



Mo–Cr isotope evidence for a reducing Archean atmosphere in 3.46–2.76 Ga black shales from the Pilbara, Western Australia

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ARTICLE INFO

Article history:

Received 14 March 2012

Received in revised form 27 December 2012

Accepted 28 December 2012

Available online 8 January 2013

Editor: Carla M Koretsky

Keywords:

Archean
Atmospheric oxygen
Molybdenum isotopes
Chromium isotopes

ABSTRACT

The distribution of redox-sensitive elements and their stable isotope variations in marine sediments has been employed to track the possible oxygenation of the atmosphere at, and before, the Great Oxidation Event (GOE; 2.4–2.2 Ga). Contrasting datasets have been used to advocate for and against the rise of free oxygen in the atmosphere prior to 2.4 Ga based on various geochemical tracers, and evidence for a partially oxidized environment remains elusive.

Herein, we present stable isotope datasets for Mo and Cr, in conjunction with major and trace elements from four black shale horizons spanning a time interval from 3.46 to 2.76 Ga in order to ascertain atmospheric oxygen levels through the Archean. The Mo, Cr and U elemental signatures within all sedimentary units are dominated by continental input. Both Mo isotopic values and Mo and U elemental signatures suggest anoxic conditions with no indication of redox cycling of these elements. This contradicts previous interpretations of an oxidized atmosphere based on published sulfur isotopic data (Ohmoto et al., 2006) and oxidized hematite occurrences at ~3.45 Ga (Hoashi et al., 2009).

Cr concentration patterns within the sample suites are controlled by continental provenance composition rather than by an authigenic Cr seawater contribution. This interpretation is supported by the relatively homogeneous Cr isotopic compositions across all sample suites and is consistent with high temperature controlled Cr isotopic ratios. Identification of redox cycling processes within detrital dominated sediments with Cr isotopes is likely to be less sensitive compared to Mo isotopes, due to the much smaller authigenic/crustal enrichment factors for Cr.

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1. Introduction

Free oxygen (O₂) influences all forms of life, either directly via respiration or indirectly through its influence on nutrient production by oxidative weathering and nutrient solubility, e.g. iron (Fe), manganese (Mn) and copper (Cu) in seawater (Nielsen, 2000; Anbar and Knoll, 2002). Knowing the time and extent of the accumulation of O₂ is crucial for reconstructing the evolution of the atmosphere, hydrosphere and biosphere systems. For almost half of Earth history, O₂ levels are widely considered to have been less than 0.001% of the present atmospheric level (PAL) (Farquhar et al., 2000). Oxygenation of the atmosphere is thought to have occurred in several steps. The first major step occurred at around 2.4 Ga, when O₂ concentration

rose from 0.001% to ~1% PAL, the level required to oxidize rock surfaces on the continents (Holland and Beukes, 1990; Farquhar et al., 2000; Bekker et al., 2004). However, the question of how, when, and to what extent O₂ accumulated on early Earth's surface prior to that time is a matter of debate and rather poorly constrained (Farquhar et al., 2000; Ohmoto et al., 2006; Holland, 2009).

In recent years, several new redox sensitive proxies have been developed and applied to reconstruct the early Earth's redox history (Siebert et al., 2003; Farquhar et al., 2007; Johnson et al., 2008; Frei et al., 2009). The disappearance of mass independent sulfur isotope fractionation (S-MIF) in marine sedimentary rocks (Farquhar and Wing, 2003; Bekker et al., 2004; Papineau et al., 2007; Domagal-Goldman et al., 2008) and the absence of detrital minerals such as uraninite, and of pyrite in paleosols (Rye and Holland, 2000) have been taken as evidence for the rise of atmospheric oxygen after ~2.4 Ga (Holland and Beukes, 1990). Although it is widely accepted that atmospheric O₂ was very low before this so-called "Great Oxidation Event" (GOE), recent studies have indicated that the redox history of early Earth's atmosphere and hydrosphere was possibly more complicated than a single stage transition from anoxic in the Archean to oxic in the Paleoproterozoic

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(Siebert et al., 2005; Ohmoto et al., 2006; Wille et al., 2007; Hoashi et al., 2009; Kato et al., 2009; Duan et al., 2010; Voegelin et al., 2010).

The processes that led to a rise in atmospheric oxygen are not well understood, although it is widely accepted that photoautotrophic microbes were the main trigger (Dutkiewicz et al., 2006). Significantly, however, there are indications that O₂ producing cyanobacteria might have emerged hundreds of millions of years prior to the GOE (Brocks et al., 1999; Grassineau et al., 2001; Buick, 2008; Schwartzman et al., 2008; Waldbauer et al., 2009) and that O₂ possibly accumulated in regions with high biological productivity, such as along continental margins where elevated nutrient levels may have stimulated oxygenic photosynthesis (Kaufman et al., 2007; Coogan, 2009). This view is advocated by several recent publications, which promote evidence for the existence of significant amounts of O₂ (few to a few tens of μM within the marine photic zone (Czaja et al., 2012)) hundreds of millions of years prior to 2.4 Ga (Siebert et al., 2005; Ohmoto et al., 2006; Anbar et al., 2007; Kaufman et al., 2007; Wille et al., 2007; Frei et al., 2009; Hoashi et al., 2009; Kato et al., 2009; Duan et al., 2010; Voegelin et al., 2010).

