



The constancy of upper mantle fO_2 through time inferred from V/Sc ratios in basalts

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Abstract

The geochemical behaviors of V and Sc during partial melting are more similar to each other than to most other elements but, in detail, the partitioning of V is redox-sensitive whereas that of Sc is not. The V/Sc ratio in basalts is shown here to be a sensitive and robust recorder of the oxygen fugacity (fO_2) of their mantle source regions. The use of V/Sc ratios differs from the use of V and/or Cr elemental systematics in basalts because the latter, strictly speaking, provide information on the fO_2 of the erupted magma and not necessarily that of the mantle source. V/Sc ratios on the other hand can “see through” magmatic differentiation processes, such as olivine crystallization, and therefore, provide a better memory of the fO_2 of the mantle. The V/Sc ratios of mid-ocean ridge basalts (MORBs) are shown here to average 6.74 ± 1.11 (1σ), which constrains the fO_2 of the modern mantle to roughly 0.3 ± 0.5 (1σ) log units below the fayalite–magnetite–quartz (FMQ) buffer. Archean basalts (up to 3.5 Ga) are shown to have identical V/Sc ratios (6.34 ± 0.62 , 1σ) to within error indicating that the fO_2 of the mantle source to Archean basalts differ from that of modern convecting mantle by no more than 0.3 log unit. The constraints based on V/Sc systematics represent an improvement on studies using V or Cr elemental systematics, which constrain the fO_2 of Archean and modern mantles to be identical, but only to within ± 0.5 to 1 log unit. These observations show that there has been little or no secular evolution of the fO_2 of the upper mantle, at least since the early Archean.

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1. Introduction

The history of atmospheric O_2 levels on Earth has always been of interest as it bears directly on the

evolution of life (cf. [1]). It is generally agreed that the Earth’s atmosphere contained little free oxygen (O_2) initially and that atmospheric O_2 levels rose markedly ~2.3 billion years ago in an event known as the Great Oxidation Event (GOE) (e.g., [1] and references therein). This is evidenced by the fact that reduced detrital minerals (pyrite and uraninite) and Fe-rich

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sedimentary deposits are better preserved in the weathering environment prior to 2.3 Gy, but are largely oxidized afterwards. What caused the GOE is a matter of continuing debate. Central to this debate is the nature of the inputs, F_{in} , and outputs, F_{out} , of O_2 from the atmosphere: if $F_{out} > F_{in}$, there will be no free O_2 in the atmosphere, and if $F_{out} < F_{in}$, O_2 levels will rise. This means that O_2 inputs were lower and/or O_2 sinks were higher before the GOE.

Of interest here is the role of volcanic degassing as an atmospheric O_2 sink. Volcanic gases serve as O_2 sinks because a certain proportion of the gas consists of reduced volatile species (e.g., CO , H_2 , S_2 , H_2S , CH_4), which will react with O_2 in the atmosphere. In general, there are two ways to increase the volcanic sink for O_2 . One is to increase the total volcanic emissions. Another is to decrease the oxygen fugacity (fO_2) of the volcanic gases, keeping total volcanic emissions constant. This is because lower fO_2 results in a greater proportion of reduced volatile species, which increases the reducing power of volcanic gases. For example, Kump et al. [2] suggested that the transition from a reduced atmosphere ($F_{out} > F_{in}$) to an oxygenated atmosphere ($F_{out} \leq F_{in}$) can be explained if the fO_2 of volcanic gases before the GOE was 2 log units lower than the present day fO_2 of volcanic gases. This hypothetical rise in mantle fO_2 could be due to progressive oxidation of the mantle by the subduction recycling of oxidized components from the surface of the Earth [2]. However, Canil [3] and Delano [4] have used the redox sensitive behaviors of V and Cr, respectively, to infer that the fO_2 of late Archean magmas are identical to the present day to within roughly ± 0.5 log unit.

