

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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A I C L E I N F

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

A B A C

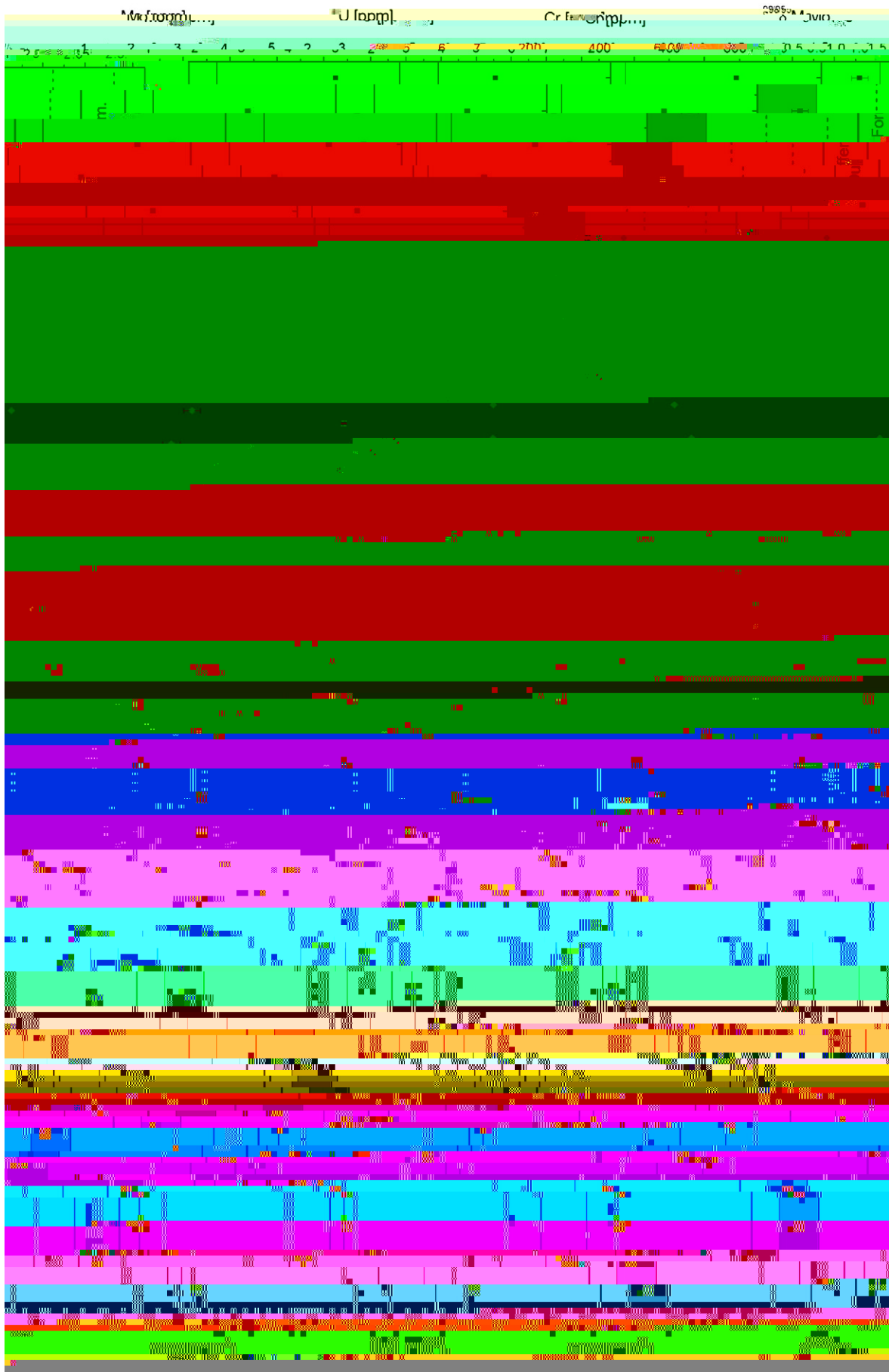
The distribution of redox-sensitive elements and their stable isotope variations in marine sediments has been employed to track the possible oxygenation of the atmosphere at, and before, the Great Oxidation Event (GOE; 2.4–2.2 Ga). Contrasting datasets have been used to advocate for and against the rise 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).

(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

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



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

al., 2011

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 be-

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