A shale-hosted Cr isotope record of low atmospheric oxygen during the Proterozoic

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ABSTRACT

The emergence and expansion of animal life on Earth represents a dramatic shift in the structure and complexity of the biosphere. A lack of firm constraints on surface oxygen levels during the mid-Proterozoic has resulted in heated debate as to whether the rise and earliest diversification of animals was directly linked to a change in environmental oxygen levels or, instead, simply reflects the timing of innovations in gene expression and developmental regulation and was independent of a direct environmental trigger. Here, we present chromium (Cr) isotope data from marine black shales that provide evidence for minimal Cr oxidation throughout the mid-Proterozoic leading up to the diversification of eukaryotes and the rise of animals during the late Neoproterozoic. This observation requires very low background oxygen levels (<1% of present atmospheric levels). Accepting previously proposed estimates of $p\mathrm{O}_2$ levels needed to induce Cr isotope fractionation, our data provide support for the persistence of an Earth system in which baseline atmospheric $p\mathrm{O}_2$ would have been low enough to inhibit the diversification of animals until ca. 800 Ma. More generally, evidence for a delayed rise of atmospheric oxygen strongly suggests that environmental factors have played a fundamental role in controlling the emergence and expansion of complex life on Earth.

INTRODUCTION

There has been a surge of work over the past two decades aimed at better understanding and quantifying Earth's protracted oxygenation. Despite major advances (e.g., Holland, 2006; Lyons et al., 2014), quantitative understanding of Earth surface oxygen levels during the ~1 g.y. leading up to the rise and early diversification of metazoan (animal) life remains fragmented and imprecise, impeding our ability to evaluate the relationship between environmental change and biologic innovation during a critical interval in eukaryotic evolution. Molecular divergence estimates place the appearance and early diversification of basal metazoans between ca. 800 and 700 Ma, ~1 g.y. after the first emergence of eukaryotes (Erwin et al., 2011). Furthermore, these estimates coincide with a burst in microfossil diversity and emergence of sponges in the biomarker record, providing additional evidence for significant biotic diversification during the middle Neoproterozoic (Knoll, 2014; Love et al., 2009). However, lack of a continuous quantitative history of Earth surface $p\mathrm{O}_2$ prior to and during this period has precluded a direct test of the role of environmental oxygen levels in spurring the early evolution and ecological expansion of animal life.

Atmospheric oxygen is now generally accepted to have risen from trace levels (<10^5 present atmospheric levels [PAL]) near the Archean-Proterozoic boundary following the Great Oxidation Event (ca. 2.4 Ga) (e.g., Lyons et al., 2014), yet oxygen levels throughout the mid-Proterozoic remain the subject of debate. Traditional estimates for mid-Proterozoic oxygen range between a lower bound of ~1% PAL based on iron retention in paleosols (though poorly constrained assumptions could allow for even lower $p\mathrm{O}_2$ (Zbinden et al., 1988; Lyons et al., 2014), and an upper bound of ~40% PAL based on inferred ocean anoxia and steady-state ocean ventilation models (Holland, 2006; Kump, 2008). Recently, a preliminary, low-resolution Cr isotope record from iron-rich chemical sediments was used to suggest an upper limit on atmospheric oxygen of ~0.1% PAL through the mid-Proterozoic (Planavsky et al., 2014). Most significantly, this upper limit is below theoretical limits for the survival of earliest metazoan phyla, making the Cr isotope signal a powerful tool for resolving the relationship between biologic and environmental evolution. Of equal or greater importance, a baseline of

low atmospheric $p\mathrm{O}_2$ would have resulted in extreme spatiotemporal variability in surface redox conditions, likely placing likely stringent environmental constraints on early complex life (Reinhard et al., in press).

Tantalizing evidence for very low atmospheric $p\mathrm{O}_2$ during the mid-Proterozoic (<1% PAL; Lyons et al., 2014; Planavsky et al. 2014), if true, would overturn several widely accepted notions about the evolution of Earth's biogeochemical cycles. However, evidence for low Proterozoic oxygen levels is derived from iron-rich sedimentary systems that are only sporadically deposited throughout Earth's history, making it difficult to constrain the long-term persistence of low baseline atmospheric O_2. Herein we present a record of Cr isotope data from black shales—common throughout Earth history—to examine large-scale changes in Cr cycling through time and further our understanding of evolving atmospheric oxygen levels.

