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Evidence for a reducing Archean ambient mantle and its effects on the carbon cycle

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ABSTRACT

Chemical reduction-oxidation mechanisms within mantle rocks link to the terrestrial carbon cycle by influencing the depth at which magmas can form, their composition, and ultimately the chemistry of gases released into the atmosphere. The oxidation state of the uppermost mantle has been widely accepted to be unchanged over the past 3800 m.y., based on the abundance of redox-sensitive elements in greenstone belt–associated samples of different ages. However, the redox signal in those rocks may have been obscured by their complex origins and emplacement on continental margins. In contrast, the source and processes occurring during decompression melting at spreading ridges are relatively well constrained. We retrieve primary redox conditions from metamorphosed mid-oceanic ridge basalts (MORBs) and picrites of various ages (ca. 3000–550 Ma), using V/Sc as a broad redox proxy. Average V/Sc values for Proterozoic suites (7.0 ± 1.4, 2σ, n = 6) are similar to those of modern MORB (6.8 ± 1.6), whereas Archean suites have lower V/Sc (5.2 ± 0.4, n = 5). The lower Archean V/Sc is interpreted to reflect both deeper melt extraction from the uppermost mantle, which becomes more reduced with depth, and an intrinsically lower redox state. The pressure-corrected oxygen fugacity (expressed relative to the fayalite-magnetite-quartz buffer, ΔFMQ, at 1 GPa) of Archean sample suites (ΔFMQ –1.19 ± 0.33, 2σ) is significantly lower than that of post-Archean sample suites, including MORB (ΔFMQ –0.26 ± 0.44). Our results imply that the reducing Archean atmosphere was in equilibrium with Earth's mantle, and further suggest that magmatic gases crossed the threshold that allowed a build-up in atmospheric O_2 levels ca. 3000 Ma, accompanied by the first "whiffs" of oxygen in sediments of that age.

INTRODUCTION

The speciation of volatiles in Earth's mantle, among them carbon, plays a pivotal role in triggering melting of mantle rocks at lower temperatures than in analogous dry systems and in the associated variety of CO_2-rich melts that can form (Wyllie and Huang, 1975; Canil and Scarfe, 1990). It is controlled mainly by the oxidation state of the mantle, which is gauged as the partial pressure (or fugacity) of oxygen (f_{O_2}) and buffered by the coexisting Fe-bearing minerals mainly within peridotite rocks (Luth et al., 1990; Stagno et al., 2013). This establishes an intimate link between changes in the redox state of the terrestrial mantle through time and the carbon cycle and, ultimately, the origin and diversification of life (Kasting et al., 1993; Holland, 2002).

The redox state of the uppermost mantle is connected to the atmosphere via its effect on the speciation of volatiles degassed in volcanic systems, with the proportion of reduced species (e.g., CH_4, H_2S, H_2) decreasing and oxidized species (e.g., CO_2) increasing with increasing f_{O_2} (Li and Lee, 2004). It has been suggested, based on broadly basaltic magmas from a variety of tectonic settings, that the uppermost Archean mantle was oxidized to present-day levels by ca. 3800 Ma (Canil, 1997, 2002; Delano, 2001; Li and Lee, 2004). This poses a conundrum because, in the presence of a reducing atmosphere prior to the Great Oxidation Event (GOE; ca. 2.4–2.3 Ga) (Lyons et al., 2014), it would suggest that the mantle and ocean-atmosphere system were not in secular equilibrium, contrary to expectations (Sleep and Zahnle, 2001; Canil, 2002). It has also prompted the dismissal of a link of the rise in atmospheric O_2 to the mantle oxidation state (Kasting, 2013). Recent evidence for a reducing Archean uppermost mantle source, from a single eclogite xenolith suite with mid-ocean ridge–derived protoliths (Aulbach and Viljoen, 2015), provides the impetus to revisit this issue, employing additional carefully chosen sample suites reported in the literature.