Here, we utilize redox-sensitive Mo and Cr isotopes and trace element signatures from four Archean low grade metamorphic black shale successions from Western Australia to determine the environmental redox conditions through a large part of the Archean (3.46 to 2.76 Ga). All samples are black shales obtained from diamond drill cores from the Pilbara region of Western Australia. These sample are complementary to other recent publications that use Mo or Cr isotopic signatures for paleo-redox reconstruction, which have indicated increased Mo and/or Cr mobility due to partial oxidation of the atmosphere since around 2.7 Ga (Anbar et al., 2007; Wille et al., 2007; Frei et al., 2009; Duan et al., 2010; Kendall et al., 2010; Voegelin et al., 2010). Our aim is to investigate the source and mobility of redox sensitive elements such as Mo, Cr and U in order to decipher the redox state of Archean oceanic basins and to address the question as to the existence of free oxygen prior to 2.7 Ga.

2. Material and methods

2.1. Geological setting and samples

Samples originate from drill cores of the Achaean Biosphere Drilling Project (ABDP) stored at the Geological Survey of Western Australia's core library facility in Perth. Nineteen black shale samples were collected from four different sedimentary horizons.

2.1.1. ~3.47 Ga Duffer Formation, Warrawoona Group (ABDP core #2)

The 3.47 Ga Duffer Formation is up to 8 km thick succession, consisting of predominantly felsic volcanoclastic rocks that lie within the middle part of the 3.52–3.42 Ga, dominantly volcanic, Warrawoona Group (Hickman, 1984; Van Kranendonk et al., 2007). Subordinate felsic volcanic flows, pillow basalts, and sedimentary rocks occur within the formation, including a 200 m thick black shale unit in the lower part of the formation (Van Kranendonk, 2010) and local black shales imbedded within volcanoclastic sandstones and siltstones. Five black shale samples, each between 10 and 20 cm long, were collected across a depth of 58.1–219.25 m in ABDP core 2 (Table 1). A recent investigation reported the existence of primary hematite from the Marble Bar Chert Member of the Duffer Formation, interpreted as evidence for free O₂ in seawater at this time (Hoashi et al., 2009), although the principal argument in support of this has been disputed since the oxidation of the Marble Bar Chert Member and overlying Apex Basalt did not occur in the Archean (Van Kranendonk et al., 2008; Li et al., 2012).

2.1.2. 2.94 Ga Nullagine Group, De Grey Supergroup (ABDP core #5)

The 3.02–2.93 Ga Nullagine Group occupies the Mosquito Creek Basin in the southeastern part of the Pilbara Craton, between the East Pilbara Terrane and the Kurrana Terrane (Van Kranendonk et

al., 2007). This group is one of several that have been collectively placed within the De Grey Supergroup, which spans the Pilbara Craton. The Nullagine Group is predominantly a siliciclastic succession that consists of the lower Cundaline Formation and the overlying Mosquito Creek Formation. Age constraints are only available from the Mosquito Creek Formation and indicate a depositional age younger than 2940 Ma (Van Kranendonk et al., 2007). The Nullagine Group was deposited across an unconformity on the East Pilbara Terrane. Stratigraphic analysis suggests a mostly deep-water depositional environment dominated by turbidites of a fan-delta origin (Bagas et al., 2008; Nijman et al., 2010). Sulfur isotope data from this group have been interpreted as evidence for an oxic Archean atmosphere (Ohmoto et al., 2006), but this interpretation has been challenged by Farquhar et al. (2007). Five black shale samples, each between 10 and 20 cm in length, were collected over a depth range of 98.3–141.25 m in ABDP core #5 (Table 1).

2.1.3. 2.77 Ga Mount Roe Basalt & 2.76 Ga Hardey Formation, Fortescue Group, Mount Bruce Supergroup (ABDP core #6 & #3)

The 2.77–2.63 Ga Fortescue Group is a thick succession of interbedded flood basalts and clastic and carbonate sedimentary rocks that were deposited across a regional unconformity on the Pilbara Craton (Thorne et al., 2001). Sedimentary rocks within the Fortescue Group were deposited under a mixture of lacustrine and deep shelf-type conditions (Eriksson et al., 1999). The basal formation of the Fortescue Group is the undated Bellary Formation, which consists of clastic sedimentary rocks. This is overlain across a conformable to unconformable contact by the ~2.77 Ga, predominantly subaerial, Mt. Roe Basalt (Blake et al., 2004; Van Kranendonk et al., 2007). Local pillows and interbeds of black shale indicate lacustrine environments during eruption. The overlying ~2.76 Ga Hardey Formation comprises mostly conglomerates, sandstones, siltstones and shales deposited in fluvial and lacustrine environments (Thorne et al., 2001).

Paleo-redox reconstructions of sedimentary rocks from these two formations yield contradictory findings. Evidence for an oxic Archean atmosphere was interpreted from black shales of the Hardey Formation using sulfur isotopes (Ohmoto et al., 2006), whereas a redox sensitive element investigation of Mount Roe paleosols claimed evidence for low, or no, oxygen (Yang et al., 2002).

In order to reconcile these conflicting results, four black shale samples, each between 10 and 20 cm long, were collected over a depth range of 98.3–141.25 m in ABDP core #3 (Hardey Formation) and five samples of black shale, each between 10 and 15 cm long, were collected over a range of depth of 85.2–267.81 m in ABDP core #6 (Table 1).

2.2. Methods

Major elemental concentrations were made by taking 1.5 g sample powder mixed with 7.5 g lithium tetraborate and fused at a temperature of 1050 °C. The glass disks were analyzed for major element compositions by a Bruker AXS Pioneer 4 kW X-ray fluorescence spectrometer (XRF) hosted by the isotope geochemistry group at the University of Tübingen.