THE Cr ISOTOPE SYSTEM AS A TRACER OF ATMOSPHERIC OXYGEN

In Earth's crust, Cr exists within minerals in its reduced and poorly soluble state [Cr(III)]. Following exposure of Cr(III)-bearing minerals at Earth's surface, nearly all oxidation to Cr(VI) occurs during oxidative weathering via interaction with manganese (Mn) oxides in terrestrial environments where dissolved Cr(III) interacts with solid-phase Mn oxides at acidic or circumneutral pH (e.g., Kotaś and Stasicka, 2000). The resulting Cr(VI) forms highly soluble chromate oxyanion species ($HCrO_4^-$, CrO_4^-) which are ^{53}Cr enriched and readily delivered to the ocean via riverine transport. Soluble Cr(VI) species can be reduced back to insoluble Cr(III) in surface and ground waters during transport with a strong preference for light isotopes, further enriching the mobile Cr(VI) pool in isotopically heavy Cr if that reduction is incomplete (Zink et al., 2010).

The net result of these processes is $\delta^{53}Cr$ seawater values strongly fractionated from the bulk silicate Earth pool (BSE) on a planet with

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widespread and pervasive Cr redox cycling, providing an isotopically distinct surface Cr reservoir that will be transferred to the authigenic component of reducing marine sediments (i.e., black shale; Reinhard et al., 2014). In contrast, though there are mechanisms for the transport of Cr(III) in surface waters, including low pH and Cr(III) complexation with ligands (Yusof et al., 2007), a lack of surface oxidative cycling will strongly restrict Cr isotope fractionation during transport to the ocean. As a result, sedimentary authigenic Cr on a reducing Earth surface would be expected to show limited fractionation relative to BSE, reflecting transport and burial of Cr(III) species but a lack of Cr redox cycling.

Available constraints on the coupled Cr-Mn system suggest that a relatively low oxygen threshold is needed to induce Cr redox cycling and resulting fractionations in surface environments. More specifically, it has been estimated that extensive Cr redox cycling should occur on time scales of regolith development if atmospheric oxygen is above ~0.1% PAL (Crowe et al., 2013; Planavsky et al., 2014). Such a threshold makes the Cr isotope proxy ideally suited to identifying baseline shifts in pO_2 during Earth's early history as significant Cr redox cycling should occur a threshold below that required for basal animals to thrive. A sustained presence or absence of fractionation from BSE values can then provide vital information about the relationship between pO_2 and the timing of metazoan diversification (Crowe et al., 2013).

Identifying such baseline shifts in the oxidative cycling of Cr requires an archive both reliable and temporally continuous through deep time. Previous work has focused on Cr isotope systematics in iron formations and ironstones, which are thought to capture the terrestrial oxidative weathering signal in $\delta^{53}Cr$ (Frei et al., 2009; Planavsky et al., 2014). Chromium scavenging is rapid and quantitative in the presence of Fe(II), leaving iron-rich chemical sediments relatively enriched and well buffered with respect to Cr, providing an important archive. However, the stratigraphic record of these sediments is sparse and nearly nonexistent through much of the critical Meso-Neoproterozoic interval presaging the emergence of metazoan life. We have avoided the use of carbonate sedimentary rocks in our study, as transition metal concentrations tend to be low and poorly buffered in these lithologies and their signatures are traditionally viewed as products of diagenetic alteration, thus requiring extreme caution in their interpretation (e.g., Brand and Veizer, 1980; Derry et al., 1992; Jahn and Cuvellier, 1994). Instead, we have exploited the well-constrained trace element systematics and stratigraphic abundance of reducing marine siliciclastic sedimentary rocks (black shales) to reconstruct long-term baseline shifts in the Earth surface Cr cycle.
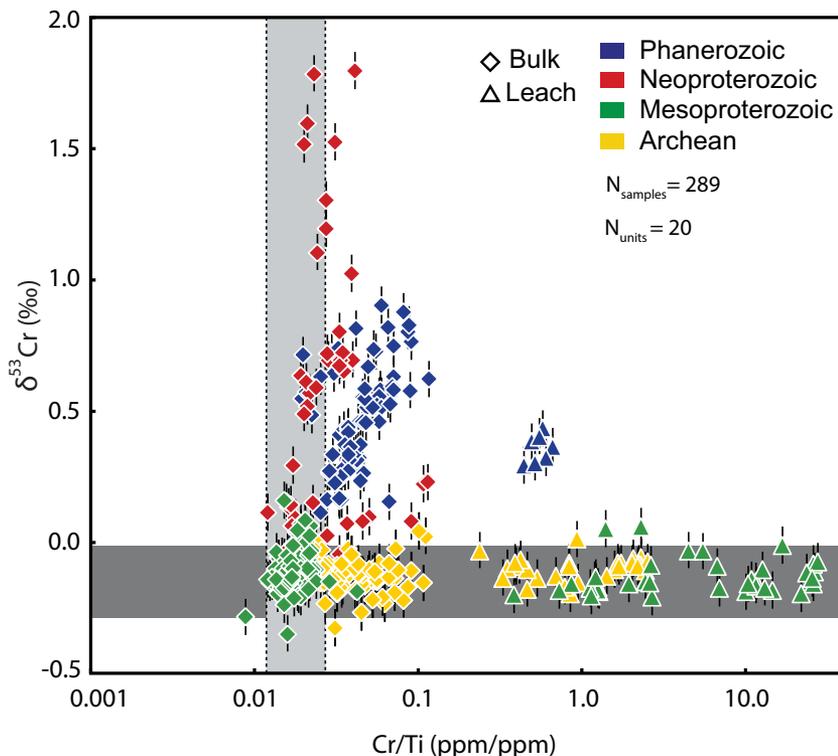

