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

Geoffrey J. Gilleaudeau[1,*], Robert Frei[1], Alan J. Kaufman[2], Linda C. Kah[3], Karem Azmy[4], Julie K. Bartley[5], Pavel Chernyavskiy[6], Andrew H. Knoll[7]

[1]Department of Geosciences and Natural Resource Management, University of Copenhagen, Øster Voldgade 10, 1350 Copenhagen, Denmark; ggillea1@gmail.com; robertf@ign.ku.dk

[2]Department of Geology, University of Maryland, College Park, MD 20742, USA; kaufman@geol.umd.edu

[3]Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN 37996, USA; lckah@utk.edu

[4]Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X5, Canada; kazmy@mun.ca

[5]Department of Geology, Gustavus Adolphus College, St. Peter, MN 56082, USA; jbartley@gustavus.edu

[6]Biostatistics/Radiation Epidemiology Branch, National Cancer Institute, National Institutes of Health, Rockville, MD 20850, USA; pchern1@gmail.com

[7]Department of Organismic and Evolutionary Biology, Harvard University, Cambridge, MA 02138, USA; aknoll@oeb.harvard.edu

*Corresponding author: ggillea1@gmail.com
Current address: School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85281, USA

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}Cr-enriched mobile Cr(VI) to solution (Izbicki *et al.*, 2008). Cr(VI) (dominantly as chromate; CrO_4^-) is then carried to the oceans via rivers, thus imparting a positively fractionated δ^{53}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}Cr, leaving residual Cr(VI) ^{53}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

92 metazoan evolution prior to the Neoproterozoic Era (Lyons *et al*., 2014; Planavsky *et al*.,
93 2014; Tang *et al*., 2016), whereas others argue that oxygen levels required by early
94 animals were in place long before their Neoproterozoic appearance (Butterfield, 2009;
95 Mills *et al*., 2014; Zhang *et al*., 2016). Mid-Proterozoic Cr-isotope data have the potential
96 to inform this debate because estimates of the pO_2 threshold needed for Cr-isotope
97 fractionation are roughly similar to experimental and theoretical estimates of the O_2
98 requirements of early animals (0.3 to 4 % PAL) (Levin, 2003; Palma *et al*., 2005;
99 Sperling *et al*., 2013a; Mills *et al*., 2014).
100
101 Thus far, studies have largely focused on iron-rich sedimentary rocks as an archive for
102 ancient seawater $\delta^{53}Cr$ values (Planavsky *et al*., 2014; Frei *et al*., 2009; 2016). In the
103 presence of Fe(II), seawater Cr(VI) is reduced to Cr(III) and can be co-precipitated with
104 Fe-oxyhydroxides (Døssing *et al*., 2011). Cr reduction favors the light ^{52}Cr isotope, so
105 that iron-rich rocks record seawater $\delta^{53}Cr$ values only if Cr reduction is quantitative.
106 Ironstone and iron formation data have thus far provided important constraints on
107 Archaean 'whiffs' of oxygen and the subsequent GOE, as well as new clues about the
108 NOE (Frei *et al*., 2009; Planavsky *et al*., 2014). Sparse ironstone data from the mid-
109 Proterozoic suggest a lack of Cr-isotope fractionation (Planavsky *et al*., 2014). Iron-rich
110 rocks are rare in mid-Proterozoic successions, however, limiting our ability to generate
111 data for the crucial period preceding the NOE.
112
113 The impetus of this study, then, is to test the reliability of Cr-isotopes in an alternative
114 lithology (marine carbonate rocks) that is 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 (coral, bivalves, gastropods) reveal that Cr-isotope fractionation does occur during biomineralization, making skeletal carbonates an unreliable archive of seawater δ^{53}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 δ^{53}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; 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 pO_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.