METHODS

V/Sc Redox Proxy

The speciation of multivalent elements, such as Fe and V, depends on the local redox state, which determines their valence and cation radius and the degree to which they are retained in the solid mantle residue or transferred into the basaltic melt (Canil, 1997, 2002; Mallmann and O'Neill, 2009). The ratios of some multivalent over homovalent elements, such as the first transition row elements V and Sc, respectively, show little dependence on the degree of partial melting and separation from their mantle source, olivine fractionation, degassing, or later overprint (Li and Lee, 2004; Lee et al., 2005). The V/Sc redox proxy is based on the knowledge that V becomes more incompatible with increasing valence state as a function of f_{O_2}, whereas Sc partitions independently of f_{O_2}, with the result that melts leaving more oxidized sources have higher V/Sc than those leaving more reduced sources.

Identification of Samples with Ambient Mantle-Derived Protoliths

In analogy with modern mid-oceanic ridge basalt (MORB), basalts and picrites from spreading ridges should have flat middle and heavy rare earth element (REE) patterns (partial melting of spinel peridotite), mild depletion in the lightest REEs (partial melting of a depleted mantle source), lack of enrichment in incompatible elements (indicative either of enriched sources, advanced degree of differentiation, or within-plate settings) or thorium (crustal contamination), and no negative Nb or Ta anomalies (convergent margin settings) (Pearce, 2008). Because clinopyroxene (cpx) partitions V over Sc, the proxy should not be applied to basalts showing evidence for cpx fractionation or accumulation (Li and Lee, 2004). To ensure that the samples chosen here from literature data comply with these assumptions and requirements, we have filtered those derived from (1) nonprimitive, pyroxenite-rich sources or those that have undergone cpx accumulation or fractionation, using CaO-MgO relationships, (2) metasomatized or enriched sources or by small degrees of partial melting, using chondrite-normalized Ce/Yb > 1, and (3) gabbroic (cumulate) protoliths, using positive chondrite-normalized Eu anomalies. The filtered samples have protoliths that left a dry peridotite source and fractionated only olivine ± plagioclase, which is the scenario for which the V/Sc redox proxy has been developed (Li and Lee, 2004; Lee et al., 2005).

Conversion of V/Sc to f_{O_2}

Due to the convergence of V/Sc in the melt with increasing melt fraction F, the average V/Sc in each suite is converted to f_{O_2} relative to the fayalite-magnetite-quartz buffer (ΔFMQ) as a function of F, which is in turn related to the melting interval determined by the initial and final pressure of melt extraction (Aulbach and Viljoen, 2015). The initial pressure is estimated by calculating the pressure at which the mantle solidus is crossed as a function of mantle potential temperature (T_P) using a published solidus parameterization (Hirschmann, 2000), whereby the terrestrial mantle T_P evolution curve (Davies, 2009) is used to obtain T_P for a given basalt or metabasalt age. This yields moderate F of ~0.2 for Archean samples (Table DR2 in the GSA Data Repository[1]). As the uppermost convecting mantle crossed its solidus at greater depths in the warmer Archean (Davies, 2009) and also becomes more reducing with depth (Stagno et al., 2013), ancient melts are expected to have lower V/Sc than modern MORB even if the redox state of the convecting mantle had not changed (Aulbach and Viljoen, 2015; Gaillard et al., 2015). In order to isolate the intrinsic redox state of the convecting mantle and subtract the effect of deeper melting of more reducing ambient mantle in the warmer Archean, ΔFMQ is projected from the average depth of melting during generation of the protoliths to the average depth of MORB generation (1 GPa) (Foley, 2011), applying the relationship of a decrease of 0.4 units of ΔFMQ per 1 GPa pressure increase (Stagno et al., 2013) (for more details on methods, uncertainties, and sample selection, as well as supplemental figure and tables, see the Data Repository).

