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Oxygenation of the mid-Proterozoic atmosphere: clues from chromium isotopes in carbonate rocks

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Abstract

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 $pO_2$ exceeds a threshold value. This is a useful system when applied to rocks of mid-Proterozoic age, where fundamental questions persist about atmospheric $pO_2$ and its relationship to biological innovation. Whereas previous studies have focused on temporally limited iron-rich sedimentary rocks, we present a pilot study of Cr-isotopes in 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 $\delta^{53}$Cr values in four carbonate successions, extending the mid-Proterozoic record of Cr-isotope fractionation—and thus $pO_2$ above threshold values—back to ~1.1 Ga. These data suggest that $pO_2$ sufficient for the origin of animals was transiently in place well before their Neoproterozoic
appearance, although uncertainty in the \( pO_2 \) 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.

**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 (Izbicki *et al.*, 2008). Cr(VI) (dominantly as chromate; \( \text{CrO}_4^{2-} \)) is then carried to the oceans via rivers, thus imparting a positively fractionated \( \delta^{53}\text{Cr} \) signal on modern seawater (+0.13 to +1.55‰ compared to crustal values of −0.123 ± 0.102‰) (Schoenberg *et al.*, 2008; Bonnand *et al.*, 2013; Scheiderich *et al.*, 2015; Wang *et al.*, 2016; Paulukat *et al.*, in prep.). Terrestrial Cr(III)-oxidation occurs by reaction with manganese (Mn) oxides (Oze *et al.*, 2007), and it is thought that Mn-oxide formation requires a threshold level of \( O_2 \) in the atmosphere. Frei *et al.* (2016) suggested that Cr-oxidation by Mn-oxides is thermodynamically possible at \( pO_2 \) as low as \( 10^{-5} \) of the present atmospheric level (PAL). Kinetic considerations dictate, however, that 0.1 to 1 % PAL is necessary to oxidize 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). Thus, the Cr-isotope system serves as a sensitive binary indicator of atmospheric \( pO_2 \) above or below these threshold values. Upon entering the marine environment, Cr(VI) can be reduced back to particle-reactive Cr(III)—a process that preferentially utilizes \( ^{52}\text{Cr} \), leaving residual Cr(VI) \( ^{53}\text{Cr} \)-enriched.
As a result, differing degrees of *in situ* Cr-reduction control Cr-isotope heterogeneity in the modern oceans (Scheiderich *et al*., 2015; Paulakut *et al*., *in prep*.).

Because terrestrial Cr-oxidation is sensitive to atmospheric oxygen, the Cr-isotope composition of seawater through time—as recorded in marine sedimentary rocks—is a potentially powerful tool for reconstructing ancient atmospheric $pO_2$. This is particularly useful for testing hypotheses about atmospheric oxygenation during the Proterozoic Eon, where fundamental questions persist about the $O_2$ 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). Two first-order oxygen pulses have been identified from the Proterozoic geologic record. During the Great Oxidation Event (GOE) at ~2.4 Ga, $pO_2$ was sustained above $10^{-5}$ PAL for the first time in Earth history (Pavlov and Kasting, 2002), although transient ‘whiffs’ of $O_2$ have been recognized from the Archaean geochemical record (Anbar *et al*., 2007). During a subsequent Neoproterozoic oxygenation event (NOE) at ~635-550 Ma, $pO_2$ began to rise to near-modern levels—a transition that continued into the Palaeozoic Era (Och and Shields-Zhou, 2012).

Empirical constraints remain limited, however, on $pO_2$ during the prolonged period in between. Constraining $pO_2$ 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 $pO_2$ was a direct impediment to
metazoan evolution prior to the Neoproterozoic Era (Lyons et al., 2014; Planavsky et al., 2014; Tang et al., 2016), whereas others argue that oxygen levels required by early animals were in place long before their Neoproterozoic appearance (Butterfield, 2009; Mills et al., 2014; Zhang et al., 2016). Mid-Proterozoic Cr-isotope data have the potential to inform this debate because estimates of the \( pO_2 \) threshold needed for Cr-isotope fractionation are roughly similar to experimental and theoretical estimates of the \( O_2 \) requirements of early animals (0.3 to 4 % PAL) (Levin, 2003; Palma et al., 2005; Sperling et al., 2013a; Mills et al., 2014).

