



# Chromium isotope fractionation between modern seawater and biogenic carbonates from the Great Barrier Reef, Australia: Implications for the paleo-seawater $\delta^{53}\text{Cr}$ reconstruction

Juraj Farkaš<sup>a,b,c,\*</sup>, Jiří Frýda<sup>d</sup>, Cora Paulukat<sup>e,1</sup>, Ed C. Hathorne<sup>f</sup>, Šarka Matoušková<sup>g</sup>, Jan Rohovec<sup>g</sup>, Barbora Frýdová<sup>d</sup>, Michaela Francová<sup>a</sup>, Robert Frei<sup>e</sup>

<sup>a</sup> Department of Geochemistry, Czech Geological Survey, Prague, Czech Republic

<sup>b</sup> Department of Earth Sciences, University of Adelaide, North Terrace, Adelaide, Australia

<sup>c</sup> TRaX – Centre for Tectonics, Resources and Exploration, University of Adelaide, North Terrace, Adelaide, SA 5005, Australia

<sup>d</sup> Department of Environmental Geosciences, Czech University of Life Sciences, Prague, Czech Republic

<sup>e</sup> Department of Geosciences and Natural Resource Management, University of Copenhagen, Denmark

<sup>f</sup> GEOMAR, Helmholtz Centre for Ocean Research, Kiel, Germany

<sup>g</sup> Institute of Geology, Academy of Sciences of the Czech Republic, Czech Republic

## ARTICLE INFO

### Article history:

Received 18 January 2018

Received in revised form 22 June 2018

Accepted 22 June 2018

Available online xxx

Editor: D. Vance

### Keywords:

chromium  
isotopes  
REE  
carbonates  
seawater  
Great Barrier Reef

## ABSTRACT

This study investigates chromium isotope variations ( $\delta^{53}\text{Cr}$ ) and REE patterns in present-day biogenic carbonates and ocean waters from Lady Elliot Island (LEI) located in the southern Great Barrier Reef (GBR), Australia, which is one of the world's largest carbonate-producing shelf ecosystems. Our results from thoroughly cleaned biogenic carbonates collected at LEI, with no detectable evidence for lithogenic Cr and/or Mn–Fe oxide coating contamination, revealed a systematic and statistically significant correlation ( $r^2 = 0.83$ ,  $p < 0.05$ ) between  $\delta^{53}\text{Cr}$  and cerium anomaly ( $\text{Ce}/\text{Ce}^*$ ) data in molluscan shells (i.e., gastropods). This in turn implies a redox-controlled incorporation of Cr from seawater into a shell during mineralization mediated by the organism. In particular, shells with higher  $\delta^{53}\text{Cr}$  values, which approach the Cr isotope composition of local seawater, tend to be associated with more negative  $\text{Ce}/\text{Ce}^*$ . Importantly, the intercept of the above  $\delta^{53}\text{Cr}$  vs.  $\text{Ce}/\text{Ce}^*$  correlation points to the Cr isotope composition of local ocean water, which has an average  $\delta^{53}\text{Cr}$  of  $+0.82 \pm 0.13\%$  ( $2\sigma$ , relative to SRM 979). These findings thus indicate that the above multi-proxy approach could be used to reconstruct the  $\delta^{53}\text{Cr}$  signature of local paleo-seawater based on  $\text{Ce}/\text{Ce}^*$  and  $\delta^{53}\text{Cr}$  data in a set of well-preserved fossil skeletal carbonates (i.e., molluscan shells) collected at a specific site. Interestingly, the only calcifying organism from LEI that yielded identical  $\delta^{53}\text{Cr}$  vs.  $\text{Ce}/\text{Ce}^*$  values as those in ambient ocean water was a microbial calcitic carbonate produced by red coralline algae (*Lithothamnion* sp.). This organism thus seems to incorporate Cr isotopes and REE from seawater without additional biological discrimination and/or isotope fractionation effects. Considering that calcite is a more stable  $\text{CaCO}_3$  polymorph during post-depositional alteration and diagenetic stabilization of marine carbonates (compared to aragonite), the fossil counterparts of these algal-microbial carbonates (microbialites) might thus represent ideal natural archives of the paleo-seawater  $\delta^{53}\text{Cr}$  and  $\text{Ce}/\text{Ce}^*$  variations over geological time.

Finally, our compilation of  $\delta^{53}\text{Cr}$  data from recent marine biogenic carbonates originating from the main oceanic provinces (South/North Pacific, South/North Atlantic, Caribbean, Mediterranean Sea) confirms that marine carbonates tend to be systematically enriched in light Cr isotopes relative to local ocean waters. Trace element constraints, however, indicate that some of these shifts to lower  $\delta^{53}\text{Cr}$  values (i.e., approaching  $-0.1$  per mil) are related to a presence of lithogenic Cr in the shells, causing a diagenetic overprint of the primary marine  $\delta^{53}\text{Cr}$  signal.

