

## Introduction

The chromium (Cr) isotope system functions as an atmospheric redox proxy because oxidative weathering of crustal Cr(III)-bearing minerals results in the release of  $^{53}\text{Cr}$ -enriched mobile Cr(VI) to solution. Cr(VI) (dominantly as chromate;  $\text{CrO}_4^-$ ) is then carried to the oceans via rivers, thus imparting a positively fractionated  $\delta^{53}\text{Cr}$  signal on modern seawater (+0.41 to +1.55 ‰ compared to crustal values of  $-0.123 \pm 0.102$  ‰) (Schoenberg *et al.*, 2008; Bonnand *et al.*, 2013; Scheiderich *et al.*, 2015). Terrestrial Cr(III)-oxidation occurs by reaction with manganese (Mn) oxides, and it is thought that Mn-oxide formation requires a threshold level of  $\text{O}_2$  in the atmosphere. Frei *et al.* (2016) suggested that Cr-oxidation by Mn-oxides is thermodynamically possible at  $p\text{O}_2$  as low as  $10^{-5}$  of the present atmospheric level (PAL). Kinetic considerations dictate, however, that 0.1 to 1 % PAL is necessary to oxidise Cr(III) within typical soil residence times (Planavsky *et al.*, 2014) and between 0.03 and 0.3 % PAL is necessary to export Cr without re-reduction by Fe(II) (Crowe *et al.*, 2013). Because the delivery of positively fractionated Cr(VI) to seawater is dependent on a threshold level of atmospheric oxygen, the Cr-isotope composition of seawater through time – as recorded in marine sedimentary rocks – can serve as a sensitive indicator of ancient atmospheric  $p\text{O}_2$ . This is particularly useful for testing hypotheses about atmospheric oxygenation during the Proterozoic Eon, where fundamental questions persist about the  $\text{O}_2$  content of Earth's atmosphere and its relationship to temporal patterns of biological innovation.

The oxygenation of Earth surface environments was a protracted process that occurred over >2 billion years (Ga) (see Lyons *et al.*, 2014). Two first-order oxygen pulses have been identified from the Proterozoic geologic record. During the Great Oxidation Event (GOE) at ~2.4 Ga,  $p\text{O}_2$  was sustained above  $10^{-5}$  PAL for the first time in Earth history, although transient 'whiffs' of  $\text{O}_2$  have been recognised from the Archaean geochemical record. During a subsequent Neoproterozoic oxygenation event (NOE) at ~635–550 Ma,  $p\text{O}_2$  began to rise to near-modern levels – a transition that continued into the Palaeozoic Era.

Empirical constraints remain limited, however, on  $p\text{O}_2$  during the prolonged period in between. Constraining  $p\text{O}_2$  during the mid-Proterozoic Eon has major implications for understanding potential biogeochemical controls on the timing of animal diversification. Some argue that exceedingly low mid-Proterozoic  $p\text{O}_2$  was a direct impediment to metazoan evolution prior to the Neoproterozoic Era (Planavsky *et al.*, 2014), whereas others argue that oxygen levels required by early animals were in place long before their Neoproterozoic appearance (Butterfield, 2009; Zhang *et al.*, 2016). Mid-Proterozoic Cr-isotope data have the potential to inform this debate because estimates of the  $p\text{O}_2$  threshold needed for Cr-isotope fractionation are roughly similar to experimental and theoretical estimates of the  $\text{O}_2$  requirements of early animals (0.3 to 4 % PAL) (*e.g.*, Mills *et al.*, 2014).