Thus far, studies have largely focused on iron-rich sedimentary rocks as an archive for ancient seawater \( \delta^{53}Cr \) values (Planavsky et al., 2014; Frei et al., 2009; 2016). In the presence of Fe(II), seawater Cr(VI) is reduced to Cr(III) and can be co-precipitated with Fe-oxyhydroxides (Døssing et al., 2011). Cr reduction favors the light \( ^{52}Cr \) isotope, so that iron-rich rocks record seawater \( \delta^{53}Cr \) 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; Planavsky et al., 2014). 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 an alternative lithology (marine carbonate rocks) that is ubiquitous in the mid-Proterozoic geologic
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 (coral, bivalves, gastropods) reveal that Cr-isotope fractionation does occur during biomineralization, making skeletal carbonates an unreliable archive of seawater $\delta^{53}\text{Cr}$ values (Paulukat et al., 2015; 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 $\leq0.1$ ‰ 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; Scheiderich et al., 2015; Paulukat et al., in prep.).

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. Our data are discussed in the context of best practices regarding diagenesis and detrital contamination, and ultimately, used to provide important new constraints on atmospheric $p\text{O}_2$ during the mid-Proterozoic Eon.
Geologic Background
Samples were analyzed 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). Detailed description of the geologic setting, depositional environments, geochronology, and post-depositional history of each succession can be found in the Supplementary Information.

Analytical Methods
Chromium separation and isotopic analysis techniques were modified from Pereira et al. (2016). All Cr-isotope and Cr concentration measurements were performed at the University of Copenhagen on a thermal ionization mass spectrometer (TIMS). Ca, Mg, Fe, Sr, Mn, and Al concentrations were measured by ICP-OES on splits of the same solutions used for Cr-isotopic analysis. Ti and Zr concentrations were measured by ICP-MS at the Geological Survey of Denmark and Greenland. Additional detail can be found in the Supplementary Information.

Diagenetic Considerations
Carbonate minerals are reactive in the diagenetic environment so that care must be taken in selecting the best-preserved samples for isotopic analysis. Criteria for sample inclusion were based upon conventional petrography, carbon and oxygen isotope compositions, and trace element concentrations. Micritic to microsparitic textures characterize most samples, with the exception of discrete intervals of alteration that were excluded (Figs.
Similarly, $\delta^{13}$C, $\delta^{18}$O, and trace element signatures are in line with typical least-altered mid-Proterozoic limestone and dolostone (Kah et al., 1999) with some exceptions that were considered altered, and thus excluded (Fig. SI-3). A total of 17 samples were excluded based on diagenetic criteria, including 13 from the Vazante Group. Interestingly, samples that are considered altered—with lower than average $\delta^{18}$O values—tend to have unfractionated $\delta^{53}$Cr values that approach average crust ($-0.12 \%$e) (Fig. SI-4). This may indicate that discrete intervals of alteration (particularly in the Vazante Group) were characterized by a resetting of the $\delta^{53}$Cr signal to crustal values. Future study should investigate this possibility, but for the purposes of this study, these samples were excluded based on standard diagenetic criteria. Additional textural and geochemical information can be found in the Supplementary Information.

The only previously published study on Cr-isotopes in carbonate rocks (Frei et al., 2011) demonstrated stratigraphic $\delta^{53}$Cr trends that mirror primary $\delta^{13}$C trends across a mixed limestone-dolostone interval. Because the C-isotope signal is thought to reflect seawater, co-variation with $\delta^{53}$Cr speaks to the fidelity potential of Cr-isotopes in both limestone and dolostone and suggests that, in the absence of further study on Cr-isotope behavior during diagenesis, standard petrographic and geochemical criteria can be used as a starting point for Cr-isotope diagenetic screening.