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## 1. Introduction

Chromium (Cr) is a redox-sensitive transition metal with four naturally occurring isotopes ( $^{50}\text{Cr}$ ,  $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$ ) that could

\* Corresponding author.

E-mail address: juraj.farkas@adelaide.edu.au (J. Farkaš).

<sup>1</sup> Current address: ALS Scandinavia AB, Aurorum 10, 977 75, Luleå, Sweden.

be used as tracers to constrain present and past redox conditions on Earth and other solar system objects (Bonnand et al., 2016; Schoenberg et al., 2016; Crowe et al., 2013; Planavsky et al., 2014; Frei et al., 2009). Stable Cr isotopes can also be utilized to monitor the sources and biogeochemical pathways of chromium within terrestrial reservoirs including geological, hydrological and biological systems (Paulukat et al., 2016; Holmden et al., 2016; D'Arcy et al., 2016; Wang et al., 2016; Pereira et al., 2015; Scheiderich et al., 2015; Farkaš et al., 2013; Bonnand et al., 2013; Schoenberg et al., 2008; Ellis et al., 2002). Although Cr can occur in numerous oxidation states (ranging from  $-2$  to  $+6$ ; cf., Daulton and Little, 2006), in most near-surface terrestrial environments including the oceans, it is typically present either as trivalent Cr(III) or hexavalent Cr(VI) species, depending on local redox conditions (Kotaš and Stasicka, 2000; Elderfield, 1970; Pettine and Millero, 1990).

Importantly, there is a systematic fractionation of stable Cr isotopes (i.e.,  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios or  $\delta^{53}\text{Cr}$ ) in nature due to redox processes, where the reduction of Cr in near-surface environments produces dissolved Cr(VI) that is isotopically heavier, relative to a less soluble Cr(III) species (Ellis et al., 2002; Zink et al., 2010; Døssing et al., 2011). The Cr isotope composition of seawater thus reflects a complex signal of oxidation/reduction processes operating within the oceans (Scheiderich et al., 2015; Paulukat et al., 2016), and the  $\delta^{53}\text{Cr}$  record of marine sedimentary archives has potential to be used to infer the past redox conditions of the ocean–atmosphere system through geological time (Frei et al., 2009, 2011, 2013, 2016; Bonnand et al., 2013; Van Zuilen and Schoenberg, 2013; Planavsky et al., 2014; Holmden et al., 2016; D'Arcy et al., 2016; Rodler et al., 2016; Gilleaudeau et al., 2016).

Due to a basically continuous geological record of marine carbonates throughout most of the Earth's history, i.e., the last  $\sim 3.7$  billion years (Nutman et al., 2016; Shields and Veizer, 2002), Cr isotope studies of marine carbonate archives are particularly appealing for paleo-redox reconstructions. However, as shown by recent studies (Rodler et al., 2015; Pereira et al., 2015; Wang et al., 2016), the actual mechanism(s) of Cr incorporation and redox-controlled isotope fractionation during the formation of inorganic and biogenic carbonates is rather complex and poorly understood, thus requiring further systematic investigations in both natural and laboratory-controlled settings. Available results from inorganic calcite precipitation experiments have revealed that the incorporation of Cr from a solution into  $\text{CaCO}_3$  is facilitated as chromate anion ( $\text{CrO}_4^{2-}$ ), which replaces carbonate anion ( $\text{CO}_3^{2-}$ ) in the calcite lattice (Tang et al., 2007). This process of inorganic calcification tends to preferentially incorporate heavy  $^{53}\text{Cr}$  isotopes into the mineral, yielding a  $\delta^{53}\text{Cr}$  of calcite which is thus up to  $\sim 0.3\%$  more positive compared to the fluid (Rodler et al., 2015). In contrast, biologically produced marine  $\text{CaCO}_3$  minerals, such as foraminiferal calcite (Wang et al., 2016), coral aragonite (Pereira et al., 2015) and bulk carbonate sediments (Holmden et al., 2016), are all systematically enriched in light Cr isotopes compared to ambient seawater. This fractionation trend is thus the exact opposite of the situation observed in inorganic calcite (cf., Rodler et al., 2015).