The findings of Canil and Delano seem to independently suggest that the GOE was not linked to changes in mantle fO_2 . However, making such a conclusion may not be so simple. First, Holland [5] more recently suggested that only a 0.5 log unit difference between the Archean and the present may be needed to explain the transition from a reducing to an oxygenated atmosphere. Second, in Canil's study of Archean komatiites [3], he investigated the behavior of V during olivine accumulation or fractional crystallization, and hence the inferred fO_2 corresponds to magmatic fO_2 s during differentiation and not necessarily to the fO_2 s of the mantle source regions to the komatiites. Similarly, Delano's study of

Cr in Archean basalts and komatiites [4] is based on the Cr concentration of the magma at Cr-spinel saturation; again, there is no necessity that this fO_2 directly reflects that of the mantle source region. Given the possibility that magmas can oxidize during ascent by degassing or interaction with crustal materials, it is possible that post-emplacement magmatic fO_2 s are maximum estimates of mantle fO_2 ; hence, the fO_2 of gases emitted directly from the mantle.

A more direct sample of the mantle is through mantle rocks in the form of xenoliths or obducted mantle slivers. One approach in inferring the fO_2 of mantle samples is to use various oxybarometers (which we term here thermobarometric fO_2 s). However, this approach provides information only on the fO_2 of last equilibration, which undoubtedly will reflect subsolidus conditions (as nearly all samples are derived from the lithospheric mantle rather than from upwelling mantle where melting takes place) and contain no memory of the original fO_2 during partial melting. In an attempt to determine the fO_2 of the upwelling part of the mantle, where melts are generated, Canil [6] and Lee et al. [7] investigated the melting systematics of V in Archean and Phanerozoic peridotites. They showed that there is no temporal difference in fO_2 of melting, but due to interlaboratory biases, there was a ± 1 log unit uncertainty in fO_2 . Although this uncertainty may be sufficient to rule out Kump et al.'s hypothesis, a change in mantle fO_2 of 0.5 log unit as suggested by Holland is still permitted.

In order to "see through" the effects of magmatic differentiation to more precisely constrain mantle fO_2 , we investigate the V/Sc systematics of basaltic magmas. V and Sc systematics are chosen for the following reasons. (1) Their geochemical behaviors during partial melting of the mantle are more similar to each other than to any other elements. (2) In detail, V partitioning is redox-sensitive, whereas that of Sc is not [3,6,8]; hence, the V/Sc ratios of primary magmas will be controlled to a large extent by the fO_2 during partial melting. (3) Because V and Sc are not volatile and are not highly enriched in continental crust, it is likely that the magma remains largely closed to V and Sc during ascent. (4) Fractional crystallization of olivine cannot significantly change the V/Sc ratio of the parent magma because V and Sc are highly

incompatible in olivine; hence, the V/Sc ratios of basalts should “see through” early magmatic differentiation processes and provide a robust window to the mantle. (5) Finally, unlike the valence states of redox-sensitive elements, which can be affected by fO_2 , V and Sc abundances are not affected by changes in redox during weathering or metamorphism, provided the system remains closed to V and Sc during such processes. Except for high degrees of open system weathering and metamorphism, V and Sc are generally immobile as attested by the lack of V and Sc mobility in highly serpentinized peridotites [9].

Here, we present a melting model for predicting V/Sc ratios of primitive magmas as a function of fO_2 . This model is used to better understand the V/Sc systematics of mid-ocean ridge basalts (MORBs) and Archean basalts in an attempt to quantify any temporal changes in the fO_2 of the convecting mantle. Our results are then examined in the context of how changes in mantle fO_2 may affect the composition of volcanic gases and consequently the amount of O_2 present in the atmosphere.

2. V/Sc as a precise paleo- fO_2 barometer of partial melting

Oxygen fugacity is an intensive variable that provides a measure of the redox potential within a given system. One way to measure fO_2 is indirectly by O_2 thermobarometry wherein one measures the activities of Fe^{3+} and Fe^{2+} in minerals or glasses [10,11]. It is assumed that thermobarometric fO_2 reflects the last equilibrium state. In the case of peridotites, thermobarometric fO_2 can be easily reset by the passage of oxidizing fluids. In the case of magmas, thermobarometric fO_2 records the fO_2 of the magma just prior to quenching. However, the fO_2 of magmas upon emplacement may have changed from their mantle source regions during ascent because of the differentiation processes mentioned in the introduction [12]. In particular, dissociation of volatile species during decompression, e.g. $H_2O=H_2+0.5O_2$, can potentially change the fO_2 of the magma even if there has been little or no fractional crystallization and crustal assimilation. Some have suggested that these effects are minimal [13]. However, there is still considerable debate on whether these processes

significantly alter the fO_2 of the magma; thus, an independent approach is needed.