For trace element measurements, including Rare Earth Elements (REE), organic carbon was removed from the sample powder by combustion at 800 °C for several hours. Subsequently, carbon-free sample powder was sequentially dissolved by 6 mol L⁻¹ hydrochloric acid (HCl) and a mixture of concentrated hydrofluoric acid (HF) and nitric acid (HNO₃). The decomposed samples were re-dissolved in 2% HNO₃ and trace element concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS) on a Varian 820-MS instrument at the Research School of Earth Sciences, Australian National University using enriched isotope internal standardization (Eggins et al., 1997).

For Mo isotopic analysis ~200 mg of sample powder was weighed into a Teflon beaker and tagged with a molybdenum double-spike enriched in the ⁹⁷Mo and ¹⁰⁰Mo isotopes. Samples were digested

using a combination of HCl and HF + HNO₃ dissolution steps. For Mo purification, the decomposed samples were taken up in 4 mol L⁻¹ HCl for element-matrix separation using Dowex 1X8, 200–400 mesh, anion exchange resin. In a second step, sample material was taken up in 0.5 mol L⁻¹ HCl and Dowex 50Wx8 200–400 mesh, cation exchange resin (Dowex 50Wx8 200–400 mesh) was used for further purification of Mo, especially from iron (Fe). Stable molybdenum isotope ratio and concentration measurements were carried out on a multi-collector ICP-MS (Thermo Scientific Neptune, Research School of Earth Sciences, Australian National University) in combination with an ESI Apex desolvating system using the protocol described by Siebert et al. (2001) and Wille et al. (2007). A 2σ external reproducibility of 0.12‰ δ^{98/95}Mo was determined by repeated analyses of the in-house J&M Mo standard.

For Cr isotopic analysis, 10–20 mg of sample powder was spiked with a ⁵⁰Cr–⁵⁴Cr double spike and digested in HF:HNO₃ in closed PFA vials. After ensuring complete digestion, Cr separation and purification from matrix elements was performed using liquid–liquid extraction with the trialkylphosphine oxide Cyanex® 923 and anion exchange purification with Dowex AG 1X8 resin. A detailed description of the Cr separation procedure is published in Schoenberg et al. (2008). Chromium isotopic measurements were determined by thermal ionization mass spectrometry (TIMS; Finnigan MAT 262, Isotope Geochemistry Group, Department for Geosciences, University of Tübingen) using Re single filaments. Chromium separates were loaded with a mixture of 3 μL silica-gel, 1 μL 0.75 mol L⁻¹ H₃BO₃ and 1 μL 0.5 mol L⁻¹ H₃PO₄ and subsequently dried down at room temperature following the procedure described by Frei et al. (2011). A 2σ external reproducibility of 0.1‰ on the ⁵³Cr/⁵²Cr ratio was determined by repeated analyses of the certified SRM 979 standard and an in-house Cr(III) standard. Reported isotope compositions (Table 2) are given relative to the certified SRM 979 standard and the average value for the Cr(III) standard is -0.418‰ in δ^{53/52}Cr, which is in excellent agreement with the value of -0.443‰ in δ^{53/52}Cr reported by Schoenberg et al. (2008).

Total organic carbon (TOC) was analyzed on decarbonated samples using an Elementar® Vario L at the Laboratories in Applied Geosciences (ZAG), University of Tübingen.

3. Results

3.1. Redox sensitive elements Mo, U and Cr

Molybdenum and U concentrations show variations throughout the different sample suites, ranging from 4.5 to 1.5 ppm Mo and from 6 to 1.9 ppm U. These concentrations are lower than average Mo and U abundances of sapropels collected from recent reducing sedimentary settings in which Mo concentrations range between 42 and 117 ppm and U concentrations range between 10.5 and 14.8 ppm (Brumsack, 2006). All samples, except for black shales from the 2.94 Ga Nullagine Group, show up to three times higher Mo and U concentrations than that of Archean juvenile upper crust (Condie, 1993). A good correlation between Mo and U concentrations can be identified throughout the whole dataset ($r = 0.79$; $n = 19$). Both elements also correlate with incompatible and immobile elements such as Th, Ta and Nb and the Rare Earth Elements (REE). Aluminum normalization of Mo and U concentrations (Fig. 1) leads to homogeneous element ratios throughout the entire sample set, which are identical to element ratios for Archean juvenile upper crust, but lower than average recent sapropels (Brumsack, 2006) and 2.5 Ga black shales (Anbar et al., 2007).

The Mo isotopic composition of the samples (Fig. 1), which range from 0.24 to 0.58‰ in δ^{98/95}Mo, is within the isotopic field of >3 Ga sedimentary rocks and is close to the average Mo isotopic composition of the continental crust (~0.2 δ^{98/95}Mo; Siebert et al., 2003, 2005; Wille et al., 2007). All samples are isotopically significantly lighter than modern oceanic seawater and the average δ^{98/95}Mo of 2.5 Ga euxinic sedimentary rocks (Anbar et al., 2007).

Shale samples from the 2.94 Ga Nullagine Group show overall higher concentrations of Cr, together with Fe, Sb and Mn (see Tables 1 and 2 in the Supplementary material) compared to the other sample suites. This behavior is opposite to the overall concentration patterns of the immobile elements, as well as that of other redox sensitive elements including Mo and U (Fig. 1).