Figure 1. Cr isotope data of Archean, Mesoproterozoic, Neoproterozoic, and Phanerozoic time bins. Shown are $\delta^{53}Cr$ data of both bulk analyses (diamonds) and leach analyses (triangles) plotted against Cr/Ti ratios. Bulk silicate Earth (BSE) values are represented by dark gray bar ($\delta^{53}Cr = 0.124‰ ± 0.101‰$), while light gray bar shows range of Cr/Ti used for statistical analyses of bootstrap resampled mean values (Fig. 2). Phanerozoic data from Gueguen et al. (2016) and Reinhard et al. (2014).

A SHALE $\delta^{53}Cr$ RECORD THROUGH TIME

We have divided our shale $\delta^{53}Cr$ data into four time bins: Archean (4–2.5 Ga), Mesoproterozoic (1.6–1.0 Ga), Neoproterozoic (1.0–0.541 Ga), and Phanerozoic (0.541 Ga to present), to highlight distinct shifts in $\delta^{53}Cr$ values. Samples ($n = 289$) were chosen from previously examined, well-preserved, organic- and sulfide-rich black shale formations ($n = 20$), which have the most potential to develop authigenic Cr enrichments. Our samples represent a global distribution of localities and are taken from multiple cratons and ocean basins: Australia, China, India, Africa, North America, and Cenozoic sediment from deep-sea drill cores. Samples from multiple formations in each time bin were analyzed using a bulk rock dissolution and a separate weak acid leach, designed specifically to isolate authigenic Cr, which is more susceptible to dissolution than detrital Cr-bearing minerals (Reinhard et al., 2014). We have compared $\delta^{53}Cr$ values to Cr/Ti ratios (Fig. 1), as this ratio has been used to resolve the relative contribution of detrital and authigenic phases to Cr isotope values. Given that there is no evidence for a shift in the Cr/Ti ratio of the upper continental crust in the Proterozoic, studies (e.g., Gueguen et al., 2016; Reinhard et al., 2014) have typically utilized the upper continental crust value of

0.02 (Rudnick and Gao, 2014) as a baseline for detrital flux. However, variability in estimates for this value do exist, and it is important to recognize that our analysis allows for recognition of non-negligible authigenic enrichments (see GSA Data Repository[1]).

All $\delta^{53}Cr$ values in pre–1.0 Ga shale samples fall within error of the isotopic composition of BSE (Fig. 1). Specifically, isotopic compositions of Mesoproterozoic (mean $\delta^{53}Cr = 0.15‰ ± 0.09‰$) and Archean (mean $\delta^{53}Cr = 0.12‰ ± 0.06‰$) samples determined by both bulk and leach extractions are indistinguishable from BSE ($\delta^{53}Cr = 0.124‰ ± 0.101‰$; Schoenberg et al., 2008). In stark contrast, Neoproterozoic samples show significant fractionations (up to +1.80‰), with a mean value of +0.47‰ ± 0.56‰. Phanerozoic samples also show significant fractionation from crustal values with a mean of +0.48‰ ± 0.23‰ (Fig. 1).