One approach is to use V/Sc systematics in magmas. As discussed in the introduction, the magmatic system should remain closed to exchange of V and Sc during degassing (V and Sc are not volatile); hence, the V/Sc systematics of primitive magmas may reflect the original fO_2 conditions in mantle source. Because V becomes more incompatible at high fO_2 and Sc partitioning is independent of fO_2 , the higher the fO_2 of melting, the higher the V/Sc should be in the melt for a given degree of melting. We can assess the sensitivity of V/Sc to fO_2 by modeling the partitioning of V and Sc during partial melting. It is well-known that MORBs are generated by adiabatic decompression. However, the exact pressure–temperature path of melting is not known very well. Thus, to model V/Sc systematics, we assume that the melting process that forms MORBs can be approximated by assuming that the average melt composition can be modeled by isobaric non-modal batch melting (aggregate fractional melts are indistinguishable from batch melts). We also assume that the temperature range of melting is small. We thus ignore the effects of changing pressure and temperature on mineral partition coefficients. Finally, we assume that MORBs (and Archean basalts) largely originate from the spinel stability field, so we adopt the melting stoichiometry of fertile spinel peridotite (olivine+orthopyroxene+clinopyroxene+spinel) at 1.5 GPa, as used in Lee et al. [7]. The parametrizations of V partitioning for olivine, orthopyroxene, clinopyroxene and spinel as a function of fO_2 were adopted from Canil and co-workers [3,6,14–16]. The following partition coefficients for Sc were used: 0.17 for olivine [17], 0.69 for orthopyroxene [18], 1.31 for clinopyroxene [19,20] and 0 for spinel.

These parameters were then inserted in the non-modal batch melting equation, $C_m/C_0=(D_B^0+F(1-P))^{-1}$, where C_m is the concentration of a given element in the melt, C_0 is the initial concentration in the mantle source, F is the melt fraction, D_B^0 is the initial bulk partition coefficient at $F=0$ ($D_B^0=\sum_j X_j^0 D_j$ where X_j^0 is the weight fraction of mineral j at $F=0$ and D_j is the partition coefficient of mineral j), and P is the melt “partition coefficient” given by $P=\sum_j (X_j^0 - X_j) D_j / F$ (where X_j is the weight fraction at a given F relative to the entire melt+residue

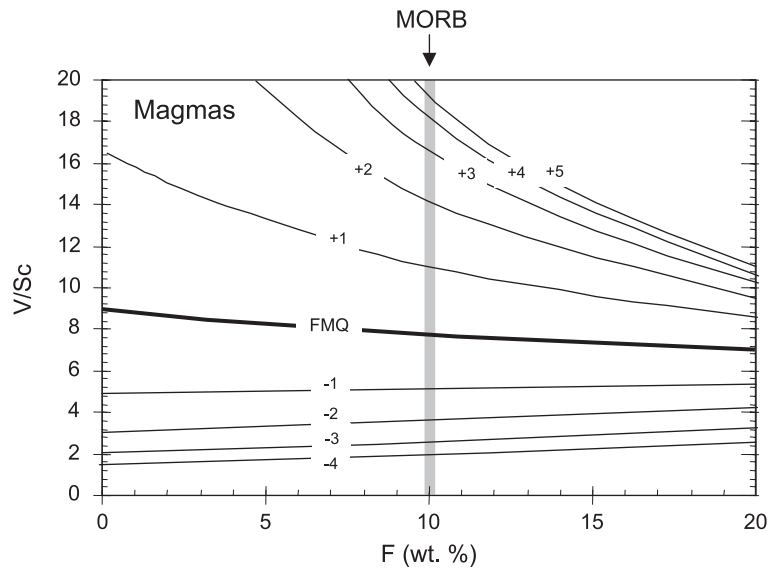


Fig. 1. The calculated V/Sc ratios of a partial melt as a function of F and contoured for different oxygen fugacities (fO_2) and a constant V/Sc of 5 for the initial mantle composition. Oxygen fugacities are denoted in terms of \log_{10} deviations from the FMQ buffer at a given temperature.