Black shale samples from all of the different sample suites are enriched in Cr (221 to 603 ppm) compared to PAAS (110 ppm) and Archean upper crust (140 ppm). However, Cr/Al ratios are similar to that of Archean upper crust, with the exception of the Nullagine Group, which have 2 to 3 times higher ratios. Significantly, the average Fe₂O₃ content of the Nullagine Group samples is 8.64 wt.%, which is nearly twice than that of Archean upper crust (4.88 wt.%) and significantly higher than that of PAAS (6.50 wt.%), suggesting a unique composition for these rocks. The average Sb concentration of the Nullagine Group samples is also high (8.8 ppm), at values that are ~20 times more concentrated than the upper continental crust ~0.4 ppm (Rudnick and Gao, 2003).

δ^{53/52}Cr values of the whole sample set are homogeneous, with values ranging from -0.16 to 0.03‰. The average δ^{53/52}Cr value of -0.10 ± 0.11‰ ($n = 18$) corresponds perfectly to the isotopic range reported for igneous rocks (-0.12 ± 0.10‰; Schoenberg et al., 2008) and is isotopically light compared to modern open ocean seawater (~0.5‰).

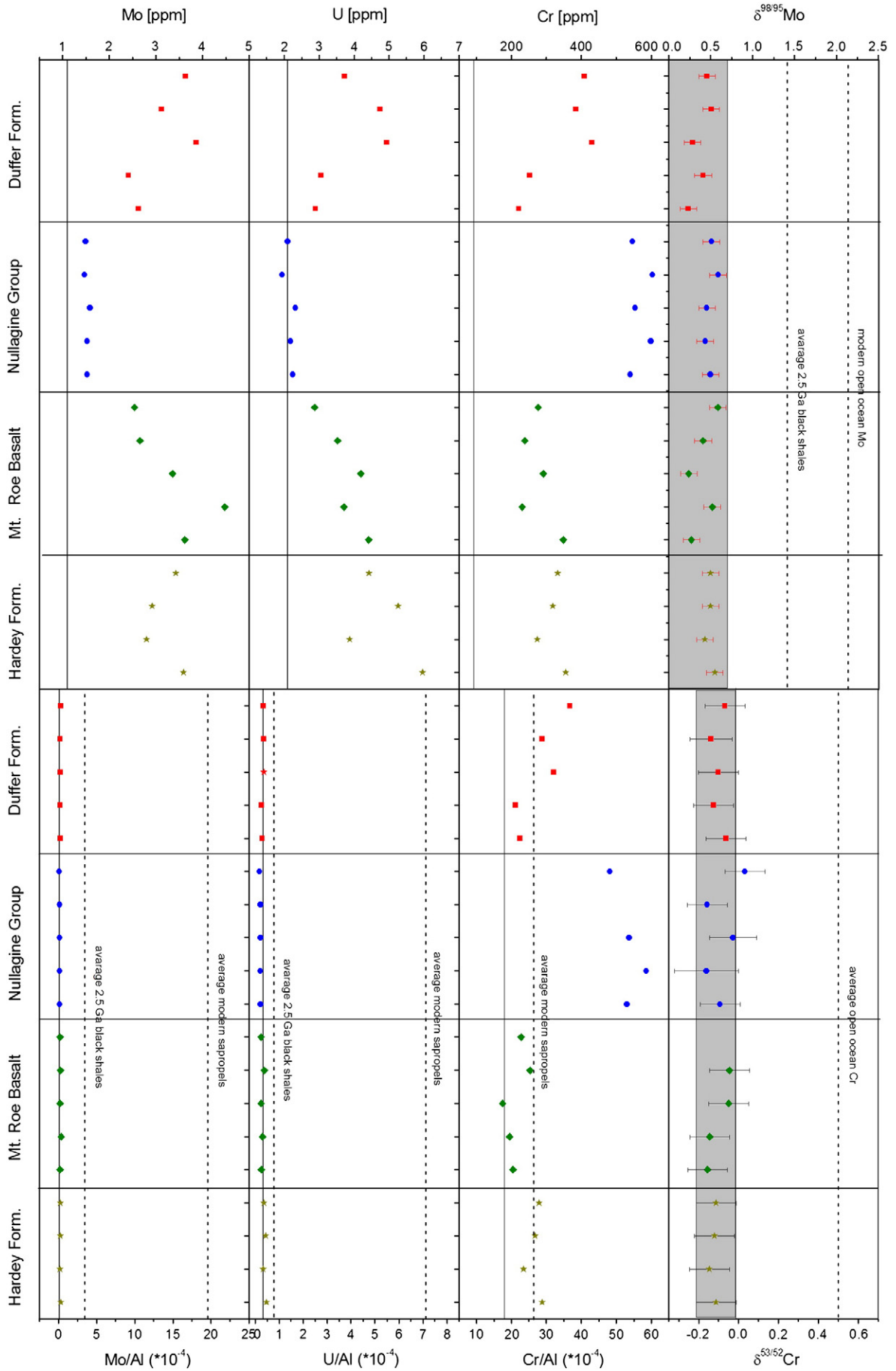
4. Discussion

4.1. Concentration pattern of redox sensitive elements Mo, U and Cr

Mo and U are enriched in the crust (1.1 ppm Mo and 2.2 ppm U) by a factor of 25.6 and 41.2 (Palme and O'Neill, 2007), respectively, compared to the depleted upper mantle. This high crust-to-mantle enrichment factor is caused by the incompatible behavior of these elements during magmatic processes. U is preferentially retained in oxides, such as uraninite, or as an accessory mineral, whereas Mo preferentially resides in sulfide phases and the remaining rock matrix due to its chalcophile behavior and incompatible character during melting. In contrast, Cr is depleted in the crust, compared to the primitive mantle, by a factor of 0.073, with an average upper crust concentration of 92 ppm compared to ~2500 ppm in the primitive mantle (Palme and O'Neill, 2007). Cr is preferentially stored in oxides such as spinel, or pyroxene, in the Cr(III) valence state.