Furthermore, due to local redox cycling and biological uptake of Cr in the oceans (Semeniuk et al., 2016), the Cr isotope signature of present-day seawater is not globally homogeneous (Scheiderich et al., 2015; Paulukat et al., 2016), further complicating the application of the  $\delta^{53}\text{Cr}$  proxy in marine carbonate archives. Considering the abovementioned issues and limitations, the full potential of Cr isotopes for paleo-redox studies can only be realized with more detailed calibration work done on the modern seawater–carbonate system from different oceanographic settings, by analyzing  $\delta^{53}\text{Cr}$  data from both local seawater and precipitated marine carbonates.

This study is the first to present such a comprehensive Cr isotope investigation of the seawater–carbonate system from one of the world's largest carbonate-producing shelf ecosystems, the Great Barrier Reef (Lady Elliot Island, Australia), where  $\delta^{53}\text{Cr}$  data were acquired from local ocean waters and selected recent biogenic carbonates (i.e., gastropods, cephalopods, corals, and calcifying algae). In addition, an alternative and complementary redox proxy, i.e., Cerium anomaly ( $\text{Ce}/\text{Ce}^*$ ), is applied here to further test and quantify the possible role of redox processes during Cr incorporation into marine biogenic carbonates. Elemental abundances of selected elements (Al, Mn, Fe, and REE), coupled with  $^{87}\text{Sr}/^{86}\text{Sr}$  analysis, are also used as indices to evaluate possible contamination by non-marine Cr sources originating from lithogenic (detrital minerals, clays) and/or Mn–Fe oxide components (Pereira et al., 2015; Wang et al., 2016; Rodler et al., 2016; Gilleaudeau et al., 2016). The Cr isotope data acquired from the seawater–carbonate system at Lady Elliot Island are complemented by additional  $\delta^{53}\text{Cr}$  analyses of marine skeletal carbonates (i.e., bivalves, gastropods) collected from the main oceanic provinces including: North and South Atlantic, North and South Pacific Oceans, and the Mediterranean Sea. Finally, these are then compared to published seawater  $\delta^{53}\text{Cr}$  signatures for the above oceanic provinces (Scheiderich et al., 2015; Paulukat et al., 2016), and conclusions are made about the redox-controlled mechanism(s) behind the Cr isotope fractionation in a seawater–carbonate system, with implications for paleo-seawater  $\delta^{53}\text{Cr}$  reconstructions.

## 2. Study sites and samples

Lady Elliot Island ( $24^\circ 06' 47''\text{S}$ ,  $152^\circ 44' 50''\text{E}$ ) is the southernmost tropical coral cay of the Great Barrier Reef (GBR), which is the largest coral reef ecosystem on Earth with in-situ production of skeletal carbonates within an area comprising about  $344,400\text{ km}^2$ , stretching along  $\sim 2300\text{ km}$  off the coastline of Queensland, Australia (Fig. 1) (De'ath et al., 2012; Chivas et al., 1986). Lady Elliot Island (LEI) represents a particularly interesting and unique site for Cr isotope studies mostly because of (i) its remote location from the Australian mainland (ca.  $80\text{ km}$  from the nearest coastline), and (ii) the effect of prevailing south-easterly trade winds blowing from the open ocean towards the mainland (Kench and Brander, 2006). Together these presumably result in a minimal input of possible continentally-derived Cr sources (i.e., mineral dust, silicate detritus) into the studied seawater–carbonate system. This unique setting of LEI, in turn, minimizes potential contamination of our samples with lithogenic/detrital Cr, which has been proven to impact  $\delta^{53}\text{Cr}$  measurements in naturally Cr-poor marine carbonates (Pereira et al., 2015; Wang et al., 2016; Rodler et al., 2016).

The reef platform of LEI is kidney-shaped, measuring  $\sim 1.2\text{ km}$  along its longest (NE–SW) and  $\sim 0.8\text{ km}$  along its shorter (SE–NW) axis, with typical water depths ranging from  $<1$  to about  $25\text{ m}$ , across the reef-flat and reef-slope areas, respectively (Hamilton, 2014). Seawater samples analyzed in this study (Fig. 1C) were collected in 2015 by the LEI's Eco Resort scuba-diving team on (i) the leeward side of the island from the reef-flat and slope areas (near Coral Garden), and also on (ii) the windward side from the northeast lagoon (i.e., a reef-flat) and the northerly surf-break area (i.e., near a reef slope) (see also Table 1).

The main shallow-water calcifying organisms and benthic carbonate producers at the LEI's reef platform are: (i) scleractinian corals, (ii) red coralline algae, (iii) green calcifying algae (*Halimeda*), and marginally also (vi) benthic foraminifera, bivalves, and gastropods (Hamilton, 2014). Samples of recent biogenic carbonates were collected in 2013 from the leeward side of LEI, in an area called the 'Coral Gardens' (Fig. 1), and these specimens were sampled under the Queensland Museum general purposes permit.

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