## Oxygenation of the mid-Proterozoic atmosphere: clues from chromium isotopes in carbonates

G.J. Gilleaudeau<sup>1,2\*</sup>, R. Frei<sup>1</sup>, A.J. Kaufman<sup>3</sup>, L.C. Kah<sup>4</sup>,  
K. Azmy<sup>5</sup>, J.K. Bartley<sup>6</sup>, P. Chernyavskiy<sup>7</sup>, A.H. Knoll<sup>8</sup>



### Abstract

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Chromium (Cr) isotopes in marine sedimentary rocks can be used as a sensitive proxy for ancient atmospheric oxygen because Cr-isotope fractionation during terrestrial weathering only occurs when  $p\text{O}_2$  exceeds a threshold value. This is a useful system when applied to rocks of mid-Proterozoic age, where fundamental questions persist about atmospheric  $p\text{O}_2$  and its relationship to biological innovation. Whereas previous studies have focused on temporally limited iron-rich sedimentary rocks, we present new Cr-isotope data from a suite of mid-Proterozoic marine carbonate rocks. Application of the Cr-isotope proxy to carbonate rocks has the potential to greatly enhance the temporal resolution of Proterozoic palaeo-redox data. Here we report positive  $\delta^{53}\text{Cr}$  values in four carbonate successions, extending the mid-Proterozoic record of Cr-isotope fractionation – and thus  $p\text{O}_2$  above threshold values – back to ~1.1 Ga. These data suggest that  $p\text{O}_2$  sufficient for the origin of animals was transiently in place well before their Neoproterozoic appearance, although uncertainty in the  $p\text{O}_2$  threshold required for Cr-isotope fractionation precludes definitive biological interpretation. This study provides a proof of concept that the Cr-isotopic composition of carbonate rocks can provide important new constraints on the oxygen content of the ancient atmosphere.

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1. Department of Geosciences and Natural Resource Management, University of Copenhagen, Øster Voldgade 10, 1350 Copenhagen, Denmark
2. Current address: School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85281, USA
- \* Corresponding author: (email: ggillea1@gmail.com)
3. Department of Geology, University of Maryland, College Park, MD 20742, USA
4. Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN 37996, USA
5. Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X5, Canada
6. Department of Geology, Gustavus Adolphus College, St. Peter, MN 56082, USA
7. Biostatistics/Radiation Epidemiology Branch, National Cancer Institute, National Institutes of Health, Rockville, MD 20850, USA
8. Department of Organismic and Evolutionary Biology, Harvard University, Cambridge, MA 02138, USA



Thus far, studies have largely focused on iron-rich sedimentary rocks as an archive for ancient seawater  $\delta^{53}\text{Cr}$  values. In the presence of Fe(II), seawater Cr(VI) is reduced to Cr(III) and can be co-precipitated with Fe-(oxyhydr)oxides. Cr-reduction favours the light  $^{52}\text{Cr}$  isotope, so that iron-rich rocks record seawater  $\delta^{53}\text{Cr}$  values only if Cr-reduction is quantitative. Ironstone and iron formation data have thus far provided important constraints on Archaean 'whiffs' of oxygen and the subsequent GOE, as well as new clues about the NOE (Frei *et al.*, 2009). Sparse ironstone data from the mid-Proterozoic suggest a lack of Cr-isotope fractionation (Planavsky *et al.*, 2014). Iron-rich rocks are rare in mid-Proterozoic successions, however, limiting our ability to generate data for the crucial period preceding the NOE.

The impetus of this study, then, is to test the reliability of Cr-isotopes in marine carbonate rocks that are ubiquitous in the mid-Proterozoic geologic record. A potential advantage of using carbonate rocks as a Cr-isotope archive is that chromate can be incorporated into the lattice of carbonate minerals with no change in oxidation state. Studies of modern invertebrate shells reveal that Cr-isotope fractionation does occur during biomineralisation, making skeletal carbonates an unreliable archive of seawater  $\delta^{53}\text{Cr}$  values (Pereira *et al.*, 2016). Mohanta *et al.* (2016) showed that modern bulk biogenic carbonate is as much as 0.45 ‰ lighter than seawater. Co-precipitation experiments involving chromate incorporation into calcite have shown, however, that abiogenic carbonate has the potential to record  $\delta^{53}\text{Cr}$  values of the ambient solution (Rodler *et al.*, 2015). In experiments with the lowest initial Cr concentration (8.6 ppm), precipitates were <0.1 ‰ heavier than the solution, suggesting that minimal fractionation occurs during chromate incorporation into calcite at low Cr concentrations typical of seawater (0.08 to 0.5 ppm).