SI-1, SI-2). 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 ‰) (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 ‰) to strongly positive values (up to +1.77 ‰). 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}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 $\delta^{53}Cr$ values and, in samples where there is evidence for diagenesis, unfractionated $\delta^{53}Cr$ 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 $\delta^{53}Cr$ 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. 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

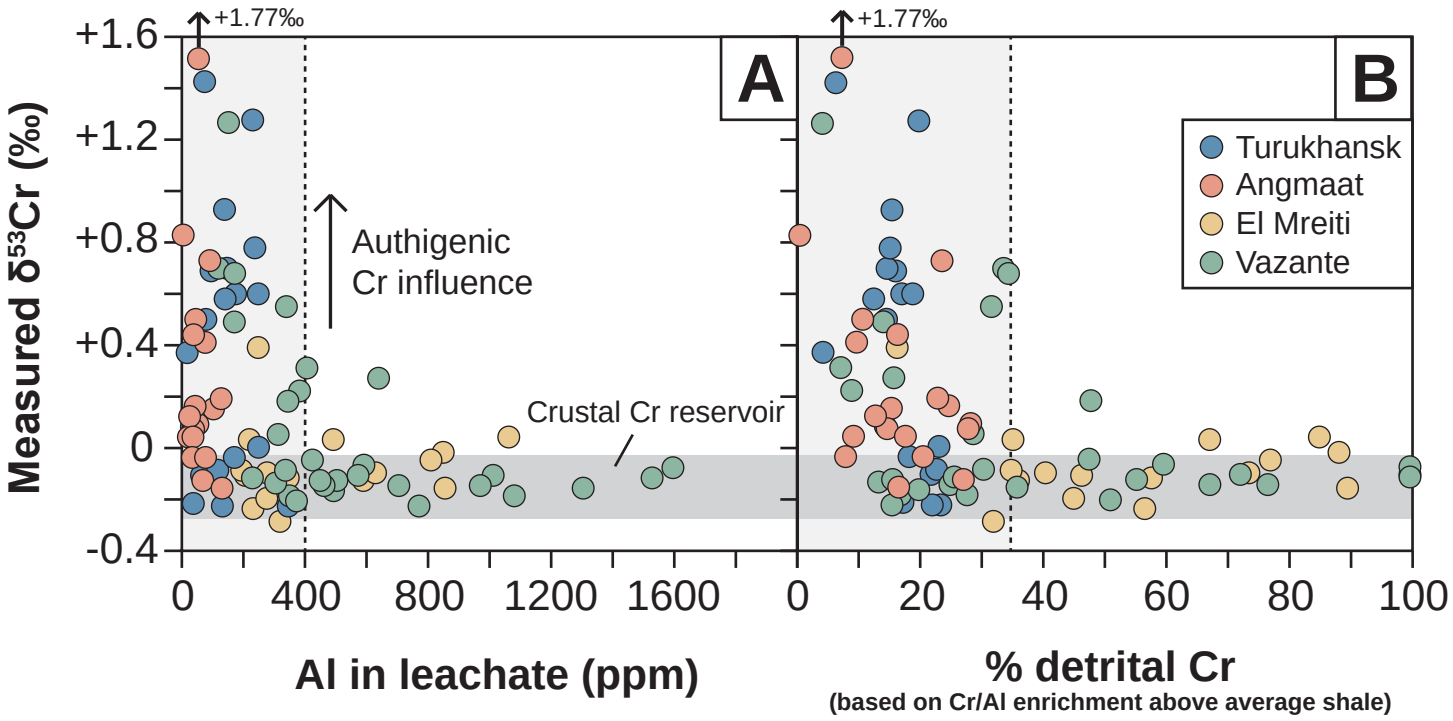

+1.77‰
+1.77‰
A
B
Turukhansk
Angmaat
El Mreiti
Vazante
Authigenic
Cr influence
Crustal Cr reservoir
Measured δ53Cr (‰)
+1.6
+1.2
+0.8
+0.4
0
-0.4
0
400
800
1200
1600
0
20
40
60
80
100
Al in leachate (ppm)
% detrital Cr
(based on Cr/Al enrichment above average shale)