In order to test that the shift from unfractionated to fractionated $\delta^{53}Cr$ values in the early Neoproterozoic tracks a shift in surface

Cr cycling instead of varying authigenic Cr enrichments, we performed a statistical analysis of δ⁵³Cr values within a range of Cr/Ti values across sample bins. We chose a Cr/Ti interval of 0.015–0.025 for our statistical comparison of δ⁵³Cr values— a range well represented by samples in all time bins. This range of Cr/Ti ratios allows for authigenic Cr enrichments that will lead to analytically resolvable Cr isotope signatures—evidenced by the abundance of post-850 Ma samples in this Cr/Ti bin that show fractionated δ⁵³Cr values. We find a statistically significant difference between the fractionated δ⁵³Cr values of the Neoproterozoic and Phanerozoic samples and the unfractionated δ⁵³Cr values of the Mesoproterozoic within this Cr/Ti bin ($p = 4.5 \times 10^{12}$) (Fig. 2). Further, within this range of Cr/Ti ratios, samples should have equal potential to capture fractionated δ⁵³Cr values based on the overlap of bootstrap resampled mean Cr/Ti values (see Data Repository). We do note the presence of small (0.1‰) isotopic fractionations in some Proterozoic shales; while these could be linked to an oxidative Cr cycle, such variations are difficult to interpret as they fall within the range of fractionations observed during non-redox-dependent processes (e.g., Saad et al., 2016). Regardless, we find the clear difference in δ⁵³Cr values when comparing pre– and post–850 Ma samples within the same Cr/Ti range to be compelling, and view this shift as indicative of a baseline transition in oxidative cycling of Cr during the early Neoproterozoic (ca. 0.9–0.8 Ga) (Fig. 3).

Within the pre–1.0 Ga sample group, there is no correlation between Cr enrichment and δ⁵³Cr (see Data Repository), consistent with the notion that varying authigenic enrichments are independent of redox controls. Further, the reproducibility of bulk δ⁵³Cr values in leachates, which preferentially extract authigenic Cr, supports the idea of limited Cr isotope variability (Gueguen et al., 2016; Reinhard et al., 2014). As a whole, the combined shale and iron-formation δ⁵³Cr records show a striking baseline shift from the very weakly fractionated to unfractionated values pre–850 Ma to highly fractionated data beginning in the Neoproterozoic—all within a single Cr/Ti range. This trend requires a secular change in oxidative Cr cycling on Earth's surface rather than changes in detrital dilution of an isotopically fractionated authigenic Cr pool.

Evidence for this base-level shift in surface oxidative processes has implications for our understanding of the relationship between the evolution of life and Earth surface environments. It has been speculated for decades that evolving ocean-atmosphere O_2 levels on Earth played a substantial role in the rise of early animals (e.g., Nursall, 1959). There is a sound basis for this idea—O_2 is by far the most efficient respiratory oxidant (Lane and Martin, 2010) and is vital for the basic biochemistry of eukaryotic
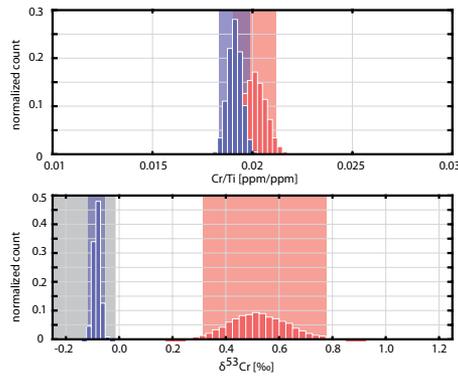

Figure 2. A: Bootstrap resampled mean values for Cr/Ti ratios in Mesoproterozoic (blue) and Neoproterozoic and Phanerozoic (red) samples with Cr/Ti ratios between 0.015 and 0.025. B: Bootstrap resampled mean values for δ⁵³Cr composition of Mesoproterozoic (blue) and Neoproterozoic and Phanerozoic (red) samples with Cr/Ti ratios between 0.015 and 0.025. Shaded regions represent 95% confidence intervals, while gray region represents the δ⁵³Cr range of bulk silicate Earth (BSE).