UPPERMOST MANTLE REDOX EVOLUTION

Reexamination of the Current Paradigm

There is considerable uncertainty regarding mantle f_{O_2} throughout Earth's history. At present, ΔFMQ of ~–0.4 (±0.4 1σ) is recorded by MORB formed in the uppermost asthenospheric mantle (Frost and McCammon, 2008; Foley, 2011). Some studies have taken modern MORB-like redox state values of ca. 3.8 Ga or younger mantle-derived melts (komatiites, picrites, and basalts) as evidence that the uppermost mantle f_{O_2} attained its present value shortly after core formation, when it had a suggested f_{O_2} of ΔFMQ –4.5 (Frost and McCammon, 2008), and remained relatively constant over time (Canil, 1997, 2002; Delano, 2001; Li and Lee, 2004). However, most of the MORB erupted >200 m.y. ago has been subducted, and the rocks sampled in Archean greenstone belts (e.g., basalts associated with komatiites) and ophiolites used in previous studies do not represent preserved oceanic crust formed within spreading ridges, and hence did not sample the ambient convecting mantle (Pearce, 2008; Foley, 2011). Rather, they reflect emplacement in intracratonic rift basins or on continental margins, with potentially significant contributions from sublithospheric mantle regions that are thermochemically anomalous and from continental lithospheric mantle, followed by assimilation, mixing, and fractional crystallization during their emplacement (Arndt, 1999; Mole et al., 2014). This masks the primary redox-derived signal and precludes application of the V/Sc redox proxy, which was devised for a primitive mantle (PM) source and processes accompanying crystallization of a dry magma after decompression melting to shallow pressures beneath spreading ridges (Li and Lee, 2004).

The recent finding of low V/Sc and corresponding f_{O_2} in a suite of 3 Ga mantle eclogites from the Kaapvaal craton (South Africa; Aulbach and Viljoen, 2015) contrasts with these earlier results and requires validation by additional data. In order to determine the oxidation state of the Archean uppermost mantle, we carefully selected those rocks from the literature that likely formed beneath spreading ridges, as outlined in the Methods section. We find that the V/Sc values of post-Archean basalts and metabasalts in this study (7.0 ± 1.4, 2σ; n = 6) are similar to those of modern MORB (6.8 ± 1.6), but that markedly lower values (5.2 ± 0.4, n = 5) are observed for Archean basalts and metabasalts (Fig. 1A), despite the difference in sample types (orogenic versus mantle eclogites) and analytical methods (measured versus reconstructed bulk rocks).

Resolvable Difference in Archean and Post-Archean Ambient Mantle Redox State

The standard deviations for V/Sc and ΔFMQ of multiple samples within single basalt and metabasalt suites are large, similar to those for modern MORB (Figs. 1A and 1B), and are interpreted to reflect f_{O_2} variability in the basalt source combined with some compositional variability (Cottrell and Kelley, 2013). However, there are at least two groups that are significantly different at the 95% level with regard to pressure-corrected ΔFMQ: post-Archean suites (including MORB) with –0.26 ± 0.44, 2σ (n = 7) and Archean suites with –1.19 ± 0.33 (n = 5; Fig. 1C), even if conservative values for V/Sc are used to calculate ΔFMQ. Low f_{O_2} retained in ferric-ferrous Fe equilibria in some mantle eclogite xenoliths have also been suggested to relate to low initial $Fe^{3+}/\Sigma Fe$ if not due to loss of incompatible Fe^{3+} during subduction-related melt loss (Stagno et al., 2015).

The redox evolution of the uppermost convecting mantle can also be illuminated from the mantle and continental crust perspective using modeling (Table DR4). The depleted mantle (DM) composition has been successfully reproduced by extraction of 3% melt from the PM, which produced the continental crust (Workman and Hart, 2005). The consequent decrease in V concentration, from 82 ppm in PM to 79 ppm in DM, is modeled for a bulk distribution coefficient for vanadium, $^{bulk}D_V$, of 0.44 for F = 0.03, which is the case for ΔFMQ –1. Thus, if the current upper mantle ΔFMQ is –0.4, and has been for billions of years, there must have been a period where mass transfer from the mantle occurred at ΔFMQ <–1. Conversely, the V concentration of the bulk continental crust (138 ppm), ~50% of which formed between ca. 3.8 and 2.5 Ga (Belousova et al., 2010), can only be produced in the model if $^{bulk}D_V$ is even lower than the estimate of 0.44, corresponding to ΔFMQ –1.3; that is, far below the present-day f_{O_2}. Thus, the weight of the geochemical evidence appears to be in favor of a more reducing uppermost mantle in the Archean.