Figure 2

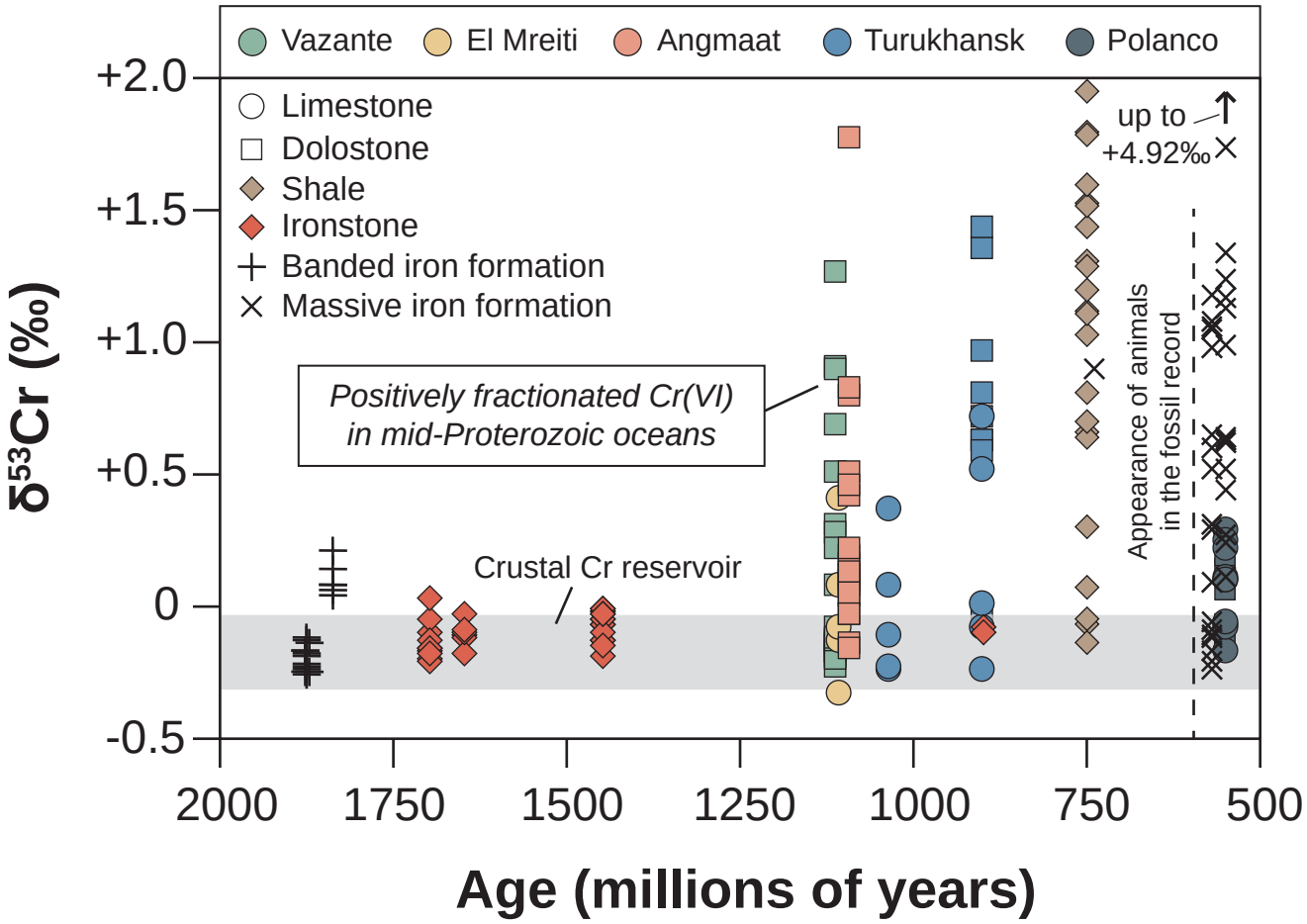

Vazante
El Mreiti
Angmaat
Turukhansk
Polanco
Limestone
Dolostone
Shale
Ironstone
Banded iron formation
Massive iron formation
Positively fractionated Cr(VI) in mid-Proterozoic oceans
Crustal Cr reservoir
up to +4.92‰
Appearance of animals in the fossil record
δ53Cr (‰)
+2.0
+1.5
+1.0
+0.5
0
-0.5
2000
1750
1500
1250
1000
750
500
Age (millions of years)