In this study, we measured the Cr-isotopic composition of marine limestone and dolostone from four geographically distinct mid-Proterozoic successions, along with a suite of major and trace elements to constrain diagenetic pathways and the influence of detrital contamination. We focused on the interval between ~1.1 and 0.9 Ga – where sea level highstand resulted in marine carbonate deposition across multiple cratons – and a variety of depositional environments to assess the consistency and reliability of the proxy. Samples were carefully selected based on known criteria for identifying diagenetic alteration and detrital contamination, and our data are ultimately used to provide important new constraints on atmospheric  $p\text{O}_2$  during the mid-Proterozoic Eon.

## Background and Methods

Samples were analysed from the Turukhansk Uplift, Siberia (~900-1035 Ma), the Angmaat Formation, Canada (~1092 Ma), the El Mreiti Group, Mauritania (~1107 Ma), and the Vazante Group, Brazil (~1112 Ma). Cr-isotope and Cr concentration measurements were performed on a thermal ionisation mass spectrometer. Ca, Mg, Fe, Sr, Mn, and Al concentrations were measured by ICP-OES, and Ti and Zr concentrations were measured by ICP-MS (see Supplementary Information).

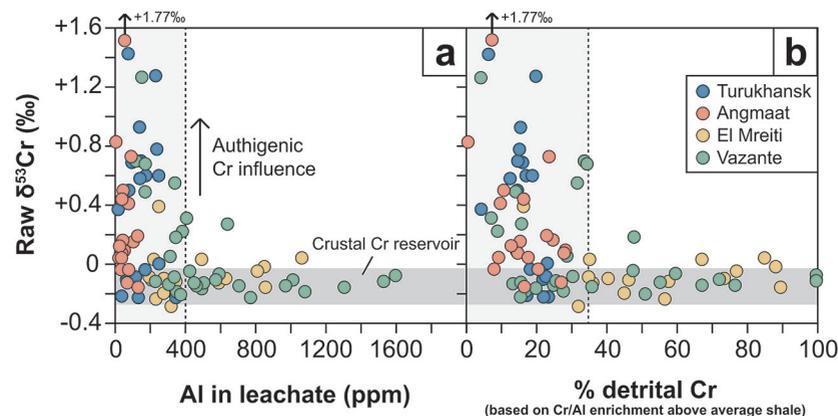
## Diagenesis

The chemical reactivity of carbonate minerals during diagenesis requires detailed understanding of potential diagenetic processes prior to selecting samples for Cr-isotope analysis. Here we employ a robust set of screening criteria for sample inclusion. Conventional light and cathodoluminescence petrography permit recognition of recrystallisation processes and secondary phases, and a combination of isotopic and elemental analyses provide evidence for fluid alteration based on the relative mobility of ions within lattice components. In short, samples containing substantial evidence for diagenetic alteration (*e.g.*, Ostwald ripening, loss of fabric details, and secondary precipitation phases) were excluded (Figs. S-1, S-2). We then compared isotopic and trace element trends that are sensitive to fluid interaction (*e.g.*,  $\delta^{18}\text{O}$ , [Sr], [Mn]; Banner and Hanson, 1990) to values recorded across a range of preservation states within Proterozoic carbonates (*e.g.*, Kaufman and Knoll, 1995; Bartley *et al.*, 2007; Kah *et al.*, 2012), conservatively excluding outliers that are depleted in  $^{18}\text{O}$ , substantially enriched in Mn, or depleted in Sr (Fig. S-3). We interpret our Cr-isotope data within the context of these standard criteria, acknowledging that additional work is necessary specifically to explore Cr behaviour during carbonate diagenesis. Detailed mineralogical, textural, and geochemical information can be found in the Supplementary Information.