WHAT CAUSED THE INCREASE IN ARCHAEAN AMBIENT MANTLE f_{O_2}?

Our data suggest that, post-core formation, the f_{O_2} of the uppermost mantle had increased by several log units by Mesoarchean time to reach modern values by Paleoproterozoic time. During Earth's accretion, disproportionation of FeO into Fe metal (~10% of which descended to the core) would have led to a corresponding increase in mantle O_2 (with ferric iron partitioned essentially into bridgmanite); subsequent upward mixing of this material could have increased the upper mantle f_{O_2} (Frost and McCammon, 2008). Figure 1C shows that sluggish upward mixing of mantle with excess Fe_2O_3, accompanied by an increase in ambient mantle f_{O_2}, mirrors evidence from the platinum group element concentrations of deep-seated komatiites for sluggish downward mixing of late accreted material (Maier et al., 2009). Both phenomena are based on observations from multiple cratons and therefore may be global expressions of a linked geodynamic process. This would be consistent with increasing evidence from geochemical data and numerical models that early-generated mantle heterogeneities can resist remixing by mantle convection for billions of years (Rizo et al., 2013; Girard et al., 2016).

SOME IMPLICATIONS

Our finding of more reducing MORBs during the Mesoarchean to Neoarchean compared to later-formed basalts warrants a closer look at the possible consequences. Figure 2A shows the redox profile predicted for an ambient mantle source with low $Fe^{3+}/\Sigma Fe$ and 10 ppm carbon

[1]GSA Data Repository item 2016244, description of sample selection and methods, Figure DR1, and Tables DR1–DR4, is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org.

