internal reference material. An average Cr(tot) concentration of $2.31 \text{ nM} \pm 0.24 \text{ nM}$ (1σ) was determined over 5 months of analysis ($n = 34$). All samples were run in triplicate and the average precision between triplicate samples was $\pm 8\%$ (1σ) (determined as the average of 40 RSD values).

With a typical concentration factor of about 5 for Cr determination in 14 mL samples, $\text{Mg}(\text{OH})_2$ coprecipitation enables detection and quantification of either Cr(III) or Cr(tot) in seawater at five times less than the detection limit of the instrument; with a typical instrumental detection limit of $\sim 0.2 \text{ nM}$ (0.01 ppb; calculated as $3*1\sigma$ of all measured blanks), this translates to a Cr detection limit of 0.04 nM . This is sufficiently low to measure Cr speciation in seawater with lower than average (2–10 nM; Cranston and Murray 1978) Cr total concentrations.

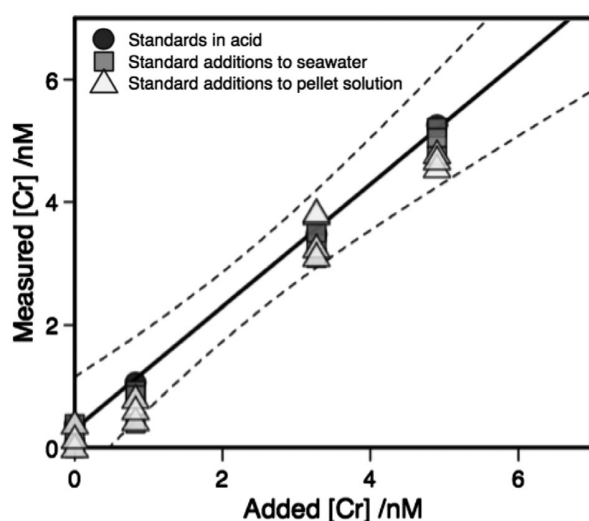


Fig. 1. The results of Cr standard additions to seawater (squares) and to pellet solutions (triangles) are plotted against an external calibration of Cr standards in 1% HNO_3 (circles). The solid black line shows the slope of the external calibration, with a 99% confidence belt shown as a dashed line. The slopes are as follows: Standards in acid = 1.00, standard additions to seawater = 1.00, and standard additions to pellet solutions = 0.98.

Recovery of organically bound Cr

We also tested the capacity of $\text{Mg}(\text{OH})_2$ coprecipitation to recover organically bound Cr, which is a category of Cr species often neglected in Cr speciation studies. To evaluate recovery of organically bound Cr, we conducted two experiments; first, we oxidized 14 mL seawater samples by UV digestion (Achterberg and Van Den Berg 1994) in order to release organically bound Cr. Second, we added model ligands to seawater to bind free Cr. The results of these two experiments were compared to Cr speciation determined in unmodified seawater to test for differences in Cr concentrations that would signify lack of organic-Cr recovery.

Samples from 10 m and 200 m depth were exposed to UV light for both 45 and 130 min to see if there was a change in recovered Cr, as the expected result of Cr release from organic complexes after UV exposure, relative to seawater without UV exposure (Sander and Koschinsky 2000; Achterberg et al. 2001). If the organically bound Cr(III) was inert to $\text{Mg}(\text{OH})_2$ coprecipitation, then release of Cr(III) due to UV radiation would cause an increase in measured Cr(tot). For reference, Saanich Inlet has DOC concentrations that range from 0.008

to 0.8 mM (Hobson 1983; Maciejewska and Pempkowiak 2014). A previous study (Achterberg et al. 2001) showed that <1% of 1.6 mM added DOC remained after 2 h of UV irradiation, indicating that 130 min exposure should completely oxidize DOC in seawater from Saanich Inlet, and effectively liberate Cr bound to UV labile DOC that may have been present. UV oxidation had no significant effect on the Cr(tot) concentrations determined at the 95% confidence interval (Table 2), regardless of sample depth or UV exposure time. This suggests that Mg(OH)₂ captures both inorganic and UV labile organically bound Cr(III), if present.