life (Summons et al., 2006). Recent work has sought to combine estimates of environmental oxygen surrounding periods of eukaryotic diversification with characterizations of oxygen requirements for discrete life stages of basal metazoans (Mills et al., 2014; Planavsky et al., 2014). Generally, these efforts are framed in terms of a threshold pO_2 value, above which complex life has the potential to flourish. These pO_2 cutoffs range from theoretical estimates of 0.14%–0.36% PAL based on diffusion (Sperling et al., 2013) to ~0.5%–4% PAL from experimental work with modern demosponges (Mills et al., 2014). Our data are consistent with limited Cr

oxidation prior to ca. 800 Ma, which, based on recent estimates of pO_2 levels needed to induce Cr oxidation (Crowe et al., 2013; Planavsky et al., 2014), suggest that low (<1% PAL) surface oxygen levels were a temporally pervasive feature of the Proterozoic Earth. Persistently low pO_2 values would likely result in considerable spatiotemporal variability in oxygen availability, with frequent anoxia throughout most marine systems (Reinhard et al., in press).

A smaller atmospheric oxygen reservoir would have been inherently poorly buffered, and would likely have been characterized by dynamic variance around still low baseline pO_2 levels. Recently, higher atmospheric pO_2 (>4% PAL) for an interval in the mid-Proterozoic has been suggested (Zhang et al., 2016), but there are potential problems with both the interpretive framework and analytical protocols (Planavsky et al., 2016). There is evidence for an excursion to higher atmospheric pO_2 levels during a protracted interval in the Paleoproterozoic (Partin et al., 2013), an interval not examined in this study. However, regardless of evidence for transient intervals of relatively high pO_2 during Proterozoic time, we suggest that it is the baseline Earth surface oxygen level during the mid-Proterozoic that is likely to be the key factor in controlling the long-term evolutionary landscape (Reinhard et al., 2016).

CONCLUSIONS

Our black shale δ⁵³Cr record provides a comprehensive new archive of large-scale changes in the extent of oxidative Cr cycling. Both the widespread distribution of our sample localities and the continuity of the data in each time bin suggest a delayed onset of pervasive and
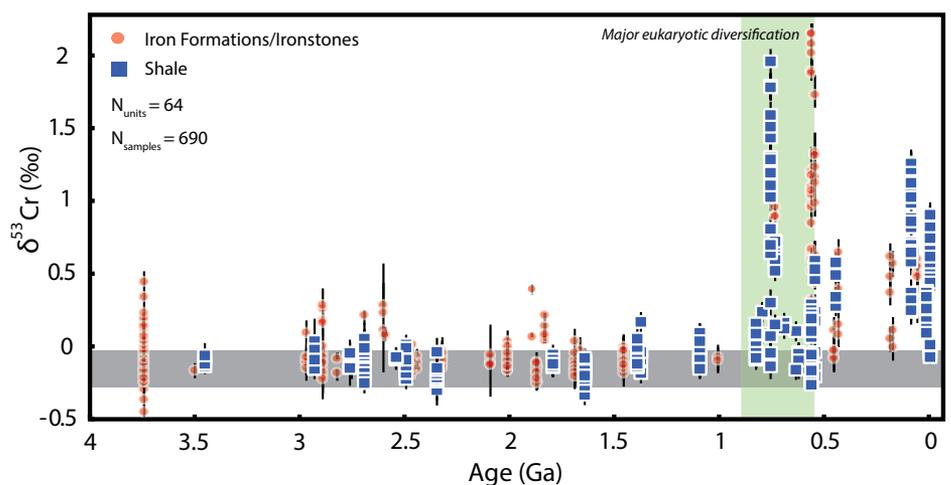

Figure 3. Cr Isotope data from shale and iron-rich chemical sediments through time. Shown are Cr isotope data from shales (blue) of this study and Frei et al. (2011, 2013), Gueguen et al. (2016), and Wille et al., (2013), and Cr isotope data from iron formations and ironstones (red) of Frei et al. (2009, 2016), Crowe et al. (2013), and Planavsky et al. (2014). Gray bar indicates bulk silicate Earth (BSE) range. Green bar indicates interval of major eukaryotic diversification based on molecular clock estimates (Erwin et al., 2011) and appearance of early metazoan body fossils (Knoll, 2014).

sustained terrestrial oxidative Cr cycling prior to the late Proterozoic. Although intermittent oxidative Cr cycling is likely to have occurred before this interval (e.g., Crowe et al., 2013), and some fractionated Cr data may ultimately appear from the mid-Proterozoic and are predicted in the immediate wake of the Great Oxidation Event, we suggest that the fundamental shift in the shale and iron-formation records in the early Neoproterozoic signals a secular change in background surface oxygen levels, highlighting a critical transition in the composition of Earth's atmosphere.

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