Figure SI-1

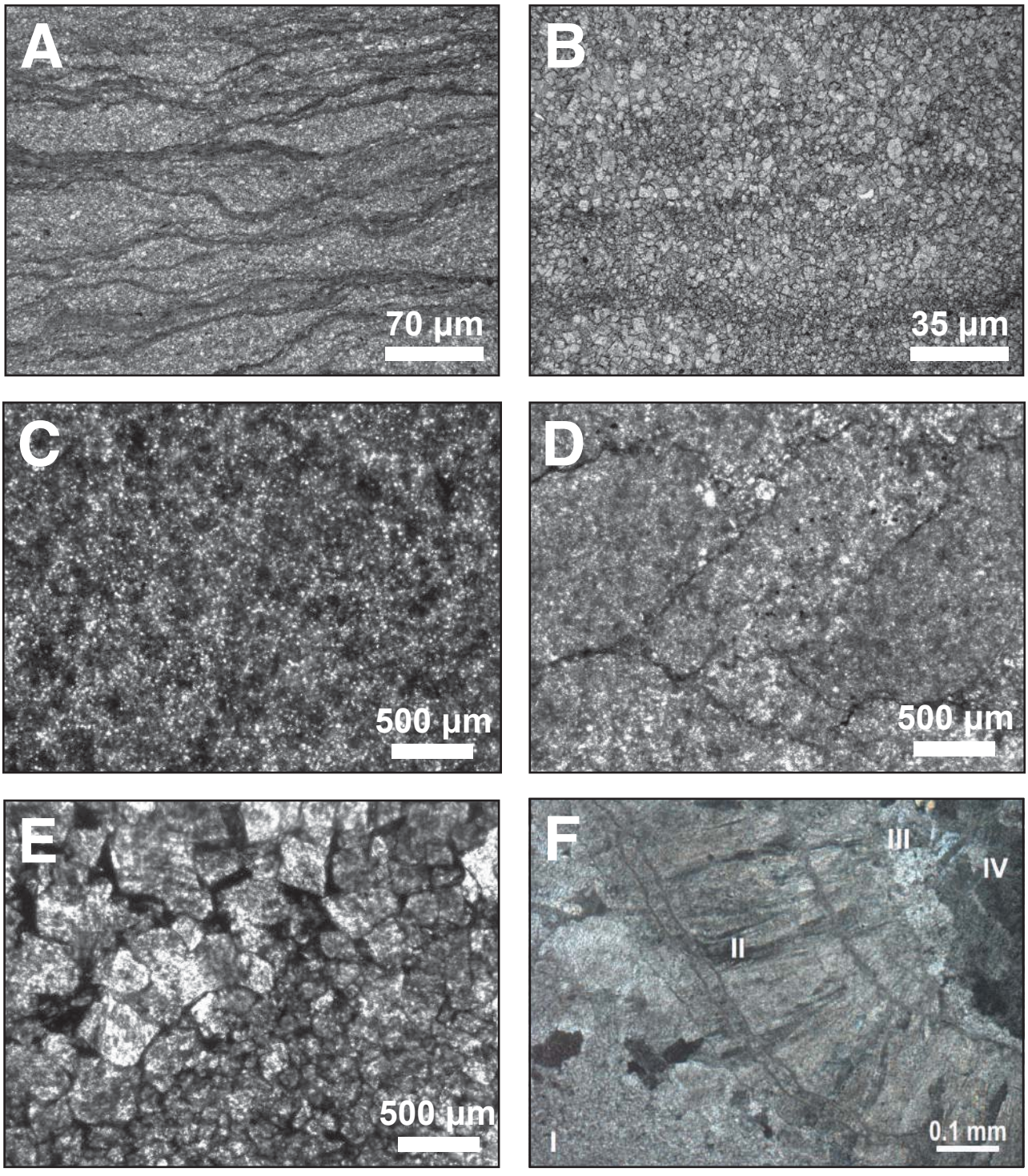


Figure SI-2