Recovery of organically bound Cr by Mg(OH)₂ coprecipitation was also tested through the amendment of seawater with four different model ligands (NTA, DFB, EDTA, and citrate) representing a variety of binding strengths to Cr. Binding strengths for Cr(III) complexes are not precisely known, but are estimated to follow the order: citrate < NTA < EDTA < DFB, with citrate representing a relatively weak chelating ligand and DFB (a siderophore) a very strong one (see Supplemental Information for further discussion) (Yamazaki et al. 1980; Silva et al. 2009; Begum et al. 2012; Duckworth et al. 2014; Resende et al. 2014). Again, if organically bound Cr was inert to Mg(OH)₂ coprecipitation, we would expect ligand-amended samples to exhibit lower measured Cr(tot) concentrations than the unamended seawater, assuming that 72 h was an adequate amount of time for ligand-Cr complexes to equilibrate with free Cr (see Supplemental Information for discussion). Each ligand was spiked into 14 mL of seawater yielding excess (5 μM; see further discussion in Supplemental Information) ligand and allowed >72 h to react at room temperature and form Cr(III)-ligand complexes (see Supplemental Information for discussion on adequate reaction times). Cr was coprecipitated and measured Cr(tot) concentrations compared between seawater with and without added ligand. Measurements of Cr(tot) in seawater containing NTA, DFB, EDTA, and citrate, as well as unamended seawater were statistically indistinguishable at the 95% confidence level (Table 3). This result was consistent with the UV oxidation experiments, and these observations together imply that Mg(OH)₂ coprecipitation captures organically bound Cr within the dissolved Cr(tot) fraction. It is possible that acidification prior to Mg(OH)₂ coprecipitation, in these experiments, liberated Cr from Cr-org complexes rendering the Cr(III) released reactive toward Mg(OH)₂. We view this as unlikely, particularly

Table 3. Samples exposed to various organic ligands are expressed as a recovery ratio normalized to the control sample (no added ligands).

	NTA	DFB	EDTA	Citrate
Recovery of Cr(III)	1.04	1.03	0.98	1.01
1SD	0.09	0.09	0.10	0.09

for stronger ligands like DFB, which by analogy to Fe (Raymond et al. 1984), should dissociate slowly on acidification. Assuming slow dissociation, it is likely that even organically bound Cr(III) would be captured in the Cr(III) fraction, but this should be verified through further testing.

Application of Mg(OH)₂ coprecipitation

We applied Mg(OH)₂ coprecipitation to determine Cr(VI) and Cr(III) concentrations in Saanich Inlet (Torres-Beltrán et al. 2017). Saanich Inlet is a persistently anoxic fjord that often experiences deep-water renewal and oxygenation in the fall. Throughout much of the year, anoxic conditions persist, and the deep basin becomes sulfidic with a well-defined oxic-anoxic boundary layer between 110 and 130 m depth. Under stratified conditions, thermodynamic considerations suggest that Cr(VI) should be dominant species in the upper oxic layer, while the presence of sulfide (HS⁻) or iron (II) (Fe (II)) is expected to convert all Cr(VI) to Cr(III) below the oxic-anoxic boundary (Elderfield 1970; Cranston and Murray 1978). During renewal, deep, oxygenated waters are likely to bring new Cr(VI) to the depths of Saanich Inlet, while oxidation of existing Cr(III) could be catalyzed by newly formed Mn oxides (Schroeder and Lee 1975). Saanich Inlet thus provides a wide range of redox conditions across which to test the Mg(OH)₂ coprecipitation method.

Profiles of Cr species concentrations (Fig. 2a) generally reflect profiles of major redox active species oxygen (O₂), nitrate (NO₃), and sulfide (HS⁻) (Fig. 2c) in Saanich Inlet. Total Cr concentrations are just over 2 nM in the surface waters and decrease with increasing depth toward the redox boundary below which there is likely Cr removal linked to reduction. This behavior is supported by the distribution of [Cr(VI)], which decreases across the redox boundary and [Cr(III)],

Table 2. Samples from 10 and 200 m that were UV irradiated for 45 min or 130 min compared to a control sample, which saw no UV radiation. Samples show no significant difference and are all within 1SD of each other.

