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

1. SAMPLE DESCRIPTION

In order to obtain constraints on the redox state of the convecting mantle, a spreading ridge origin has to be ascertained for the samples to which the V/Sc redox proxy is applied (Foley, 2011). We rely on literature reports of regional tectonic evolution and on geochemical indicators (e.g. LREE-depleted REE patterns with flat MREE-HREE, depleted initial radiogenic isotope compositions, lack of Ti-Nb-Ta depletions) to find appropriate eclogite and ophiolite suites that may represent fragments of oceanic crust that was subducted (ophiolites) or exhumed (orogenic metabasalts) during the closure of past ocean basins, or emplaced during the amalgamation of cratons (mantle eclogites) (Table DR1). Only non-plume-, non-subduction-related orogenic eclogites, and ophiolites that are allochthonous to the continental rocks with which they now occur, can provide unambiguous constraints on conditions of melting of the ambient convecting mantle (Pearce, 2008; Kamber, 2015). This does not apply to “ophiolites” occurring in Archaean greenstone belts, or to basalts associated with komatiites, which are (par)autochthonous and do not represent Archaean oceanic crust (Bickle and Nisbet, 1994; Pearce, 2008; Kamber, 2015). The mantle eclogites used in this study fulfil the requirement of a low-pressure origin (Jacob, 2004; Aulbach and Viljoen, 2015) and have ages that often correlate with periods of craton amalgamation or collisions at craton margins (Table DR1).

2. METHODS

Bulk rock reconstruction

In order to obtain kimberlite-free bulk mantle eclogite compositions, it is common practise to reconstruct these from mineral compositions weighted by their modal abundances (Jacob, 2004). The procedure and rationale has been outlined in detail in Aulbach and Viljoen (2015). The chosen mineral mode of 55% garnet plus 45% cpx is dictated by the picritic rather than basaltic nature of mantle eclogites (Jacob, 2004), lies within the range of measured modes and reproduces the major-element compositions of picrites produced in experiments at ~2 to 3 GPa and ~1400 to 1450° C (similar to the conditions determined for ambient Archaean mantle from mantle eclogites from the Kaapvaal craton; Aulbach and Viljoen, 2015), with SiO₂ of ~46-48 wt% and MgO of 14-16 wt% (Falloon and Green, 1988; Hirose and Kushiro, 1993). Rutile does not control the concentrations of V and Sc in the residue (Aulbach et al., 2011), but its presence will have an effect on bulk rock V/Sc, increasing this ratio by 0.15 in eclogites from the Lace kimberlite, Kaapvaal craton (n = 3; Aulbach and Viljoen, 2015) and by 0.14 in eclogites from the central Slave Craton (n = 6; Aulbach et al., 2011). The average V/Sc of each eclogite xenolith suite in this study was therefore adjusted by +0.15 to account for the likely presence of rutile. In contrast, spinels, which also have high D_V (Mallmann and O’Neill, 2009), are rarely reported for eclogite xenoliths and such samples are not included here.
Data filtering

Samples (including MORB) with chondrite-normalised Ce/Yb > 1 are possibly metasomatised (Aulbach and Viljoen, 2015) and are therefore filtered from the data-set. Assuming that true peridotite-derived melts emplaced in spreading ridges should have Ce/Yb ≤ 1, the Ce/Yb filter further removes samples having protoliths (1) derived from enriched sources, to which the V/Sc redox sensor cannot be applied, (2) emplaced mid-plate beneath a thick lithospheric lid allowing only low melt fractions to be achieved, which do not represent ambient convecting mantle or (3) that assimilated evolved crustal material (Pearce, 2008).

For some sample suites, a range of ages is reported, and median age values are used in Figure 1 along with the range as the associated uncertainty. When isochron ages are available, associated one-sigma uncertainties are plotted. Additional uncertainty (of no consequence to the conclusions reached in this paper) derives from the fact that in metamorphosed samples, isochron ages date metamorphism, whereas the protolith could be up to several 100 Ma older (by analogy with the age of modern ocean basins).

Fractionation or accumulation of cpx has a marked effect on V/Sc (Li and Lee, 2004). Herzberg and Asimow (2008) published equations that define the upper and lower limits of MgO-CaO relationships that are expected for melts from a dry peridotite source that experienced only olivine fractionation. These equations were applied to filter samples from the database that either experienced cpx accumulation (high CaO/MgO) or fractionation (low CaO/MgO), or that have a pyroxenite component in their source (low CaO/MgO). Data were filtered to exclude gabbroic (cumulate) samples with positive Eu anomalies; following Li and Lee (2004), MORB was additionally filtered to exclude samples with MgO < 8 wt%.