Weathering under oxidized atmospheric conditions oxidizes Mo, U and Cr, making them soluble as oxyanions. This is in contrast to Al, which is highly particle reactive. The low chemical reactivity of Mo and U oxyanions in solution leads to a homogeneous seawater concentration for both metals of ~105 nM (Emerson and Husted, 1991) and ~14 nM (Morford and Emerson, 1999), respectively. Their conservative behavior is illustrated in their high mean ocean residence times of ~750 kyr for Mo and ~400 kyr for U (Algeo, 2004). The average Cr concentration in seawater ranges between 2 and 5 nM (Cranston and Murray, 1978; Sander et al., 2003) and is much lower compared to Mo and U. The mean ocean residence time

Fig. 1. Mo, U, Cr concentration data, Mo/Al, U/Th, Cr/Al ratios and Mo and Cr isotopic values for Archean black shales. Solid line indicates element concentrations for Archean juvenile upper crust (Condie, 1993), gray field in the δ^{98/95}Mo plot indicates Mo isotopic composition range of >3 Ga Archean marine sediments (Siebert et al., 2005; Wille et al., 2007), gray field in the δ^{53/52}Cr plot indicates Cr isotopic composition range in igneous source rocks (Schoenberg et al., 2008). Dashed lines represent modern open ocean seawater isotopic values (Barling et al., 2001; Siebert et al., 2003; Bonnand et al., 2010); average element concentrations and ratios from modern sapropels (Brumsack, 2006); and average element concentrations and ratios as well as Mo isotopic information from ~2.5 Ga old black shales (Mount McRae Shale, unit S1) (Anbar et al., 2007).



for Cr ranges between 7 and 40 kyr (Van Der Weijden and Reith, 1982; Campbell and Yeats, 1984), which is much longer than the average ocean mixing time of 1.2 kyr. Thus, Cr is generally regarded as conservative element (Connelly et al., 2006), particularly when compared to Al, with an overall concentration of 1 nM (Hydes, 1977), but a much shorter ocean residence time of ~3–5 years (de Jong et al., 2007). These high water column redox-sensitive metal/aluminum ratios, which contrast average crustal ratios, can be partly mirrored in reducing sediments due to a quantitative removal of these elements from the water column in a local anoxic, euxinic setting such as the Black Sea. This is mainly due to H₂S-rich waters, organic matter, or Fe colloids (Spencer et al., 1972; Emerson et al., 1979; Eary and Rai, 1989; Pettine et al., 1994; Colodner et al., 1995; Helz et al., 1996; Morford and Emerson, 1999; Kim et al., 2001; Algeo, 2004; Kim et al., 2007; Frei et al., 2009; Døssing et al., 2011).

Indeed, elevated average Mo/Al, U/Al and Cr/Al ratios of modern sapropels of 19.8×10^{-4} , 7.1×10^{-4} and 26.5×10^{-4} , respectively (Brumsack, 2006), indicate enrichment in recent organic-rich sediments compared to that of the upper continental crust (Mo/Al: 0.13×10^{-4} , U/Al: 0.33×10^{-4} , Cr/Al: 11.3×10^{-4}) (Rudnick and Gao, 2003).

Intriguingly, U and Mo abundances obtained from the four sedimentary formations of this study show Mo/Al and U/Al ratios nearly identical to that of the upper continental crust. These ratios imply no, or very little, authigenic enrichment of these elements from seawater during sediment deposition. This is interpreted to indicate an immobile behavior of these elements, thereby suggesting insufficient levels of O₂ to oxidize and mobilize these redox sensitive metals.

While Cr/Al ratios for a majority of the sample suites range between Archean continental source rock and modern sapropels, samples of the 2.94 Ga Nullagine Group show Cr/Al values that are higher than those from recent organic-rich sediments, and that are close to values found in Cretaceous black shales (Brumsack, 2006). The Nullagine Group samples show large differences in element concentrations compared to the other sample suites, with lower concentrations of mantle mineral incompatible elements (Ta, Th, Nb and U) and overall higher concentrations of more mantle mineral compatible elements such as Fe, Mn, Sb, Mg and Cr.

These data imply that, instead of an authigenic enrichment of Fe, Mn, Sb and Cr from a dissolved seawater pool – which would imply redox cycling of these elements at the time of sediment deposition – these elements were controlled by different proportions of mafic vs. felsic source components (McLennan et al., 1983). Co/Th vs. La/Sc support a significant difference of the relative proportions of these two source components (Fig. 2), indicating mixing between mafic and felsic igneous rock end-member compositions, likely sourced from the immediately unconformably underlying Pilbara Supergroup (Smithies et al., 2007). Fig. 2 reveals that Nullagine Group samples incorporate nearly 50% mafic components, while samples from the Duffer Formation and the two sedimentary rock units of the Fortescue Group are clearly dominated by felsic igneous rock components and only contain around 25% mafic material.