## Detrital Chromium

Our results indicate a broad range of  $\delta^{53}\text{Cr}$  values in each succession, ranging from crustal values (near -0.12 ‰) to strongly positive values (up to +1.77 ‰). To understand this isotopic heterogeneity, we first evaluated the degree to which measured  $\delta^{53}\text{Cr}$  values reflect authigenic Cr in carbonate vs. allochthonous Cr from detrital sources. As part of each dissolution for  $\delta^{53}\text{Cr}$  analysis, we measured a split for aluminium (Al) content to assess the degree to which clay – which can be a host phase for detrital Cr – was leached during dissolution. In a plot of Al concentration in the leachate vs. raw  $\delta^{53}\text{Cr}$  values (Fig. 1a), positively fractionated  $\delta^{53}\text{Cr}$  is only recorded in samples where less than ~400 ppm Al is leached. A similar trend is observed for other detrital indicators. Positively fractionated  $\delta^{53}\text{Cr}$  is only observed when leachate titanium (Ti) and zirconium (Zr) concentrations are generally less than 10 and 1 ppm, respectively (Fig. S-4), although the relationship is not well-defined for Zr. Assuming that Al is the most effective indicator of clay contamination, we compared sample Cr/Al ratios to an average shale composite (Cr = 90 ppm; Al = 8.89 wt. %; Wedepohl, 1991) – which serves as a first-order proxy for clay-rich detrital sediment – to derive a rough estimate of the fraction of Cr sourced from detrital material for each sample. Similarly, positively fractionated  $\delta^{53}\text{Cr}$  is only recorded in samples where less than ~35 % of measured Cr is detritally sourced (Fig. 1b).





**Figure 1** (a) Cross-plot of raw Cr-isotope values and Al concentration in the leachate. Dashed line is at 400 ppm Al. (b) Cross-plot of raw Cr-isotope values and % detrital Cr based on enrichment above average shale. Dashed line is at 35 %.

These trends represent a mixing curve where Cr in the carbonate lattice is dissolved and analysed in addition to Cr leached from clay. When detrital Cr exceeds ~35 % of total measured Cr,  $\delta^{53}\text{Cr}$  values approach average crust ( $-0.12\text{‰}$ ) and the isotopic composition of the authigenic seawater component is unresolvable. When samples have less than ~35 % detrital Cr, we can perform a basic correction of raw  $\delta^{53}\text{Cr}$  values, assuming the detrital component has a crustal  $\delta^{53}\text{Cr}$  value. This yields a first-order estimate of the isotopic composition of the authigenic Cr component ( $\delta^{53}\text{Cr}_{\text{auth}}$ ), which is thought to be derived from seawater (see Supplementary Information).

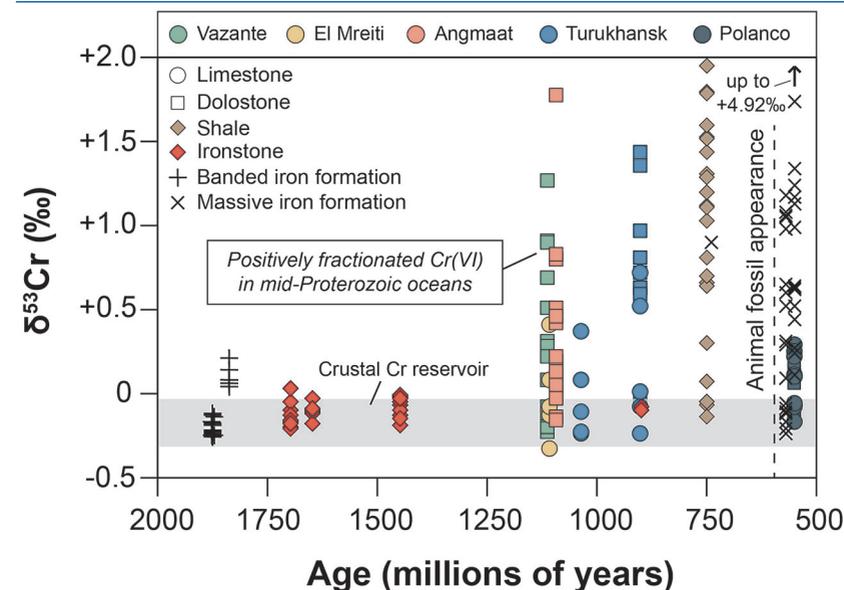
After exclusion of samples based on diagenetic and detrital contamination criteria, our dataset consisted of 62 samples that cover all four successions. These methods for assessing detrital Cr contamination represent a new set of best practices that should be applied in future Cr-isotope studies of carbonate rocks.