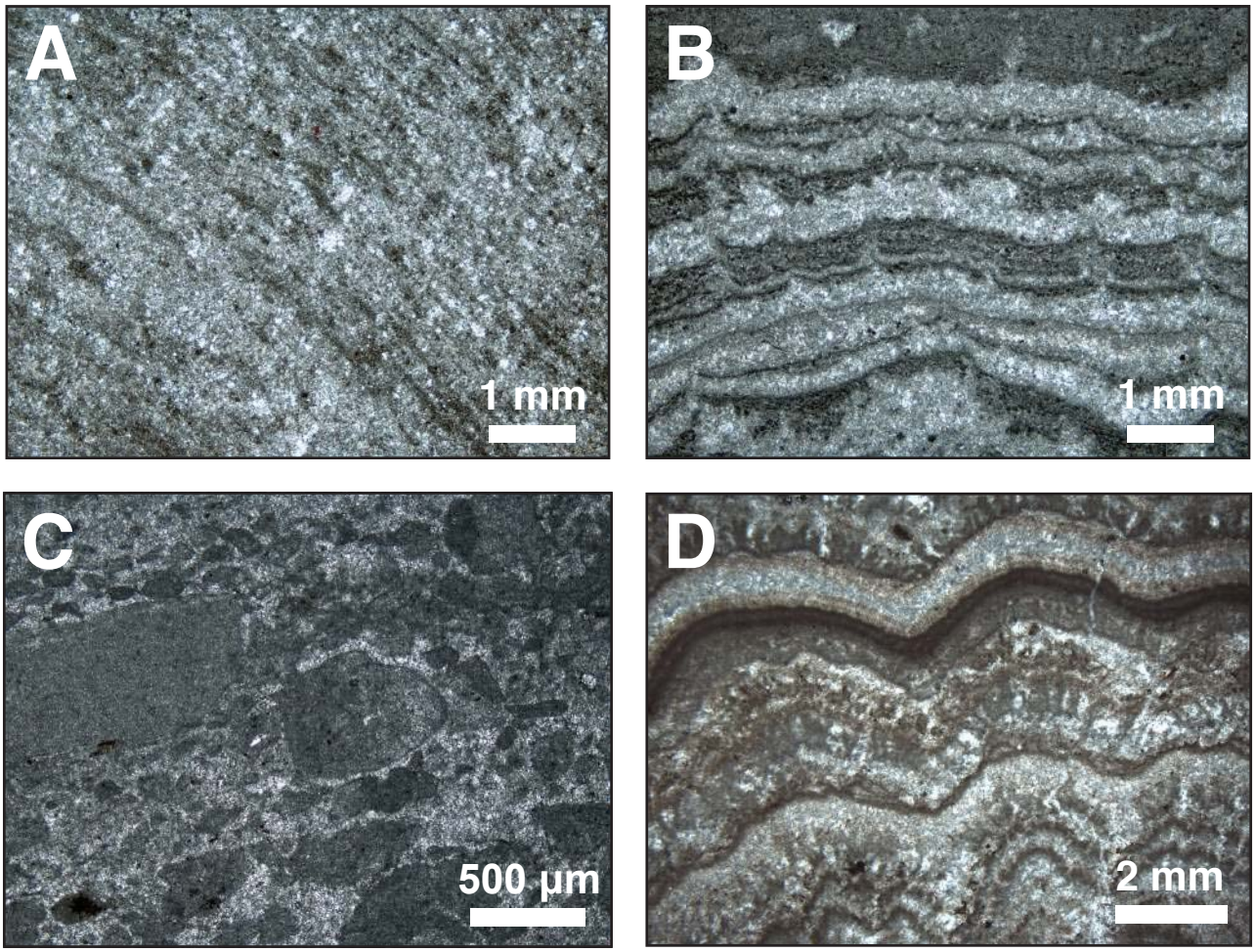
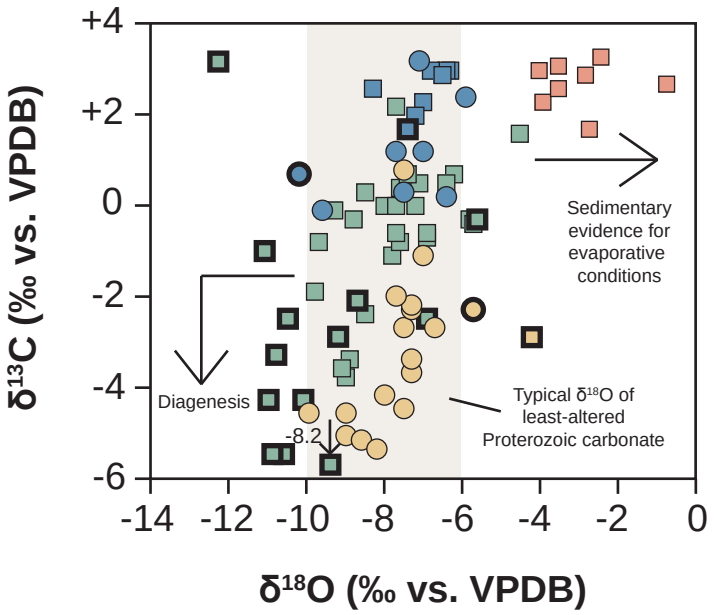