system). An initial V/Sc ratio of 5 for the MORB source region was assumed based on our observation that the V/Sc ratios of fertile peridotites are constant at a value of 5 [9]. In Fig. 1, we plot the V/Sc ratios of 1.5 GPa melts as a function of F at given constant fO_2 s. It can be seen that at low fO_2 , V is more compatible than Sc so the V/Sc ratio of the melt is low. At high fO_2 , V becomes more incompatible than Sc, leading to high V/Sc ratios in the melt. As expected, it can be seen that V/Sc ratio also depends on F , which requires that the V/Sc systematics of different magmas can only be compared if they are derived by similar degrees of melting. A standard way of estimating F is to use the reciprocal of a highly incompatible trace element, such as Na and Ti. Below, we will compare MORBs, which on average represent 10% melts [21], to Archean basalts having similar 1/Na and 1/Ti systematics.

3. Results

3.1. Mid-ocean ridge basalts

We now apply our models to real rocks. In Fig. 2A, we plot V/Sc ratios of MORBs (taken from the RidgePetDB database [22]) as a function of MgO

(corrected for loss of ignition). It can be seen that V/Sc rises slightly as MgO decreases below 8 wt.% MgO. This is due to the onset of clinopyroxene crystallization, which increases V/Sc in the melt because it prefers Sc over V. In order to eliminate the effect of clinopyroxene crystallization, we select only those samples with MgO contents between 8 and 12 wt.% (shaded region in Fig. 2A,B). This selection criteria does not eliminate the effects of early olivine crystallization. However, as noted above, even though olivine crystallization increases the concentrations of V and Sc in the melt, it cannot change the V/Sc ratio of the melt significantly because these elements are highly incompatible in olivine (e.g., the exponent in the fractional crystallization equation $(V_m/Sc_m)/(V_m/Sc_m)_0 = F^{(D_{ol}^V - D_{ol}^{Sc})}$ is nearly zero, where subscript m denotes melt and subscript 0 denotes original melt composition). It is possible that co-crystallization of spinel with olivine may fractionate V/Sc ratios to low values due to the higher compatibility of V in spinel compared to Sc. However, it can be seen that the V/Sc ratios are constant in the 8–12 wt.% MgO range, suggesting that any spinel crystallization must be small (Fig. 2A). We thus argue that the V/Sc ratios of basalts having MgO contents between 8 and 12 wt.% closely represent that of their magmatic parent and hence provide a window to mantle fO_2 .