**Detrital Chromium Contamination**

Our results indicate a broad range of $\delta^{53}$Cr values in each succession, ranging from crustal values (near $-0.12 \%$e) to strongly positive values (up to $+1.77 \%$e). To understand
this isotopic heterogeneity, we first evaluated the degree to which measured $\delta^{53}$Cr values reflect authigenic Cr in carbonate vs. allogenic Cr from detrital sources. As part of each dissolution for $\delta^{53}$Cr analysis, we measured a split for aluminum (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. measured $\delta^{53}$Cr values (Fig. 1A), positively fractionated $\delta^{53}$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 $\delta^{53}$Cr is only observed when leachate titanium (Ti) and zirconium (Zr) concentrations are generally less than 10 and 1 ppm, respectively (Fig. SI-5), 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 $\delta^{53}$Cr is only recorded in samples where less than ~35 % of measured Cr is detritally sourced (Fig. 1B).

These trends represent a mixing curve where Cr in the carbonate lattice is dissolved and analyzed in addition to Cr leached from clay. When detrital Cr exceeds ~35 % of total measured Cr, $\delta^{53}$Cr values approach average crust (~0.12 ‰) 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 measured $\delta^{53}$Cr values, assuming the detrital component has a crustal $\delta^{53}$Cr value. This yields a first-order estimate of the isotopic composition of the authigenic Cr component ($\delta^{53}$Cr$_{auth}$), which is
derived from seawater (see Supplementary Information). We also performed corrections using post-Archaean Australian shale (PAAS) values (Taylor and McLennan, 1985) instead of the average shale composite of Wedepohl (1991), but found <2 % differences in estimates of detrital Cr contribution and < 0.02 ‰ differences in corrected $\delta^{53}$Cr$_{auth}$ values.

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 studies that examine the Cr-isotopic composition of carbonate rocks.

**Constraining Atmospheric Oxygen**

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

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 $pO_2$ (Frei et al., 2009). Subsequent evidence for Cr-isotope
fractionation is not found until ~750 Ma (Planavsky et al., 2014), leading to the
suggestion that persistently low $pO_2$ inhibited Cr-isotope fractionation during the entire
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).

At present, there is no clear consensus on the $pO_2$ level required for Cr-isotope
fractionation during terrestrial weathering (e.g., Crowe et al., 2013; Planavsky et al.,
2014; Frei et al., 2016). If we take soil residence time calculations (~0.1 to 1 % PAL;
Planavsky et al., 2014) as our best estimate, we conclude that $pO_2$ 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 mild biospheric oxygenation in the
Mesoproterozoic Era (Kah et al., 1999; 2001; 2004; Frank et al., 2003; Johnston et al.,
2005; Parnell et al., 2010; Spinks et al., 2014; Zhang et al., 2016). Data are potentially
inconsistent, however, with recent estimates of $pO_2$ persistently between or below 0.1 to
1 % PAL throughout the entire mid-Proterozoic Eon (Lyons et al., 2014; Liu et al., 2016;
Tang et al., 2016), including Cr-isotope data from sparse mid-Proterozoic iron oolites
(Planavsky et al., 2014).
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 (Crowe et al., 2013), 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 (Planavsky et al., 2014). This discrepancy cannot be explained by Cr-isotope fractionation during carbonate formation, particularly if carbonates preferentially incorporate $^{52}\text{Cr}$ (Mohanta et al., 2016), which would only amplify evidence for positively fractionated Cr in mid-Proterozoic seawater. Carbonate diagenesis can also be excluded because least-altered samples in our dataset have positive $\delta^{53}\text{Cr}$ values and, in samples where there is evidence for diagenesis, unfractionated $\delta^{53}\text{Cr}$ values are recorded. This indicates 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 $\delta^{53}\text{Cr}$ 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 $\delta^{53}\text{Cr}$ 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 $\delta^{53}\text{Cr}$ 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
\( pO_2 \). Data from earlier Proterozoic carbonate successions are needed to further test the
hypothesis of Planavsky et al. (2014). Taken together with the full range of published
proxy data (Frank et al., 2003; Kah et al., 2004; Johnston et al., 2005; Parnell et al.,
2010; Planavsky et al., 2014; Liu et al., 2016; Tang et al., 2016; Zhang et al., 2016), 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 (Levin, 2003; Palma et al., 2005;
Sperling et al., 2013a). If we take 0.1 to 1 % PAL as the threshold required for Cr-isotope
fractionation (Planavsky et al., 2014), 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 (Narbonne, 2005). By
contrast, if we take the lower threshold value of 0.03 % PAL proposed by Crowe et al.
(2013), 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 and Outlook