Depth m	Cr(tot)					
	Control nM	SD nM	45 min nM	SD nM	130 min nM	SD nM
10	2.15	0.13	2.26	0.06	2.43	0.42
200	1.94	0.07	1.78	0.24	1.94	0.21

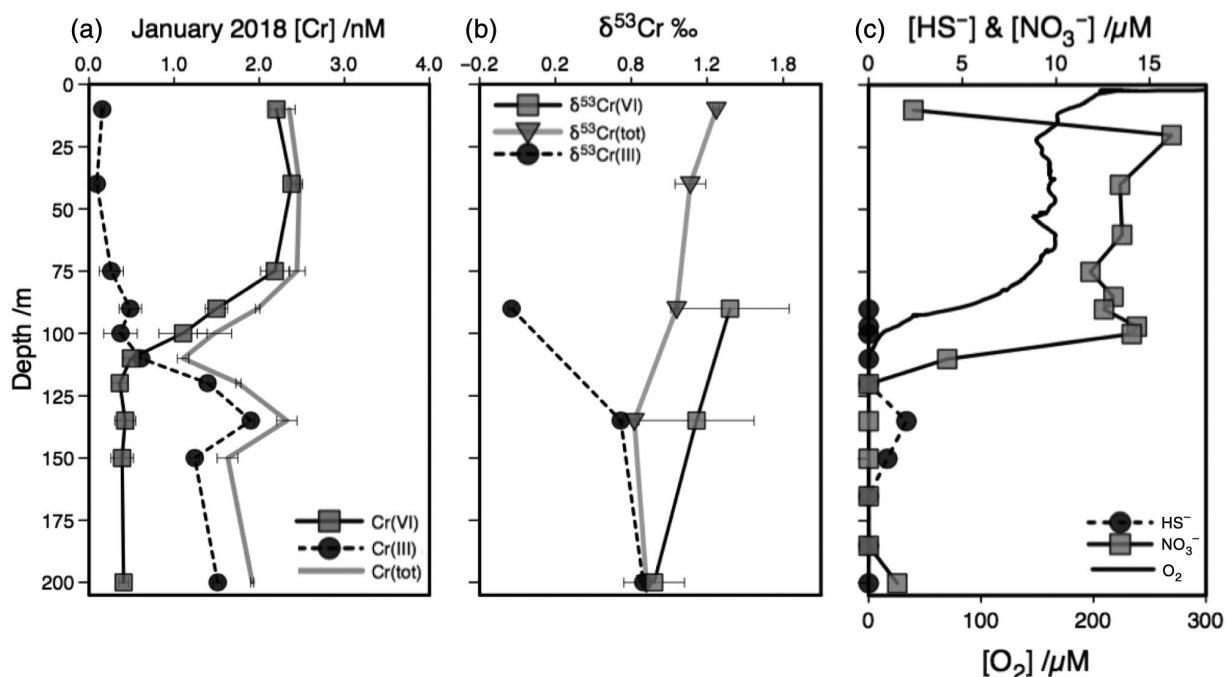


Fig. 2. Vertical profiles of Cr speciation from January 2018 (a), compared to species-specific $\delta^{53}\text{Cr}$ values from the same month at select depths (b). (c), The dissolved oxygen, sulfide, and nitrate water column profiles from January 2018.

which increases below the boundary implying Cr reduction. While Cr(III) dominates in the anoxic portion of the water column, Cr(VI) appears to persist at low (0.36–0.42 nM) concentrations. This persistence of Cr(VI), as well as irregularity in the Cr(III) concentration profile likely reflect nonsteady state processes in Saanich Inlet linked to deep-water renewal events that tend to oxygenate the deep waters (Anderson and Devol 1973). Such a renewal event occurred in October 2017, and its effects were observed in our January sampling; for example, the lingering presence of nitrate at 200 m as well as the relatively low concentrations of HS^- . Notably, Cr(VI) was likely introduced to the deep waters during renewal, and this has important implications for Cr isotope systematics, as we discuss later. Broadly, however, our Cr species measurements are consistent with previous observations of Cr speciation in Saanich Inlet (Cranston and Murray 1978; Emerson et al. 1979), and are well in line with the known redox properties and geochemical behavior of Cr.

Species-specific seawater Cr isotope ratios

We also applied $\text{Mg}(\text{OH})_2$ coprecipitation to determine the $\delta^{53}\text{Cr}$ of Cr(III) and Cr(VI) in Saanich Inlet. The $\delta^{53}\text{Cr}$ of Cr(tot) and Cr(III) were measured, while the $\delta^{53}\text{Cr}(\text{VI})$ was determined by mass balance, using the Cr(VI) concentrations obtained from the difference between Cr(tot) and Cr(III), and the measured $\delta^{53}\text{Cr}$ of Cr(tot) and Cr(III) (Table 4), as described below:

$$\delta^{53}\text{Cr}(\text{VI}) = \frac{(\delta^{53}\text{Cr}(\text{tot}) \times [\text{Cr}(\text{tot})] - \delta^{53}\text{Cr}(\text{III}) \times [\text{Cr}(\text{III})])}{([\text{Cr}(\text{tot})] - [\text{Cr}(\text{III})])}$$

Profiles of species-specific Cr isotope compositions are shown in Fig. 2b.