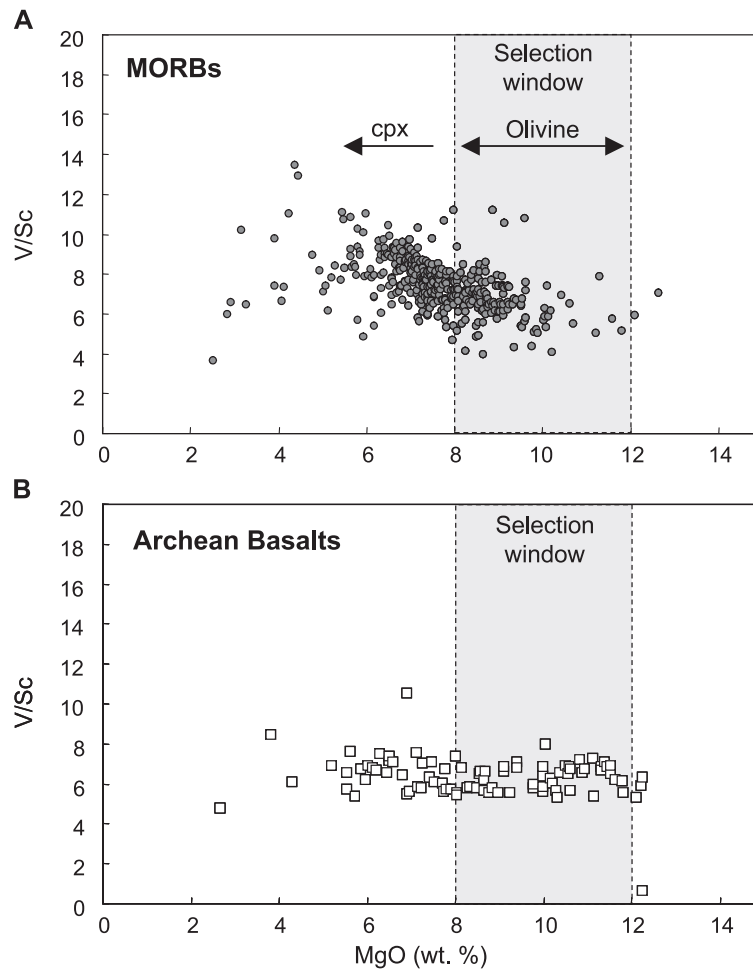


Fig. 2. The V/Sc ratio for MORBs and Archean basalts. (A) V/Sc versus MgO (volatile-free) for global MORB dataset from RidgePetDB. “Cpx” stands for clinopyroxene crystallization. (B) V/Sc vs. MgO (volatile-free) for Archean basalts. Shaded region represents the interval of MgO contents selected for comparison to melting models in Figs. 1 and 3.

In Fig. 3A and B, we plot the MgO-filtered V/Sc data as a function of $1/\text{Na}$ and $1/\text{Ti}$, which are used as proxies for melt fraction F because Na and Ti are highly incompatible during partial melting. After filtering, it can be seen that the range in V/Sc ratios decreases substantially, yielding an average V/Sc ratio of 6.74 ± 1.11 (1σ). Superimposed on Fig. 3A and B are isopleths of V/Sc ratios for a given $f\text{O}_2$ calculated at $F=10$ wt.%, which represents an estimate of the average F of MORBs [21]. Given that the predicted effects of varying $f\text{O}_2$ on V/Sc ratios are large, the small range observed in V/Sc ratios thus indicates a correspondingly small range in $f\text{O}_2$ (Figs. 1 and

3A,B). Our calculations imply that the $f\text{O}_2$ of the MORB mantle source is roughly between FMQ-1 and FMQ, which falls within the range of $f\text{O}_2$ estimated from the Fe^{3+} activity of minerals in abyssal peridotites and the Fe^{3+} activity of MORB glasses (FMQ-2.5 to FMQ+0.5 [10,11]). This suggests that the $f\text{O}_2$ of MORBs remains largely unchanged from the melt source region to emplacement in the crust.

3.2. Archean basalts

For Archean samples, we considered only those samples with MgO contents less than 13 wt.% to be