Rare Earth Element (REE) patterns are least affected by weathering processes (Nance and Taylor, 1977) and can be used to constrain differences in source rock contributions. PAAS normalized REE patterns for the four sedimentary sample suites (Fig. 3) are in the range of previously published Archean shales from the Pilbara Supergroup (McLennan et al., 1983). Although samples of the 2.94 Ga Nullagine Group show a similar REE pattern to samples from the 3.47 Ga Duffer Formation, this former features lower overall REE abundances, particularly the light REEs compared with all other sedimentary sample suites (Table 3 in the Supplementary material).

Average REE values for three different source rocks from the 3.52 to 3.42 Ga Warrawoona Group (Pilbara Supergroup) were chosen to represent ultramafic (komatiitic, Coonterunah Subgroup), basaltic (tholeiitic basalt, Coonterunah Subgroup) and felsic (Duffer

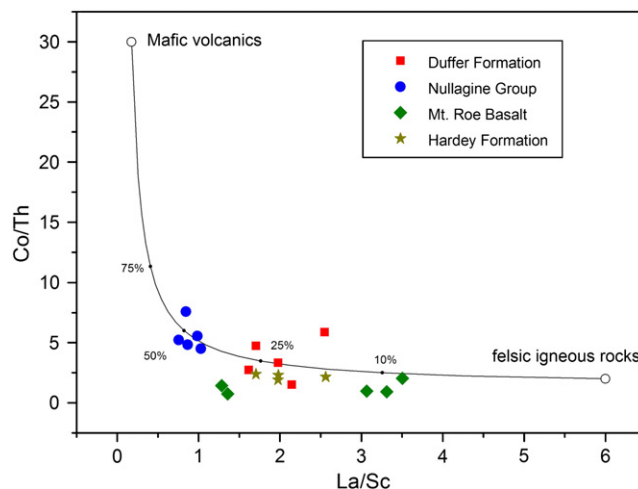


Fig. 2. Plot of Co/Th vs. La/Sc for the different sedimentary groups. Mixing line is calculated using average Pilbara mafic volcanics and felsic rocks (McLennan et al., 1983). Tick marks indicate the percentage of mafic volcanics.

Formation) sources (Smithies et al., 2007) (Fig. 3a). The best fit between calculated and measured REE values can be achieved by taking a combination of $1.229 \times$ felsic, $0.014 \times$ basaltic and $0.055 \times$ ultramafic contribution for samples of the Duffer Formation and $0.746 \times$ felsic, $0.242 \times$ basaltic and $0.104 \times$ ultramafic contribution for the Nullagine Group samples. These source rock proportions yield a good coincidence between measured and calculated REE patterns, verifying the different source rock contributions. Translating this into source rock contributions for the total sedimentary rock yield a 94.6% felsic, 1.1% basaltic and 4.2% ultramafic contribution for the Duffer Formation and a 68.3% felsic, 22.2% basaltic and 9.5% ultramafic contribution for the Nullagine Group (Fig. 3b). These findings are in good agreement with the Co/Th vs. La/Sc results, which indicate a much higher mafic content for the Nullagine Group samples.

Overall, the sedimentary Cr concentrations in the rocks studied here are related to the abundance and weathering of Cr-rich mineral phases within ultramafic host rocks that contributed material to the sedimentary formations (Oze et al., 2004). In summary, whereas elevated Cr/Al in recent sapropels and in Cretaceous black shales might be the result of authigenic Cr enrichment, Cr/Al in the Archean sample suites studied here most likely reflect a higher mafic and ultramafic detrital contribution, particularly in the Nullagine Group.

4.2. Mo and Cr isotopes

The interpretation of a detrital control of the sedimentary chemistry for the redox sensitive metals is supported by the overall homogeneous $\delta^{98/95}\text{Mo}$ and $\delta^{53}\text{Cr}$ values, which are consistent with a dominant continental detrital input. The Mo isotopic composition of the modern ocean is 2.3% heavier in $\delta^{98/95}\text{Mo}$ than the continents. This isotopic shift results from Mo adsorption on Mn-oxides and sedimentation in oxic sediments, which preferentially incorporate the lighter Mo isotope leading to a build-up of an isotopically heavy oceanic reservoir under oxidizing conditions. It has been shown that under strongly reducing conditions in the presence of H₂S, this heavy Mo isotopic seawater signature can be stored in euxinic sediments through quantitative Mo removal from the water column into the sediment by Fe–Mo sulfides (Siebert et al., 2003; Anbar, 2004; Helz et al., 2011).

Such a heavy oxygenated oceanic Mo signature is not observed in our samples. However, the complexity of Mo-adsorption and precipitation processes may alter such straight-forward interpretations of Mo isotope signals in black shales (Poulson et al., 2006; Nägler et