Figure SI-3


+4
+2
0
-2
-4
-6
-14
-12
-10
-8
-6
-4
-2
0
δ13C (‰ vs. VPDB)
δ18O (‰ vs. VPDB)
Sedimentary evidence for evaporative conditions
Diagenesis
-8.2
Typical δ18O of least-altered Proterozoic carbonate

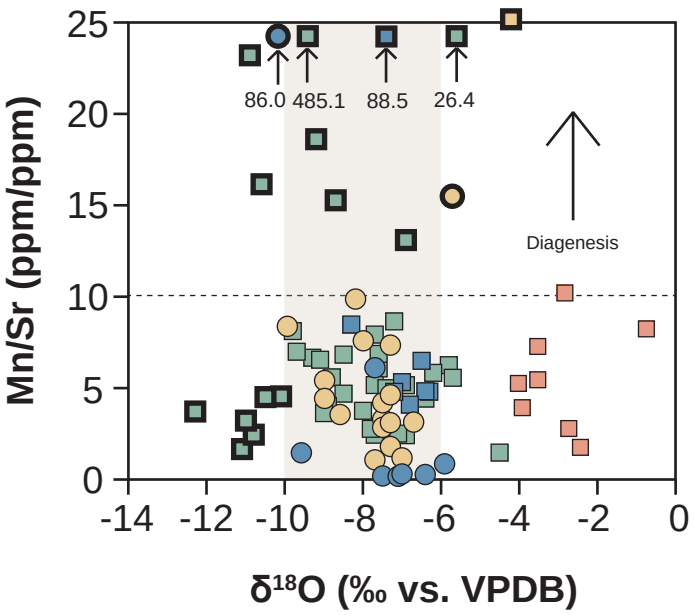

25
20
15
10
5
0
-14
-12
-10
-8
-6
-4
-2
0
Mn/Sr (ppm/ppm)
δ18O (‰ vs. VPDB)
86.0
485.1
88.5
26.4
Diagenesis