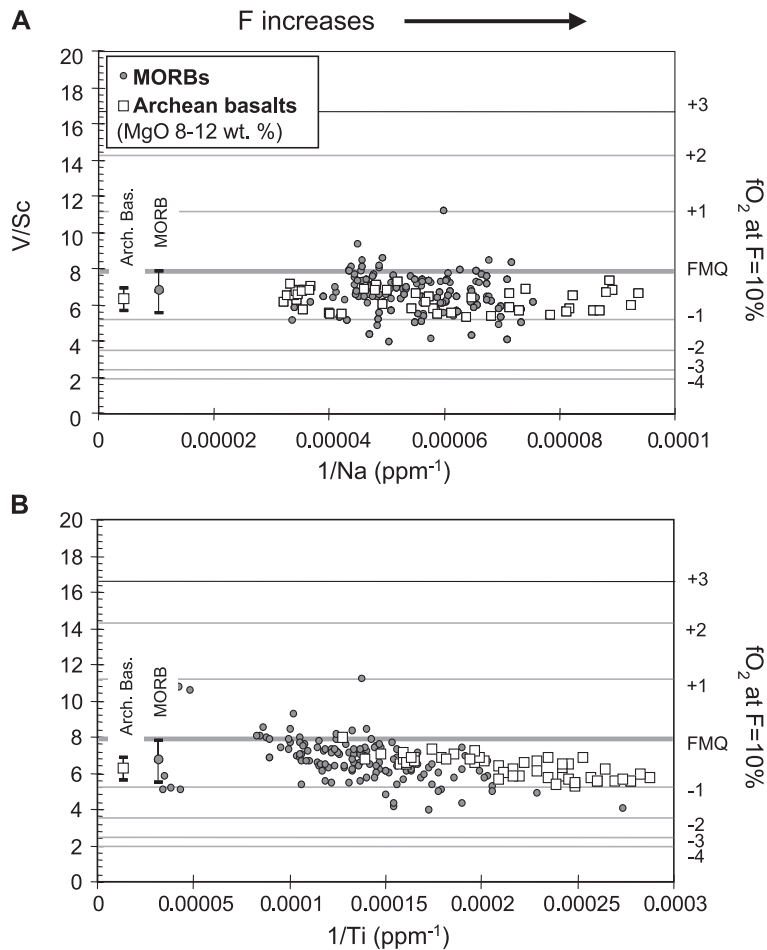


Fig. 3. (A) V/Sc versus $1/\text{Na}$ (ppm^{-1}) after selecting MORBs and Archean basalts having MgO between 8 and 12 wt.%. (B) V/Sc versus $1/\text{Ti}$ (ppm^{-1}). $1/\text{Na}$ and $1/\text{Ti}$ are used as proxies for the degree of melting F . V/Sc- $f\text{O}_2$ isopleths in A and B are calculated at $F=10\%$ and for constant initial V/Sc ratio of 5 for the mantle (as shown in Fig. 1). Average V/Sc ratios (plus 1 standard deviation) for MORBs and Archean basalts are shown on left-hand side of figures.

basaltic (see [23] for discussion). We assume that the majority of these Archean basalts are unrelated to komatiites, which have much higher MgO contents [23,24] and that Archean basalts represent low degree melts ($\sim 10\%$) similar to that of MORBs and unlike the very high degrees of melting required to generate komatiites (40–50%). It is for this reason we have chosen Archean basalts rather than komatiites for direct comparison to MORBs. We compiled V, Sc and MgO (corrected for loss of ignition) data from the 3.5 Ga Barberton complex in South Africa [25], the 3.2 Ga Nondweni greenstone belt in South Africa [26], the ~ 2.7 Ga Crixas greenstone belt in Brazil [27], the

~ 2.7 Ga Kambalda basalts in western Australia [28], the ~ 2.7 Ga basalts from Newton Township in Ontario, Canada [29], and the ~ 2.7 Ga Eastern Goldfields basaltic province in western Australia [24]. These data are shown in Fig. 2B. We recognize that some investigators have suggested that some of these Archean basalts may be the products of fractional crystallization and/or crustal contamination of parental komatiitic magmas [28,30]. However, as stated above, early fractional crystallization involving olivine does not significantly change the V/Sc ratio of the magma. In addition, crustal contamination will only slightly reduce the V/Sc ratio of the magma

because the V/Sc ratio of bulk continental crust is ~ 6.0 [31]. Nevertheless, if substantial crustal contamination has occurred, the V/Sc ratios of Archean basalts and corresponding estimates of fO_2 are minimum estimates.

As in our treatment of MORB data, the Archean basalts (Fig. 2B) are selected to include only those samples between 8 and 12 wt.% MgO in an attempt to retain the least evolved compositions. After selecting for MgO, the V/Sc data are plotted against 1/Na and 1/Ti as done with the MORB dataset (Fig. 3A,B). One question that arises is whether the geochemistry of these ancient samples have been modified by metamorphism and/or weathering. It is likely that some of the Na and Mg values have been compromised by post-emplacement mobility. However, Ti is considered to be one of the most immobile elements during such processes. Mass losses associated with extensive weathering will result in an apparent increase in the concentration of a conservative element like Ti. However, weathering is unlikely to explain the factor of ~ 3 variation in 1/Ti values in the Archean basalts (Fig. 3B) because this would imply 66% mass loss due to weathering, which would be largely manifested as a significant loss of SiO_2 . On the contrary, anomalously low SiO_2 contents are not observed. Thus, the 1/Ti concentrations are taken to be fairly robust indicators of relative melting degree. The considerable overlap between the Archean basalts and MORB in terms of 1/Ti (and 1/Na) confirms that the Archean basalts are indeed derived from similar melting degrees as MORBs (e.g., $\sim 10\%$); hence, their V/Sc ratios can be compared directly.