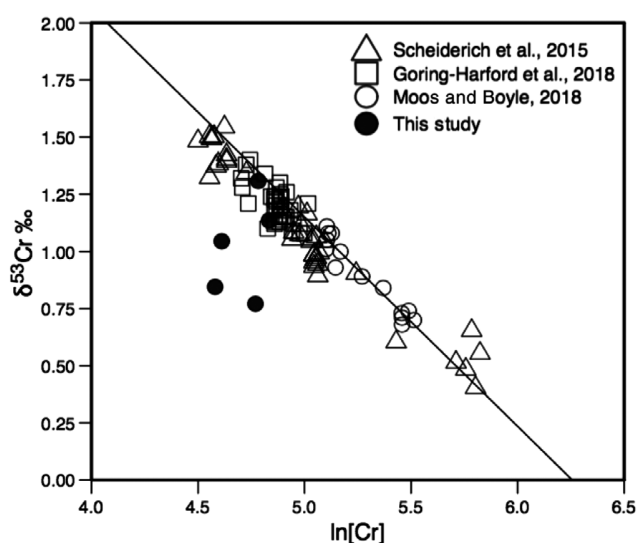
Measurements of $\delta^{53}\text{Cr}(\text{III})$ are lighter than $\delta^{53}\text{Cr}(\text{VI})$, as would be expected from the directionality of all previous assessments of equilibrium and kinetic Cr isotope fractionation associated with redox reactions (Qin and Wang 2017). Notably, however, we do not observe an increase in the $\delta^{53}\text{Cr}(\text{tot})$ at 90 m, relative to shallow waters above, that would be expected to arise from the formation and export of particle-reactive Cr(III) to deeper waters through sedimentation of sinking particles (Fig. 2b). The apparent lack of increasingly positive $\delta^{53}\text{Cr}(\text{tot})$ in light of Cr(VI) reduction implies open system behavior, and a decoupling between waters above 70 m depth that readily exchange with surface waters from the Strait of Georgia, and waters below 70 m depth that only receive episodic input of water from the Strait of Georgia during deep-water renewal (Anderson and Devol 1973). When we compare the relationship of $\delta^{53}\text{Cr}(\text{tot})$ from Saanich Inlet with seawater measurements from other locations, we find that the two surface depths, 10 and 40 m, fit well with the linear relationship between $\delta^{53}\text{Cr}(\text{tot})$ and $\ln[\text{Cr}(\text{tot})]$ defined by prior seawater measurements and referred to as the global Cr array (Fig. 3; Scheiderich et al. 2015; Goring-Harford et al. 2018;

Table 4. Select isotopic data from Cr(tot) and Cr(III) samples taken from Saanich Inlet, British Columbia in January, 2018. (Cr(VI) calculated by difference).

Depth m	Cr(tot)				Cr(III)				Cr(VI)			
	$\delta^{53}\text{Cr}$ ‰ 979	2SD ‰	[Cr] nM	SD nM	$\delta^{53}\text{Cr}$ ‰ 979	2SD ‰	[Cr] nM	SD nM	$\delta^{53}\text{Cr}$ ‰ 979	2SD ‰	[Cr] nM	SD nM
10	1.31	0.02	2.35	0.07	n/a	n/a	0.15	0.02	n/a	n/a	2.20	0.07
40	1.14	0.1	2.47	0.04	n/a	n/a	0.09	0.03	n/a	n/a	2.38	0.05
90	1.05	0.01	1.98	0.03	-0.04	0.02	0.48	0.13	1.40	0.39	1.50	0.13
135	0.77	0.02	2.32	0.12	0.68	0.02	1.90	0.04	1.18	0.38	0.42	0.12
200	0.85	0.02	1.92	0.02	0.83	0.01	1.51	0.05	0.9	0.2	0.41	0.06