### Atmospheric Oxygen

The main observation of our dataset is that all four successions record positively fractionated  $\delta^{53}\text{Cr}_{\text{auth}}$  values. The maximum isotopic difference observed by Rodler *et al.* (2015) between synthetic calcite and ambient solution was  $0.33\text{‰}$  so that, even if some fractionation did occur during carbonate formation, the preponderance of strongly positive  $\delta^{53}\text{Cr}$  values in our dataset ( $n = 24$  samples  $>0.3\text{‰}$ ) indicates that mid-Proterozoic seawater was positively fractionated. Additionally, if carbonate preferentially incorporated  $^{52}\text{Cr}$  as observed by Mohanta *et al.* (2016), then our dataset provides even stronger evidence for positively fractionated Cr in mid-Proterozoic seawater, assuming that carbonates are able to retain their original  $\delta^{53}\text{Cr}$  signature.



The record of positively fractionated Cr in seawater has recently been extended back to ~3.8 Ga, which Frei *et al.* (2016) interpret as terrestrial Cr-oxidation under an otherwise anoxic Archaean atmosphere. Banded iron formations from the Archaean-Proterozoic transition record pulses of terrestrial Cr-oxidation prior to the GOE and a lack of Cr-isotope fractionation immediately following the GOE, which is interpreted as a post-GOE decline in atmospheric  $p\text{O}_2$  (Frei *et al.*, 2009). Subsequent evidence for Cr-isotope fractionation was not found until ~750 Ma (Planavsky *et al.*, 2014), leading to the suggestion that low  $p\text{O}_2$  inhibited Cr-isotope fractionation during the mid-Proterozoic Eon. Here we extend the mid-Proterozoic record of positively fractionated Cr back to ~1.1 Ga – a revision of ~350 Ma from previous estimates (Fig. 2).



**Figure 2** Compilation of all published Proterozoic Cr-isotope data including new data presented here.  $\delta^{53}\text{Cr}_{\text{auth}}$  values (after detrital correction) are presented for data from this study.

At present, there is no clear consensus on the  $p\text{O}_2$  level required for Cr-isotope fractionation during terrestrial weathering. If we take soil residence time calculations (~0.1 to 1 % PAL; Planavsky *et al.*, 2014) as our best estimate, we conclude that  $p\text{O}_2$  at least transiently exceeded ~0.1 to 1 % PAL during the mid-Proterozoic Eon. These data are consistent with a broad range of proxies that suggest increasing biospheric oxygen in the Mesoproterozoic Era (Kah *et al.*, 2001; Johnston *et al.*, 2005; Parnell *et al.*, 2010; Zhang *et al.*, 2016). Data are potentially inconsistent, however, with recent estimates of maximum  $p\text{O}_2$  between 0.1 and 1 % PAL during the mid-Proterozoic Eon, including Cr-isotope data from sparse mid-Proterozoic iron oolites (Planavsky *et al.*, 2014; Liu *et al.*, 2016).



Potential conflict between our data and other proxies could be related to uncertainty regarding the  $pO_2$  threshold required for Cr-isotope fractionation. If we take 0.03 % PAL as the required threshold, for example, our data become compatible with the  $pO_2$  estimate of Liu *et al.* (2016) based on carbonate Zn/Fe systematics. Regardless of the threshold value, however, our data remain inconsistent with Cr-isotope data from mid-Proterozoic iron oolites. This discrepancy cannot be explained by Cr-isotope fractionation during carbonate formation, particularly if carbonates preferentially incorporate  $^{52}Cr$  (Mohanta *et al.*, 2016), which would only amplify evidence for positively fractionated Cr in mid-Proterozoic seawater. We have also robustly screened our samples for diagenesis using standard petrographic and geochemical criteria, although diagenetic effects cannot be completely discounted given uncertainty regarding Cr behaviour during carbonate diagenesis. To this end, we compared  $\delta^{53}Cr$  to  $\delta^{18}O$  as a diagenetic indicator, and found that the lowest  $\delta^{18}O$  values in our dataset – normally thought to reflect diagenetic alteration – are associated with unfractionated  $\delta^{53}Cr$  values (Fig. S-5). This could indicate that, at least in our dataset, diagenesis is more likely to give a false negative than a false positive result. Another possibility is that ironstone data do not record seawater  $\delta^{53}Cr$  because of partial Cr-reduction during precipitation of shallow water iron oolites, which may have occurred under fluctuating redox conditions. As articulated by Planavsky *et al.* (2014), however, this would be expected to generate a range of  $\delta^{53}Cr$  values – not the persistently unfractionated values that were measured.