Conversion of V/Sc to fO2

The procedure, assumptions and rationale for the conversion of V/Sc to fO2 have been described in Aulbach and Viljoen (2015) and are summarised here for the benefit of the reader; results are given in Table DR2. The main premise of the use of V/Sc as a redox sensor is that the concentrations of these mildly incompatible elements are little fractionated during igneous processes (Canil, 1997, 2002; Li and Lee, 2004; Lee et al., 2005). The fO2 sensitivity of V has been experimentally demonstrated in numerous studies and the strongest sensitivity in \( \Delta DV \) is recorded between \( \Delta FMQ-2 \) to \( \Delta FMQ+4 \) (Mallmann and O’Neill, 2009), encompassing the region of interest in our study. The V/Sc-derived average \( \Delta FMQ \) of −0.3 and standard deviation of ±0.5 for modern MORB (Li and Lee, 2004) compare well in terms of both absolute value and distribution of values with the value of −0.41±0.43 obtained from conventional Fe3+/ΣFe-based oxybarometry (Frost and McCammon, 2008).

Due to higher terrestrial mantle potential temperatures in the past (Davies, 2009), the mantle solidus was crossed at greater depths, generating higher melt fractions (F). MORB represents relatively small melt fractions (F ~0.1) leaving a spinel peridotite source at ~1.5 to < 2 GPa depth and melting on average to 0.5 GPa, whereas picrites represent larger melt fractions (0.2-0.3) (Herzberg et al., 2010). Bulk D\( V_{Sc} \) has been shown to change little for F ≤0.27, when cpx is exhausted (Lee et al., 2005). However, with increasing F, incompatible element concentration ratios in the melt converge, decreasing the sensitivity of V/Sc to fO2 (Lee et al., 2005). In order to obtain estimates of F for all samples, the ages for the (meta)basalts are inverted for \( T_P \) using the \( T_P \) profile of Davies (2009), which then yields a pressure for the
onset of partial melting for each of the suites when combined with the solidus parameterisation of Hirschmann (2000) (Table DR2). For this Tp profile at 3 Ga, the solidus is crossed at a pressure of 2.5 GPa when the mantle Tp is ~1420°C, consistent with the absence of a garnet signature during formation of the low-pressure protoliths to Archaean eclogite suites (Figure DR1). For mantle upwelling beneath mid-ocean ridges, the final melting pressure is likely shallow in the absence of a pre-existing lithospheric lid, ranging from 1 atm to 1 GPa, such that the melt fraction F should be proportional to the depth of onset of partial melting and the resulting length of the melting column (Herzberg et al., 2010). Finally, V/Sc is converted to ΔFMQ as a function of F, using the relationship derived by Li and Lee (2004).

The mantle becomes more reducing with depth (Frost and McCammon, 2008), owing to the enhanced stability of ferric iron-bearing components in garnet and pyroxene, and, in the modern mantle, reaches metal saturation at depths around 250-300 km (Ballhaus, 1995; Rohrbach et al., 2007). A meaningful comparison of the redox state of mantle-derived melts must take into account that these may have separated from a source at variable mantle depths, depending on mantle potential temperature (Tp) as a function of age. This pressure effect is corrected by projecting from the average depth of melting for the generation of the protoliths to the samples used in this study to the average depth of MORB generation, assumed here to be 1 GPa (Foley, 2011). Using a final melting pressure of 0.5 GPa and a melt productivity of 10% per GPa (Walter, 1999), the average melt extraction pressure is calculated from the melt fraction described in the previous paragraph (Table 1). A correction to 1 GPa can then be made using the ΔFMQ-depth relationship of Stagno et al. (2013), with a value of 0.4 log units per GPa. If the final melting pressure was higher, for example 1 GPa instead of 0.5 GPa, the corresponding ΔFMQ correcting to 1 GPa would increase by 0.10 log units.  

Uncertainties

The application of V/Sc as a redox proxy and conversion to oxygen fugacity has been modelled by Li and Lee (2004) assuming a primitive mantle (PM) source and isobaric non-modal batch melting in the spinel peridotite stability field, but an uncertainty estimate is not provided. Several uncertainties can be identified: (1) Related to source compositions and
Figure DR2.