Moos and Boyle 2018). This makes sense considering the effective exchange of surface seawater with the Strait of Georgia and the open Pacific Ocean (Gargett et al. 2003). The three deeper depths (90, 135, and 200 m), however, fall off the global Cr array indicating that the processes controlling the isotopic composition of Cr in the deep waters of the inlet are not the same processes that control the slope of the global Cr array. A similar effect was observed by Wang et al. (2019), where total Cr plotted above the global Cr array and only measured $\delta^{53}\text{Cr}(\text{III})$ followed the global trend. The deep inlet samples fall below the global Cr array, indicating that deep water Cr in Saanich Inlet is anomalously isotopically light and/or low in Cr concentration. This is consistent with the observation that Cr speciation in these deep waters is predominantly Cr(III), which according to the directionality of known redox associated fractionation processes is expected to be isotopically lighter than the reactive pool of Cr(VI). On the other hand, it is also evident that the

isotopic composition of Cr(VI) at 200 m is nearly equivalent to that of Cr(III) indicating that Cr(VI) and Cr(III) are neither in isotopic equilibrium (Wang et al. 2015), which would imply an isotopic difference of 5.6‰ between Cr(VI) and Cr(III), nor is there any evidence that the two pools of Cr are related by a process involving kinetic isotope fractionation, as the Cr(III) pool would still be expected to be isotopically lighter than Cr(VI) pool. One potential explanation is a decoupling of the two pools due to open system behavior, with Cr(VI) apparently retaining a relatively light composition likely inherited from its source in the Strait of Georgia as described earlier. Cr(VI) is expected to be the dominant species in oxygenated waters like those from the Strait of Georgia, and a $\delta^{53}\text{Cr} = 0.90\text{‰}$ is within observations of other seawater samples (e.g., Scheiderich et al. 2015; Goring-Harford et al. 2018; Moos and Boyle 2018), but in this case the concentration is lower than expected as the result of dilution with Cr(VI)-poor Saanich Inlet deep waters. We can estimate the [Cr(VI)] likely introduced during renewal if we assume the waters in the Strait of Georgia contain 1–4 nM Cr(VI) (similar to Saanich Inlet) and that a deep water renewal event brings in the equivalent of 30–65% of the deep water volume (Anderson and Devol 1973). This leads to estimates of [Cr(VI)] between 0.3–2.4 nM and these are within the range observed here. Cr(III) on the other hand may be largely from Saanich Inlet itself; under anoxic conditions at this depth, Cr(III) typically makes up the entire Cr pool and $\delta^{53}\text{Cr}(\text{III})$ would be expected to reflect complete reduction of Cr(VI), and therefore it is conceivable that it would also be approximately 0.9‰. While we are unable to fully resolve Cr isotope systematics in Saanich Inlet through the data generated in this proof-of-concept experiment, we demonstrate the need for more Cr speciation analysis of Saanich Inlet waters, and ocean waters more generally, to further our knowledge of the factors influencing Cr isotope fractionation in the oceans, and the origin and meaning of the global Cr array.

**Fig. 3.** Comparison of $\delta^{53}\text{Cr}(\text{tot})$ data from this study to global measurements and the global Cr array (Scheiderich et al. 2015 (all data except Arctic summer mixed layer samples); Goring-Harford et al. 2018 (outliers removed); Moos and Boyle 2018 (SAFe data only plotted)).

Comments and recommendations

We developed a Cr speciation method using $\text{Mg}(\text{OH})_2$ coprecipitation that effectively quantifies Cr(III) and Cr(VI) in

seawater and enables species-specific isotope measurements on parallel samples. Alternatively, the use of a Cr double-spike on large volume samples before precipitation would negate the need for separate Cr concentration samples and increase the precision on the determined Cr concentration when determined by isotope dilution. This requires, however, that the Cr concentration can be roughly estimated to enable the correct double-spike addition. The broader application of this method to the study of Cr speciation and isotope fractionation in seawater will undoubtedly yield new insight into the marine and global geochemical cycling of Cr, its effects on the Cr isotopic composition of seawater and marine sediments, and our ability to reconstruct past environments based on Cr isotope data. While lower salinity samples were not tested here, brackish and freshwaters in principle could be analyzed following the addition of Mg, extending the utility of the method to Cr speciation in water, generally.

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Acknowledgments

This work was financially supported by NSERC (Grant #0487). ABD was supported by a NSERC CREATE Grant (MAGNET PhD). DMS and SLJ were funded by the Swiss National Science Foundation (SNSF grants PP00P2_144811 and PP00P2_172915). We thank the captain and crew of the RV Strickland.

Submitted 24 May 2019

Revised 09 October 2019

Accepted 11 November 2019

Associate editor: Gregory Cutter