Figure SI-4

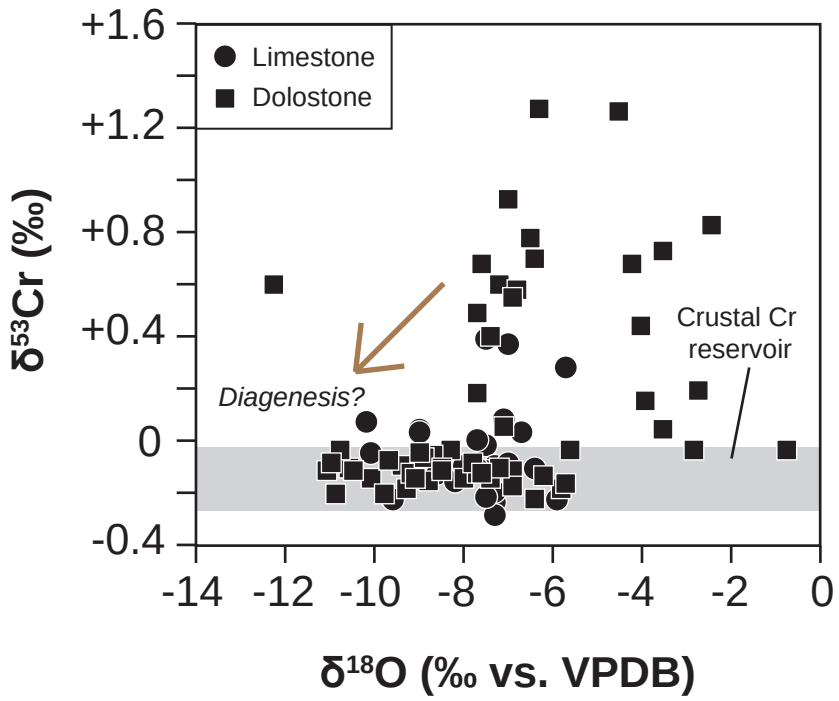
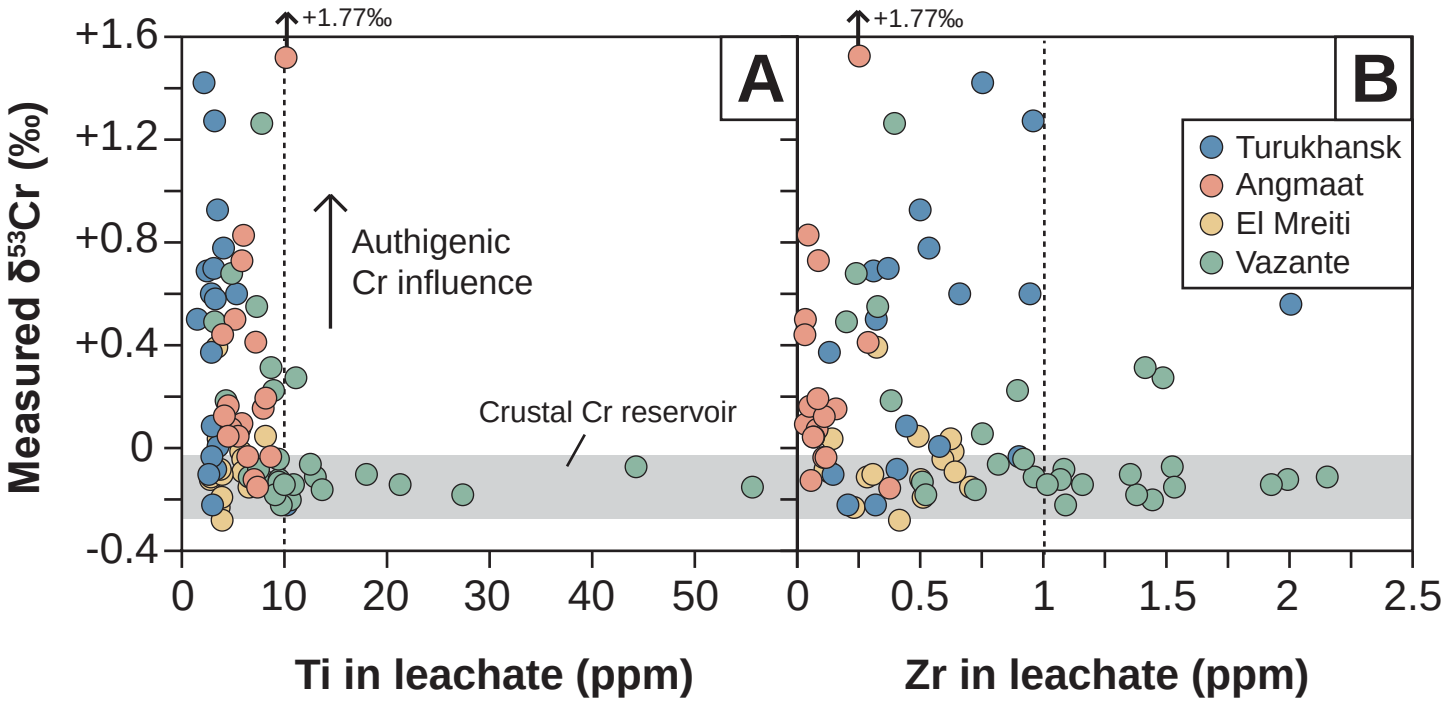

Limestone
Dolostone
Diagenesis?
Crustal Cr reservoir
+1.6
+1.2
+0.8
+0.4
0
-0.4
-14
-12
-10
-8
-6
-4
-2
0
δ53Cr (‰)
δ18O (‰ vs. VPDB)

Figure SI-5


+1.77‰
+1.77‰
A
B
Turukhansk
Angmaat
El Mreiti
Vazante
Authigenic
Cr influence
Crustal Cr reservoir
Measured δ53Cr (‰)
+1.6
+1.2
+0.8
+0.4
0
-0.4
0
10
20
30
40
50
0
0.5
1
1.5
2
2.5
Ti in leachate (ppm)
Zr in leachate (ppm)