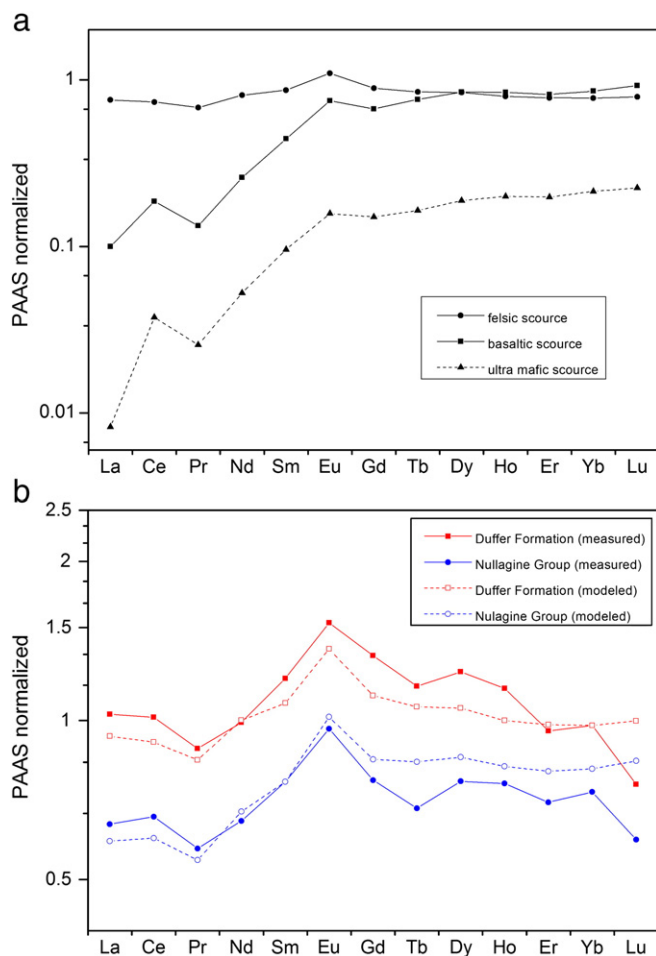


Fig. 3. a) PAAS normalized measured and modeled REE plot for the different source rocks. b) PAAS normalized measured and modeled REE plot for Nullagine Group and Duffer Formation samples.

al., 2011). The fact that anoxic sediments do not necessarily reflect the Mo isotopic composition of the contemporary seawater has been shown in recent Black Sea sediments (Neubert et al., 2008). Dependent on H_2S concentration and pH (Erickson and Helz, 2000; Helz et al., 2011), incomplete removal of Mo from the water column into the sediment, in conjunction with fractionation processes during thiomolybdate formation, can lead to lighter isotopic Mo signatures in anoxic sediments compared to the contemporary ocean. Furthermore, the Mo isotopic composition of Archean seawater may not necessarily be fractionated to the same extent as in well oxygenated Phanerozoic environments, since the euxinic/suboxic to oxic Mo sedimentation ratio was different. It has been shown, also within sediments of the Neoproterozoic Hamersley Province (Czaja et al., 2010), that isotopic data of redox sensitive metals do not necessarily reflect the whole paleo-environment due to decoupling of processes. It can also be true for Mo isotopic signature within sediments where post depositional early diagenetic Mn cycling can remobilize Mo and alter the environmental Mo information (Reitz et al., 2007; Scheiderich et al., 2010). Nonetheless, the consistently low and homogeneous Mo isotope signals close to those of average continental crust together with no indication of an authigenic Mo enrichment within the sediments show that most likely Mo was not involved in any redox cycling process either within the water column due to free oxygen or within the sediment due to microbial processes. The lack of correlation with other redox-sensitive tracers is strongly in favor of predominantly reducing weathering conditions, such that free O_2 levels were not sufficiently high enough to mobilize Mo.

This result is in agreement with published ~ 2.76 Ga Mt. Roe #2 paleosol data from the Fortescue Group (Macfarlane et al., 1994; Yang et al., 2002). In these paleosols, the distribution of redox-sensitive elements, namely U and Mo, indicates no or very low levels of atmospheric oxygen during soil formation, insufficient to mobilize elements (Macfarlane et al., 1994; Yang et al., 2002).

As for Mo and U, mobilization of Cr during oxidative continental weathering will lead to isotopic fractionation (Ellis et al., 2002; Zink et al., 2010) with a build-up of an isotopically heavy oceanic Cr reservoir ($\sim 0.5\%$ $\delta^{53}Cr$). This results from a preferential flux of heavier isotopes along with the Cr(VI) aqueous species into the ocean (Frei et al., 2011). Unlike Mo and U, the mean residence time of Cr is much lower, between 7 and 40 ka (Van Der Weijden and Reith, 1982; Campbell and Yeats, 1984; Connelly et al., 2006). Manganese and Fe oxyhydroxides, together with biogenic matter, are generally regarded as important scavenging carrier phases and deep ocean transport mechanism for Cr (Connelly et al., 2006; Døssing et al., 2011). The formation of Fe–Mn hydroxides/colloids at the chemocline/redox-interface, i.e., the transition from oxic to anoxic conditions, results in Cr being scavenged from seawater via direct precipitation, adsorption or incorporation of particle-reactive species (Spencer et al., 1972; Early and Rai, 1989; Pettine et al., 1994; Ellis et al., 2002; Brumsack, 2006; Frei et al., 2009; Døssing et al., 2011). Alternatively, kinetic measurements from laboratory experiments indicate that the half-life for Cr(VI) in H_2S -rich euxinic environments ranges from a few hours to several days (Pettine et al., 1994; Kim et al., 2001; Kim et al., 2007). Reduction and co-precipitation of dissolved Cr lead to large isotopic fractionation with the lighter isotopes favored for reduction and co-precipitation. A $\Delta^{53/52}Cr_{(solid-dissolved)}$ up to -4.5 and -4.2% has been reported for Cr reduction by ferrous iron and -3.11 for Cr reduction on organic substances (Ellis et al., 2002; Døssing et al., 2011; Kitchen et al., 2012). Ultimately, if incorporation is not quantitative, the Cr isotopic composition of sediments will vary and depend on reaction kinetics and the detrital dilution of the authigenic signal. The complexity of these processes renders systematic variations in Cr isotopes basically non-predictable, yet under oxidizing weathering conditions isotopic composition of such chemical sediments would clearly be distinct from the isotopically homogeneous continental source (Schoenberg et al., 2008). If Cr enrichments of Nullagine Group samples were due to authigenic contribution from a dissolved Cr seawater pool with an estimated $Cr_{authigenic}/Cr_{detrital}$ ratio of ~ 3 based on Cr/Al ratios compared to the Archean continental crust, a resulting isotopic difference in $\Delta^{53}Cr_{(detrital-authigenic)} < 0.15\%$ would result in an unresolvable isotopic shift from continental values. However, within analytical error, all $\delta^{53}Cr$ isotopic values are within the field of continental derived material with no indication of a significant authigenic input from a dissolved Cr seawater reservoir. This is in line with the observation that the Cr concentration within these sediments is controlled by varying detrital inputs. Testing the existence of a dissolved Cr(VI) ocean reservoir is not feasible from these whole rock analyses due to large detrital derived Cr background.