Another alternative is that mid-Proterozoic  $pO_2$  was variable around the threshold required for Cr-isotope fractionation. There is evidence for this in our dataset – the persistence of unfractionated  $\delta^{53}Cr$  values that are not related to detrital contamination (Fig. 1) could be related to transient periods of  $pO_2$  below threshold values. Indeed the only measured iron oolites that temporally overlap with samples from this study are limited samples from the ~0.9 Ga Aok Formation (Canada), implying that the coarse temporal resolution of current data may be insufficient to track short-term variability in  $pO_2$ . Taken together with the full range of published proxy data, we conclude that mid-Proterozoic  $pO_2$  was likely more dynamic than previously envisaged.

## Biological Implications

Implications of our data on biospheric evolution are similarly tied to uncertainty regarding the  $pO_2$  threshold needed for Cr-isotope fractionation. Tank experiments have shown that sponges can survive when  $pO_2$  is as low as 0.5 to 4 % PAL, leading Mills *et al.* (2014) to conclude that this level was likely sufficient for the origin of animals. Based on theoretical early annelid body plans, a small worm with a circulatory system could likely survive at  $pO_2$  as low as 0.14 % PAL (Sperling *et al.*, 2013a). Studies from modern oxygen minimum zones confirm these estimates and suggest that the bilaterian body plan would only be inhibited if  $pO_2$  were below 0.4 % PAL. If we take 0.1 to 1 % PAL as the threshold required

for Cr-isotope fractionation, then our data suggest that  $pO_2$  levels sufficient for the origin of animals were at least transiently in place by ~1.1 Ga – some 300 Ma before the origin of sponges based on molecular clock estimates (Erwin *et al.*, 2011) and >450 Ma before the first appearance of animals in the fossil record. By contrast, if we take a lower threshold value of 0.03 % PAL, then our data have less direct implications for biology. Ecological considerations are also important and modern oxygen minimum zones suggest that there is a clear linkage between oxygen availability, animal size, and the relative proportion of carnivorous taxa (Sperling *et al.*, 2013b). Based on these considerations it seems that, although the oxygen requirements of small, simple animals were likely met by ~1.1 Ga, low atmospheric  $pO_2$  may still have inhibited the development of larger, more energetic animals that have greater preservation potential in the fossil record.

## Conclusions

This study demonstrates the viability of the Cr-isotope palaeo-redox proxy as it is applied to ancient carbonate rocks. After screening for detrital contamination – and assuming that our least-altered samples are able to retain original  $\delta^{53}Cr$  values – Cr-isotope data can be interpreted in the context of ancient atmospheric  $pO_2$ . Results from four carbonate successions extend the mid-Proterozoic record of positively fractionated Cr back to ~1.1 Ga – a revision of ~350 Ma from previous estimates. If we take 0.1 to 1 % PAL as the  $pO_2$  threshold needed for Cr-isotope fractionation, then our data suggest that the oxygen requirements of small, simple animals were at least transiently met well prior to their Neoproterozoic appearance, although uncertainty regarding this  $pO_2$  threshold precludes definitive biological interpretation. Ultimately, the development of novel carbonate-based redox proxies has the potential to greatly enhance the temporal resolution of palaeo-redox data for the Proterozoic Eon.

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## Additional Information

**Supplementary Information** accompanies this letter at [www.geochemicalperspectivesletters.org/article1618](http://www.geochemicalperspectivesletters.org/article1618)

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