Series of bivariate diagrams (oxides in wt%, trace elements in ppm) used to assess the low-pressure origin and metamorphic evolution of diverse (meta)basalt suites used in this study. A-D: Archaean suites; E-H: Proterozoic suites; references in Table DR1. Shown for comparison is the MORB compilation of Jenner and O’Neill (2012). Lower average concentrations in incompatible minor and trace elements (TiO₂, Ce, Yb) indicate formation at higher melt fractions, whereas positive trends of Ce and Yb with TiO₂ indicate melt evolution during fractional crystallisation of olivine (± plagioclase), where these elements are incompatible. Lower slopes of TiO₂ with Ce compared to basalts and picrites may indicate metamorphic melt loss of highly incompatible Ce; similar slopes of TiO₂ with Yb to MORB suggests derivation by partial melting of spinel peridotite, whereas lower slopes may indicate retention of Yb by garnet in the source, hence partial melting at pressures ≥2.5-3.0 GPa; higher slopes may be due to metamorphic melt loss in the eclogite facies, during which Yb is compatible in garnet (Aulbach and Viljoen, 2015). Bottom panels show V/Sc against Sc to assess effects of degree of peridotite source melting and against chondrite-normalised Ce/Yb (denoted by subscript N) as a proxy for degree of eclogite partial melting during metamorphism. There appears to be a trend for Proterozoic samples, indicating that V behaved more incompatibly, as modelled for melting of rutile eclogite with NMORB composition at ΔFMQ+0.5 (Table DR4). A significant number of Archaean samples falls above and below the modelled melt depletion trend and shows no covariation of V/Sc as a function of Ce/YbN.
mineralogy diverging from the primitive mantle model. This is further discussed in section 4 below. (2) Uncertainty in the garnet-cpx modal abundances used in the reconstruction of mantle eclogites. The average $cpx/garnet D_V$ and $D_{Sc}$ is 3.0 and 0.27, respectively, in a suite of mantle eclogites from the Lace kimberlite (Kaapvaal craton), indicating stronger partitioning of V into cpx and of Sc into garnet, and a sensitivity of bulk rock V/Sc on mineral modes. The effect of varying the mineral mode by 10% (e.g. 60% garnet plus 40% cpx instead of equal proportions) on V/Sc is to vary this ratio on average by 1 “unit” (Aulbach and Viljoen, 2015). Unless a systematic bias is involved, this is of no consequence when average values are calculated for multiple samples per eclogite suite, as done here. (3) Within-suite spread of V/Sc values, which translate into large standard deviations as shown in Fig. 1. The modern MORB source is known to be heterogeneous with regard to mineralogy and composition (e.g. Salters and Stracke 2004) and to redox state (Cottrell and Kelley 2013). The ancient uppermost convecting mantle may have been similarly heterogeneous, giving rise to a similar spread in V/Sc. This translates into heterogeneity with regard to elemental V and Sc concentrations in the source, but also to the partitioning of V into the melt as a function of $f_{O_2}$.

3. ASSESSMENT OF INTER-LABORATORY BIAS

For the reported measured bulk rock compositions (orogenic and ophiolitic amphibolites, granulites and eclogites), most data were produced by XRF or solution ICPMS. Noack et al. (2013) present Sc results obtained by solution ICPMS on BHVO-2 (31.3 ppm) and BIR-1 (42.7 ppm), compared with GEOREM-values of 33 and 43 ppm, respectively, revealing minimal deviation. Reference values for V are not available in that study. Errors <5% are cited for solution ICPMS-derived trace-element data from the Belomorian belt (Shchipansky et al., 2012). Inter-lab comparison of rocks with matrices similar to the (meta)basalts used here (dolerite and microgabbro) demonstrate that XRF data for both V and Sc agree to within 8 and 7% (1 sigma), respectively (Govindaraju et al., 1994). Good agreement with accepted values (<7% deviation, both positive and negative) was obtained for Sc in three well-characterised basaltic reference materials (BCR-1, BHVO-1, BIR) using ICPMS (Garbe-Schoenberg et al., 1993; V was not quantified in that study), corresponding to techniques employed in the studies used here.

For eclogite xenoliths, bulk rock compositions are based on in situ analyses of constituent garnet and cpx, employing EPMA and LAM ICPMS, which are routine analyses in the labs from which such data are used (University of Alberta, Frankfurt University, Macquarie University; first author has worked in all three laboratories). V and Sc occur in both minerals at concentrations far above the limit of detection (<0.06 ppm and <0.3 ppm, respectively) and can be determined with instrumental uncertainties of ~5% (Aulbach and Viljoen, 2015). From an analytical viewpoint, there is therefore no concern that V/Sc could be systematically underestimated. Three Archaean mantle eclogite suites (Greenland/North Atlantic craton: Tappe et al., 2011; Superior: Smit et al., 2014; Kaapvaal: Aulbach and Viljoen, 2015), give lower V/Sc values than Proteorozoic suites, which agree remarkably well with V/Sc for two similarly aged orogenic eclogites and granulites (Shchipansky et al., 2012; Noack et al., 2013), the V/Sc of which was obtained using whole-rock analytical techniques in other laboratories (Table DR3). These considerations provide circumstantial evidence that inter-laboratory bias or a bias from rock type (measured orogenic vs. reconstructed xenolith) is small.
4. EFFECTS OF MANTLE SOURCE MINERALOGY

A secular change in the modal composition of the ambient convecting mantle has plausibly occurred by progressive depletion of an originally primitive “starting material” due to extraction of the continental crust (corresponding to an F of 0.03; Workman and Hart, 2005). Modelling presented in Table DR4 shows that melting of (1) depleted rather than primitive mantle, (2) pyroxene-rich source heterogeneities or (3) garnet rather than spinel peridotite will lead to higher V/Sc in the melt compared to a primitive mantle model, hence biasing the results towards higher apparent $f_{O_2}$ when the Li and Lee (2004) model is used as a redox proxy.