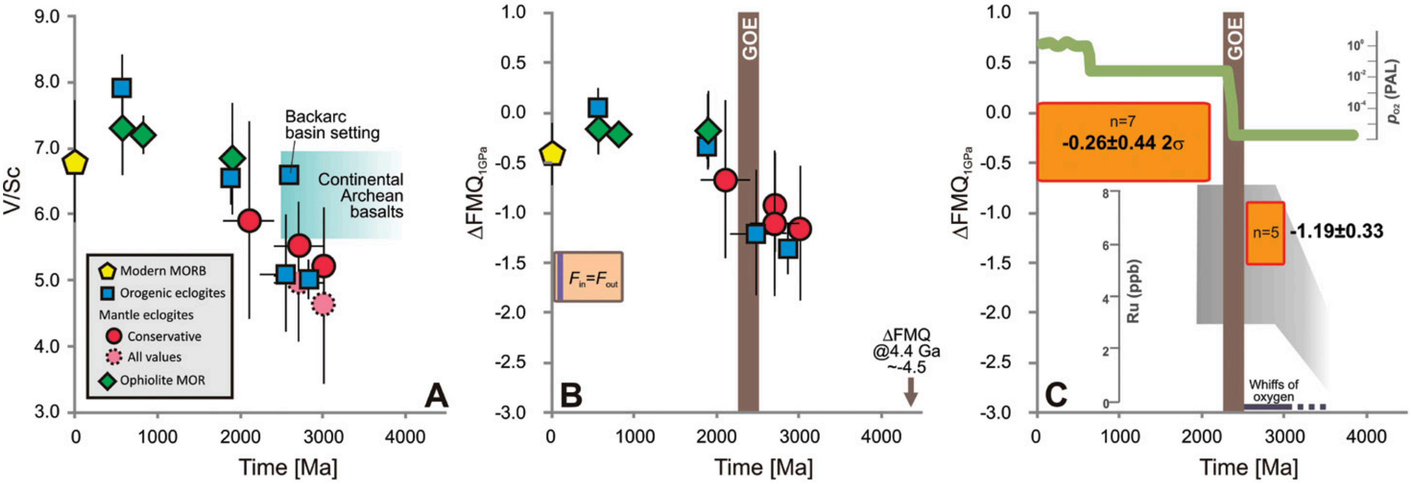

Figure 1. A: V/Sc of mid-ocean ridge (MOR)–derived metabasalts and basalts. MORB—mid-oceanic ridge basalt. B: Calculated oxygen fugacity (f_{O_2}) (relative to fayalite-magnetite-quartz buffer, ΔFMQ) corrected to 1 GPa . Error bars on V/Sc are 1σ of the mean per sample suite, those on ΔFMQ are propagated 1σ errors of V/Sc, and those on the age are the cited 1σ errors for isochron-derived ages or age ranges reported in the literature. For two mantle eclogite suites (Victor [Superior craton, Canada] and Lace [Kaapvaal craton, South Africa]), two average values were calculated, where samples with the lowest V/Sc, of uncertain nature, were excluded for a conservative estimate. The range of V/Sc for continental Archean basalts is from Li and Lee (2004), and the estimate for convecting mantle immediately after core formation is from Frost and McCammon (2008). The timings of the Great Oxidation Event (GOE) and of the first "whiffs" of oxygen are from Lyons et al. (2014). F_{in} = F_{out} (F—flux) corresponds to the crossover between volcanic gas compositions acting as oxygen sinks versus sources as a function of ambient mantle f_{O_2} (Holland, 2002; Li and Lee, 2004). C: ΔFMQ (corrected to 1 GPa) averaged for all post-Archean sample suites (including modern MORB) and for all Archean sample suites. Boxes encompass mean ΔFMQ ±2σ and age ranges for the sample suites. Gray field shows trend in Ru concentrations in mantle-derived komatiites (Maier et al., 2009); green line shows one possible evolution of atmospheric partial pressure of O_2 (pO_2) relative to the present atmospheric level (PAL) (Lyons et al., 2014).