This pilot study demonstrates the viability of the Cr-isotope palaeo-redox proxy as it is applied to ancient carbonate rocks. Once best screening practices for diagenesis and detrital contamination are applied, 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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Figure 1

- Figure 1 shows the relationship between $\delta^{53}$Cr and Al in leachate, as well as the percentage of detrital Cr, based on Cr/Al enrichment above average shale.

- The data is categorized into two sections:
  - **A**: Turukhansk, Angmaat, El Mreiti, and Vazante samples are represented.
  - **B**: The same samples are shown, with a focus on the Crustal Cr reservoir and Authigenic Cr influence.

- The graph illustrates the measured $\delta^{53}$Cr values on the y-axis and Al in leachate on the x-axis, with % detrital Cr (based on Cr/Al enrichment above average shale) indicated on the right side of the graph.
**Figure 2**

A diagram showing the variation of δ^{53}Cr values with age (millions of years) across different geological formations. The diagram includes data for Limestone, Dolostone, Shale, Ironstone, Banded iron formation, Massive iron formation, and the Crustal Cr reservoir. Key observations include:

- **Positively fractionated Cr(VI) in mid-Proterozoic oceans**
- **Appearance of animals in the fossil record**

The δ^{53}Cr values range from -0.5 to +2.0‰, with a notable peak around +4.92‰ up to 2000 million years ago. The Crustal Cr reservoir is indicated by a horizontal band at δ^{53}Cr values of -0.5 to +0.5‰.
Figure SI-3

The figure shows a scatter plot of δ¹³C (‰ vs. VPDB) and δ¹⁸O (‰ vs. VPDB) values. The scatter plot highlights typical δ¹⁸O values of least-altered Proterozoic carbonate and indicates sedimentary evidence for evaporative conditions during diagenesis. The plot also includes Mn/Sr ratios expressed in ppm/ppm.

- The δ¹³C values range from -6 to +4‰.
- The δ¹⁸O values range from -14 to 0‰.
- Mn/Sr ratios range from 0 to 25 ppm/ppm.

Key observations:
- Typical δ¹⁸O values of least-altered Proterozoic carbonate.
- Sedimentary evidence for evaporative conditions.
- Mn/Sr ratios indicating diagenesis.

The figure provides evidence for the transformation of carbonate sediments under specific environmental conditions, as indicated by the δ isotopic values and Mn/Sr ratios.
Figure SI-4

The diagram shows a scatter plot of δ⁵³Cr (‰) vs. δ¹⁸O (‰ vs. VPDB) for Limestone and Dolostone samples. The data points indicate a possible trend or pattern related to diagenesis and crustal Cr reservoir. The presence of an arrow labeled "Diagenesis?" suggests a point of interest or question in the data analysis.
Figure SI-5

The figure shows a scatter plot with two panels labeled A and B. The x-axis represents Ti in leachate (ppm) for Panel A and Zr in leachate (ppm) for Panel B. The y-axis represents measured δ53Cr (‰). The plot includes data points for Turukhansk, Angmaat, El Mreiti, and Vazante, indicated by different colors.

The plot highlights the crustal Cr reservoir and the authigenic Cr influence. Arrows indicate a δ53Cr deviation of +1.77‰.