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# Role of upper-most crustal composition in the evolution of the Precambrian ocean-atmosphere system



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#### ABSTRACT

Recent research has emphasized the potential relationships between supercontinent cycles, mountain building, nutrient flux, ocean-atmosphere chemistry and the origin of life. The composition of the Upper-Most Continental Crust (UMCC) also figures prominently in these relationships, and yet little detailed data on each component of this complex relationship has been available for assessment. Here we provide a new set of data on the trace element concentrations, including the Rare Earth

Elements (REE), in the matrix of 52 marine black shale formations spread globally through the Archean and Proterozoic. The data support previous studies on the temporal geochemistry of shales, but with some important differences. Results indicate a change in provenance of the black shales (upper-most crustal composition), from more mafic in the Archean prior to 2700 Ma, to more felsic from 2700 to 2200 Ma, followed by a return to mafic compositions from 2200 to 1850 Ma. Around 1850 to 1800 Ma there is a rapid change to uniform felsic compositions, which remained for a billion years to 800 Ma. The shale matrix geochemistry supports the assertion that the average upper-most continental source rocks for the shales changed from a mix of felsic, mafic and ultramafic prior to 2700 Ma to more felsic after 1850 Ma, with an extended transition period between. The return to more mafic UMCC from 2200 to 1850 Ma is supported by the frequency of Large Igneous Provinces (LIPs) and banded iron formations, which suggest a peak in major mantle-connected plume events and associated Fe-rich hydrothermal activity over this period. Support for the change to felsic UMCC around 1850 Ma is provided by previous geological data which shows that felsic magmas, including, A-type granites and K-Th-U-rich granites intruded vast areas of the continental crust, peaking around 1850 Ma and declining to 1000 Ma. The implications of this change in UMCC are far reaching and may go some way to explain the distinct features of the Boring Billion (1800-800 Ma). Firstly, because mafic-ultramafic rocks contain significantly higher levels of the bio-essential nutrient elements (e.g. Fe, P, Ni, Cr, Co, Cu, Se, Mn, Zn) compared with

higher levels of the bio-essential nutrient elements (e.g. Fe, P, Ni, Cr, Co, Cu, Se, Mn, Zn) compared with felsic rocks, the flux of macro- and micro-nutrients to the ocean would have decreased significantly post 1850 Ma. This would have contributed to a drop in productivity and a drop in atmosphere O<sub>2</sub> as suggested by the marine pyrite proxy. In addition, a change from mafic to felsic dominant composition of the UMCC post 1850 Ma, would have led to a decrease in the erosive flux of Ca and Mg to the ocean, affecting the oceanic carbonate equilibrium and likely contributing to a rise in atmosphere CO<sub>2</sub>.

On this basis, we speculate that the commencement of the middle Proterozoic, commonly known as the Boring Billion period from 1800 to 800 Ma, marks the start of an extended time in Earth's evolution when the UMCC became dominated by felsic rocks, particularly K–U–Th–anorogenic granites. This led to a period of anomalously low concentrations of bio-essential trace elements, but elevated REE, U, Th, Pb, Tl, Rb/Al and K/Na in the oceans.

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#### 1. Introduction

The chemistry of the Archean and Proterozoic oceans had a major influence on the evolution of early life (Anbar and Knoll, 2002; Anbar, 2008; Scott et al., 2008; Knoll, 2014). The nutrients

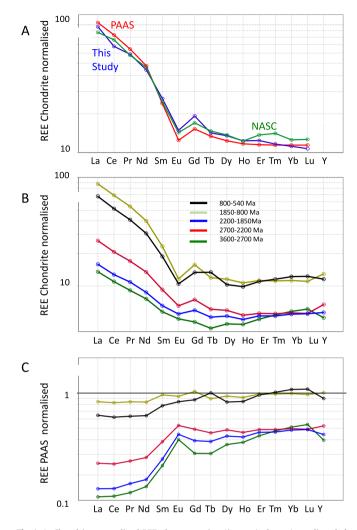
\* Corresponding author. *E-mail address:* ross.large@utas.edu.au (R.R. Large). supplied to the oceans, particularly the macronutrient P and micronutrients Fe, Co, Ni, Cu, Zn, Mn, Cd, Se and Mo, are principally sourced by oxidative weathering and erosion of the Upper-Most Continental Crust (UMCC), with additional input from seafloor hydrothermal vents (Stüeken et al., 2015). Major emphasis has been placed on the redox state of the atmosphere in controlling the type of nutrient flux into the ocean (Arnold et al., 2004; Scott et al., 2008; Sahoo et al., 2012; Planavsky et al., 2014; Large et al., 2014). Supercontinent cycles of plate collision, consolidation, cratonization, break-up and rifting are also considered to be important factors that may have controlled the variations in nutrient flux to the Precambrian oceans (Des Marais et al., 1992; Brasier and Lindsay, 1998; Bartley et al., 2001). More recently, the composition of the UMCC, how it varied through Precambrian time and its influence on the type of nutrients supplied to the oceans have been the focus of research (Dhuime et al., 2017; Tang et al., 2016; Greber et al., 2017; Hoffmann, 2017).