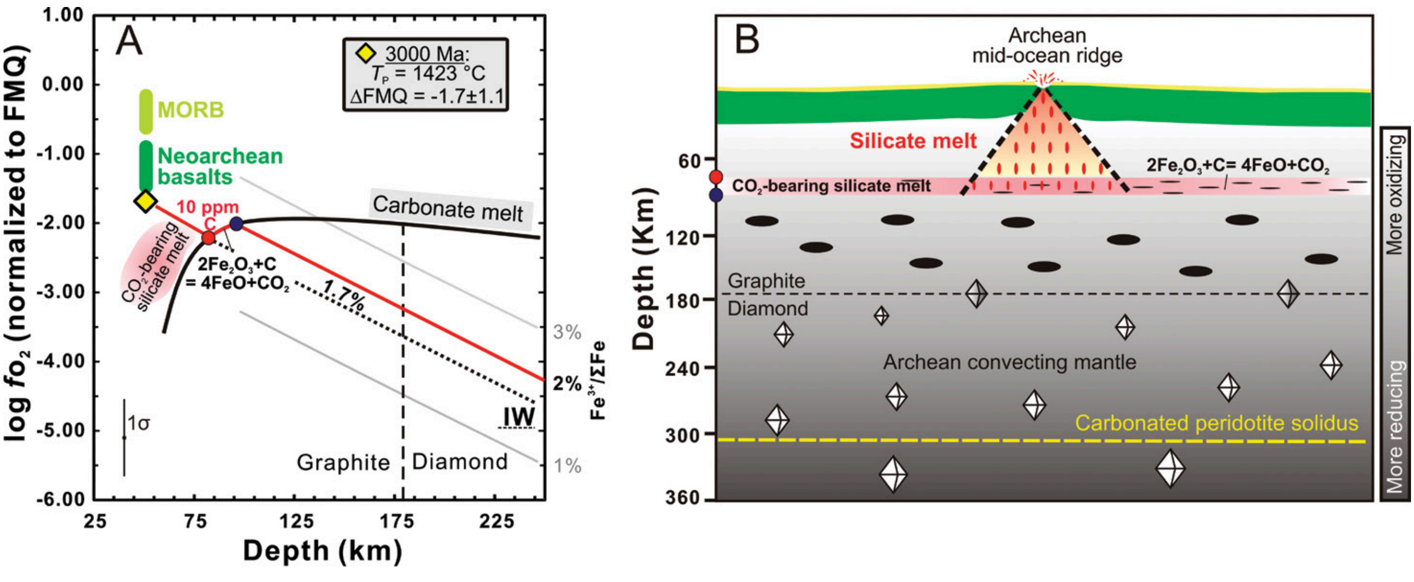

Figure 2. Speciation of carbon in the Archean mantle and origin of CO_2-bearing melts. The composition of CO_2 melts results from the parameterization of oxygen fugacity (f_{O_2}) as functions of pressure (*P*), temperature (*T*), and X_{CO_2}. A: Mantle redox profiles (f_{O_2} as a function of depth; gray lines) for different bulk rock $Fe^{3+}/\Sigma Fe$ ratios (Stagno et al., 2013) at mantle potential temperature (T_P) of 1420 °C; i.e., the temperature derived for the oldest mantle eclogite suite investigated here (3 Ga; Lace, Kaapvaal craton, South Africa; Aulbach and Viljoen, 2015). Calculations of f_{O_2} along an Archean mantle adiabat follow those of Stagno et al. (2013). Error bar shows 1σ on the oxy-thermobarometer employed. Black line indicates f_{O_2} at which graphite (or diamond) and carbonate melt (Stagno and Frost, 2010) coexist within a peridotite assemblage, calculated as function of *P*, *T*, and CO_2 content. With decreasing pressure during mantle upwelling, f_{O_2} drops owing to the increase in silica content in the melt. The ranges of f_{O_2} for mid-oceanic ridge basalt (MORB) and Archean basalts are from Lee et al. (2005) and this study, respectively. Mantle containing 2% $Fe^{3+}/\Sigma Fe$ would be in the graphite stability field at depths <170 km. Redox melting [C(graphite) + $2Fe_2O_3$(melt) = 4FeO + CO_2 (both in the melt)] (Frost and McCammon, 2008) would occur in the depth interval of ~100 km (blue dot) and ~80 km (red dot) as the f_{O_2} of upwelling mantle crosses the equilibrium between graphite and carbonate-silicate melt (CO_2 content ~10 wt%), with consequent reduction of Fe^{3+} in silicate phases (red line). The MORB f_{O_2} at 3000 Ma would result from oxidation of only 10 ppm of carbon in the depleted early mantle source (Dasgupta, 2013), which decreases the initial rock $Fe^{3+}/\Sigma Fe$ ratio by <1%. For higher carbon contents and lower T_P in the mantle source, silica-poor carbonated melts would be produced. The IW (iron-wustite) buffer is also indicated. B: Processes in the Archean convecting mantle as modeled in A (red line).

(Dasgupta, 2013), which can satisfy the ΔFMQ of –1.7 ± 1.1 at 3000 Ma (most reduced value for Lace eclogites; Kaapvaal craton, South Africa), with redox melting occurring at ~100 km, at similar pressures to MORB generation, during which small amounts of carbonate-silicate melts are produced in equilibrium with graphite in the source. Thus, redox melting is expected to occur at shallower depths for lower $Fe^{3+}/\Sigma Fe$ (Foley, 2011; Rohrbach and Schmidt, 2011). In contrast, the generation of carbonated silicate melts beneath mid-ocean ridges by redox melting would provide a possible mechanism of primordial CO_2 transfer from the uppermost mantle to the seafloor, the volume of which appears to be mainly controlled by $Fe^{3+}/\Sigma Fe$ (Fig. 2).

The ratio of reduced to oxidized volatiles escaping from pre–3000 Ma magmas after decompression melting and degassing, at appropriately shallow emplacement depths (Gaillard et al., 2015), would have been higher than today (Li and Lee, 2004). Such reducing volcanic gas mixtures were possibly propitious for the formation of organic molecules that may have become early building blocks of life (Kasting et al., 1993). The switch to a net oxidizing input occurs around ΔFMQ –2 to –1.4 (Holland, 2002; Li and Lee, 2004); that is, close to the values determined for the Mesoarchean in our study (Fig. 1B). Given these new results, a change in uppermost mantle redox state as a factor in the rise of atmospheric oxygen needs to be reconsidered.

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