5. Conclusions

Local and/or temporal occurrences of O_2 , so-called “oxygen oases”, in high bio-productive shelf settings has been postulated for the Archean (Kasting, 1993). Our Mo isotopic results for ≥ 2.76 Ga old sedimentary rocks are within the field of continentally derived detritus, indicating insufficient O_2 levels, as required to mobilize this element. These findings are in line with previous reported Mo isotopic compositions in Archean sediments older than 2.7 Ga (Siebert et al., 2005; Wille et al., 2007) (Fig. 4), and Mo and U concentrations that indicate no measurable contribution of an authigenic seawater-derived component for these elements. In contrast, Mo isotopic signatures in sediments ≤ 2.7 Ga are isotopically heavier than solely continent derived sedimentary material. Such heavier Mo isotopic signatures, in conjunction with the apparent elevated concentrations of other redox sensitive elements, such as U

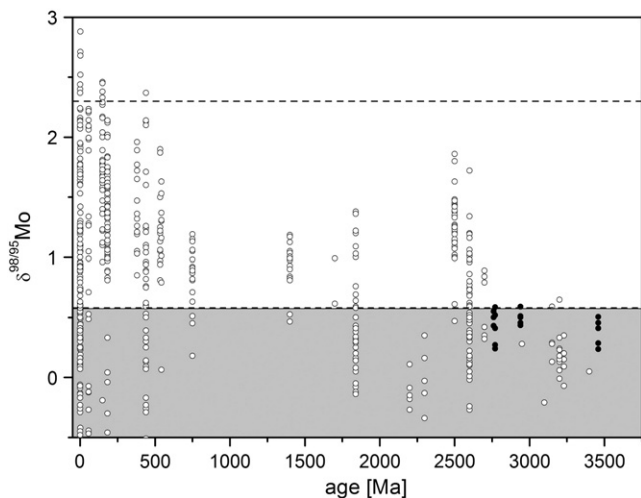


Fig. 4. Compilation of Mo isotopic composition of organic rich sediments through time; open circle = published by values (Arnold et al., 2004; Siebert et al., 2005; Lehmann et al., 2007; Wille et al., 2007; Pearce et al., 2008; Wille et al., 2008; Gordon et al., 2009; Kendall et al., 2009; Duan et al., 2010; Pearce et al., 2010; Scheiderich et al., 2010; Dahl et al., 2011; Kendall et al., 2011; Zhou et al., 2011; Dickson et al., 2012; Herrmann et al., 2012; Zhou et al., 2012); filled circles: this study.

and Re, after 2.7 Ga suggests aquatic mobilization of these elements. Modeled water-column oxygenation based on coupled iron–molybdenum isotopic investigations on 2.65–2.5 Ga old sediments varies between a few to a few tens of μM (Czaja et al., 2012). Following this approach, water column oxygen levels must have been lower for depositional conditions of the hereby studied sedimentary sequences. Although, we note that this does not exclude the presence of oxygen niches in other sedimentary setting older than 2.7 Ga.

Changes in Cr concentrations in 3.46–2.76 Ga black shales from the Pilbara Craton are not the result of an increased mobility of this element due to oxygenated weathering conditions, but rather reflect different proportions of detrital mafic vs. felsic components. Changes in sedimentary provenances, i.e., source rock composition, element redistribution in secondary phases during weathering, as well as hydraulic mineral sorting are likely reasons for the observed variations in elemental concentrations between different sedimentary units. An important implication from these observations is that Cr and Mo bear different qualities as authigenic input tracers. Whereas Mo has a low lithogenic background but a high mobility and chemical stability of its dissolved oxyanion, Cr has high lithogenic concentrations relative to low enrichment factors in reducing sediments by scavenging of dissolved Cr. In conclusion, while Mo is a sensitive redox-proxy even in sediments with a detrital component, the detection of possible authigenic Cr signals, and with this its use as a redox-proxy, is strongly limited within whole rock black shales commonly used as paleo-redox proxy archive.

Acknowledgments

Many thanks to Chantal Alibert for very helpful discussion and many thanks to Les Kingsly, Graham Mortimer and Jake Howe for their analytical help. Thanks to the Australian Research Council (Grants DP0770820 and DP0771519 awarded to Bill Maher (UC), Michael Ellwood (ANU) and Steve Eggins (ANU)) for providing funds to support this work. We further thank Clark Johnson and an anonymous journal reviewer for their insightful comments and Joel Blum for editorial handling.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2012.12.018>.

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