This contribution focuses on variations in the composition of the UMCC and highlights how they may have been critical in the changes in ocean chemistry that led to the period in the middle Proterozoic commonly known as the Boring Billion. Bioessential trace elements in sedimentary pyrite in marine black shales have been used as a micronutrient proxy through the Precambrian (Large et al., 2014, 2017; Mukherjee et al., 2017). Though we consider oxidative weathering to be one of the major drivers of such nutrient element trends, the importance of source rock composition deserves further evaluation.

Here, we use trace element ratios and Rare Earth Elements (REE) concentrations in shales to shed light on the evolution in the composition of the UMCC (Taylor and McLennan, 1985, 1995; Ronov et al., 1992; Condie, 1993). REE are relatively immobile, having a uniformly low seawater solubility and geologically short residence times in the ocean (200-2,000 years), such that they are almost quantitatively transferred from the continents to marine sediments, with the dissolved fraction rapidly deposited in the marine clay-organic-rich fine-grained component of shales (Taylor and McLennan, 1985, 1995; Freslon et al., 2014). Other low solubility trace element ratios have also been investigated here as they have been proven to be generally useful in crustal provenance studies, e.g., Th/Cr, Th/Co, Ni/Co, Cr/Sc and Cr/V (Condie and Wronkiewicz, 1990). In this study we have not measured bulk-rock REE chemistry in the conventional manner, but focused on LA-ICPMS analysis of the clay-rich matrix of fine-grained black shales. The clay matrix contains the component of REE carried by seawater and absorbed onto clays and organic matter (Taylor and McLennan, 1995; Roaldset, 1979; Freslon et al., 2014), rather than the component in detrital rock fragments and detrital heavy minerals, which has little relationship to the transfer of REE from the continents to continental margin organic-rich shales. The black shales used in this study have been selected from 52 Precambrian shale formations, 60% from Australia and 40% from other global locations (Table S1).

#### 2. Methods

The compositions of the fine matrix portion of the shales were measured in situ by Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) at the ARC Centre of Excellence in Ore Deposits, University of Tasmania. Eight to ten spots were measured per sample, on areas with the lowest pyrite and detrital phases and averaged to obtain the final result. The measurements were done using a 193 nm ArF Excimer ATL Atlex ILR laser coupled to an Agilent 7700 ICP mass spectrometer. The system is equipped with a custom-made constant-geometry Laurin Technic ablation chamber S-155 designed for 20 mounts of 2 cm size. A 50 µm spot was analyzed using a laser pulse rate of 10 Hz and a laser beam fluence  $\sim 2 \text{ J/cm}^2$  at the sample. Ablation occurred in an atmosphere of pure He flowing at a rate of 0.8 l/min immediately past the ablation point within the cell. He carrier gas was mixed with Ar (0.85 l/min) for improved efficiency of aerosol transport; both ICP-MS instruments were optimized to maximize sensitivity on mid- to high-mass isotopes (in the range 80-240 amu). Thirty seconds of measurement of background was followed by ablation for 60 seconds. External standards were measured before and after the sample run.



**Fig. 1.** A: Chondrite normalized REE plot comparing 1) post-Archean Australian shale (PAAS – red line), 2) this study, mean post Archean black shales by LA-ICPMS (blue line; n = 71) and 3) north American shale composite (NASC – green line). The close similarity of all REE patterns indicates the LA-ICPMS analytical method used here is compatible with other analytical methods. B: Chondrite normalized mean black shale matrix REE patterns for major periods of Earth history. Outlier spot analyses with  $8 < La/La^* < 0.001$  have been excluded from the mean calculation. C: PAAS normalized mean black shale matrix REE patterns for major periods of the references to color in this figure legend, the reader is referred to the web version of this article.)

The calculation of concentrations was achieved in two steps. Firstly the preliminary concentrations were obtained by the method outlined by Longerich et al. (1996) using a set of in-house and international reference materials which included GSD-1G as the primary standard for the majority of elements, Peruvian Pyrite for S and BCR-2 and NIST 612 for quality control. Instrumental drift was corrected at this stage. At the second stage, the final concentrations were calculated by normalization to 100%. The percentage of Fe present as pyrite was estimated assuming all measured S is present in pyrite with the remaining Fe assumed to be in oxide. The analyses were then normalized to total by estimating the mass of oxygen required for lithophile elements, including non-pyrite Fe, and adding concentrations of all measured elements. The resulting compositions are equivalent to whole rock compositions of the shale, excluding sulfide and lithogenic components. It is apparent from comparison of the chondrite normalized patterns of PAAS, NASC and the mean post Archean black shale analyses (n = 675)in this study (Fig. 1A), that the analytical method described here produces very similar results to the more conventional methods of McLennan (1989) and Gromet et al. (1984).

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