5. EFFECT OF PARTIAL MELT LOSS DURING OR AFTER ECLOGITISATION

The effect of metamorphic melt loss, during or after eclogitisation of warm Archaean oceanic crust where a silicic melt similar to tonalite-trondhjemite-granodiorite is produced (e.g. Sen and Dunn, 1994), is gauged using chondrite-normalised Ce/Yb (denoted with subscript N). Modelling shows that this ratio decreases to 0.65 after 5% and 0.28 after 20% partial melt extraction from a rutile-bearing eclogite (Aulbach and Viljoen, 2015). Archaean sample suites show no co-variation of V/Sc with Ce/Yb_N, indicating that the effect of melt extraction on V/Sc is insignificant, whereas post-Archaean suites appear to show a correlation (Figure DR2D, H).

Fully quantitative modelling of the effect of melt loss from eclogite is hampered by the lack of experimental partitioning data for $^{\text{Mineral-silicic melt}}D_V$ and knowledge of how the $f_{O_2}$ in subducting oceanic crust changes with depth. Preliminary modelling using coefficients for the redox-dependent distribution of V between basaltic melt and cpx plus garnet ($^{\text{garnet}}D_V = cpxD_V$; Mallmann and O’Neill, 2009), and assuming that rutileDV changes as a function of $f_{O_2}$ at the same rate as cpx (Table DR4), shows that under reducing conditions ($\Delta$FMQ-2), bulk $D_{V/Sc}$ is 0.73, whereas under more oxidising conditions ($\Delta$FMQ-0.4, corresponding to the modern MORB source) bulk $D_{V/Sc}$ is 0.28. For oxidising conditions, this leads to a decrease in V/Sc from 7.29 to 6.26 (NMORB estimate of Gale et al., 2013), whereas for more reducing conditions a weaker decrease is observed (to 7.13, both for F = 0.2). For an Archaean basalt with lower initial V/Sc of 5.50, the decrease upon melt extraction from eclogite would be smaller still (to 5.38). While the V/Sc of Proterozoic suites is well modelled for a $\Delta$FMQ+0.5 (plausibly corresponding to more oxidising conditions in subduction zones after the GOE), a significant number of Archaean samples lies below and above the trend at moderate and high degrees of melt extraction, respectively, suggesting partial melt extraction under reducing conditions when V/Sc changes little (Figure DR2D, H).

At Lace some of the lowest V/Sc values are observed for low Ce/Yb_N and these samples are excluded for a conservative estimate in order to avoid a bias toward low $f_{O_2}$, although these low V/Sc are unlikely to be due to melt loss from eclogite. Conversely, inclusion of Proterozoic samples with low V/Sc at low Ce/Yb_N may imply a small bias of the data toward lower $f_{O_2}$. Their exclusion would drive the average Post-Archaean data towards an even higher average, accentuating the difference with the Archaean data-set. Our approach is to err on the side of overestimating $f_{O_2}$ in the Archaean and underestimating $f_{O_2}$ in the post-Archaean. The fact that we still observe a resolvable difference (at the 2 sigma level) between both, after accounting for the higher melt fractions and deeper onset of partial melting leading
to the generation of Archaean picrites, suggests that the differences between the two data-sets are real and related to redox.

6. ESTIMATE OF CO² FLUX DURING THE MESOARCHEAN

It is possible to determine the asthenospheric redox profile based on the use of oxybarometry for garnet-bearing peridotite for known $f_{O2}$ of MORB (Stagno et al., 2013). At depths where the $f_{O2}$, buffered by the 4-phase mantle mineral assemblage, crosses the boundary at which carbon and carbonate coexist, redox melting is expected to occur above the solidus temperatures of carbonated peridotite. At higher Archaean mantle potential temperatures and lower $f_{O2}$ determined in this study (Table DR2), and following the parameterization of melt fraction vs T (Dasgupta, 2013) and of $X_{CO2}$ (melt) vs $f_{O2}$ (Stagno and Frost, 2010), the resulting melt composition is carbonate-silicate. The oxygen needed to oxidise graphite to carbonate causes a shift in the $Fe^{3+}/ΣFe$ of the mantle bulk composition, which depends on the initial carbon concentration. In this study, the carbon concentration is chosen to be in agreement with experiments on C partitioning between silicate and melts (Dasgupta, 2013).

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