Fig. 3A and B shows that the V/Sc ratios of MORBs (6.74 ± 1.11) and Archean basalts (6.34 ± 0.62) overlap completely. The ratio between the V/Sc of MORBs to Archean basalts is 1.06 ± 0.20 , which corresponds to only a 6% difference (or 0.4 V/Sc units). Using the V/Sc- fO_2 isopleths in Fig. 3A and B, the corresponding difference in fO_2 between the Archean and modern mantle is roughly 0.3 log unit. This conclusion is consistent with the results of Canil [3] and Delano [4], who showed that the fO_2 s of Archean and Phanerozoic magmas are also similar. In particular, the coincidence in magmatic and mantle fO_2 s shows that the fO_2 s of MORBs and Archean basalts remain unchanged from their mantle source regions. If the Archean basalts examined here are

representative of the Archean upper mantle, we are forced to conclude that the fO_2 of the modern and Archean upper mantles (up to 3.5 Gy ago) are to within error identical. However, an increase of at most 0.3 log unit in fO_2 between the Archean and the present is permitted by the V/Sc data.

4. Discussion

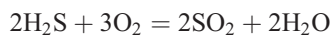
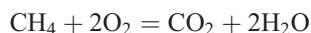
4.1. The role of mantle fO_2 in modulating the volcanic sink of O_2

The question now is whether the permitted 0.3 log unit difference between the Archean and modern mantles as discussed above is sufficient enough to influence the O_2 content of the atmosphere. We thus re-examine the role of mantle fO_2 in controlling the volcanic sink of atmospheric O_2 . Today, the production of O_2 occurs dominantly by photosynthesis ($CO_2 + H_2O = CH_2O + O_2$) and to a lesser extent by bacterial reduction of ferric to ferrous iron (e.g., $2Fe(OH)_3 + 4H_2SO_4 = 2FeS_2 + 7.5O_2 + 7H_2O$, $2Fe_2O_3 = 4FeO + O_2$). It is believed that most of this O_2 production is consumed by weathering of reduced components in rocks, and only a small proportion of today's atmospheric O_2 reacts with reduced gases released by volcanism and metamorphic processes [2]. In the Archean, however, it has been further suggested by Kump et al. [2] that oxidative weathering would not have been as important as it is today because of the lower levels of O_2 in the Archean atmosphere. If so, volcanic sinks would dominate the consumption of O_2 in Archean times.

Here, we address the sensitivity of the volcanic sink of atmospheric O_2 to variations in the fO_2 of volcanic emissions. For the purposes of modeling the volcanic sink of atmospheric O_2 , we assume that the fO_2 of the mantle source region dictates the composition of the volcanic gases that are released into the atmosphere. We begin by first considering modern volcanic gases in the balance of atmospheric O_2 . Once the modern balance of O_2 is understood, we can reexamine the Archean O_2 balance in the context of the new fO_2 constraints from V/Sc.

A thermodynamic model was constructed to study the redox processes in volcanic volatile systems. We

assume that volcanic volatiles are dominated by the species of O, C, H and S. The proportions of these species at a given fO_2 are determined by combining the mass balance equations for C, H and S with the following reactions:



Equilibrium constants for these reactions were calculated from the thermodynamic data of [32]. The total moles of C, H and S used in our model are estimated as follows. We use the estimate for the global volcanic CO_2 flux (6×10^{12} mol/year) and assume that CO_2 is the dominant C bearing species in volcanic gases [33]. We then estimate H and S fluxes by taking the average of C/H/S ratio of volcanic gases from 34 volcanoes [34,35]. For reference, the C/H/S ratios of volcanic gases are shown in Fig. 4. Because of the different tectonic conditions of continental and mid-ocean ridges, two temperature–pressure conditions were assumed. For continents, we assumed a temperature of 1500 K and a pressure of 1 bar. For mid-ocean ridges (“oceans”), we assumed 900 K and 400 bars. The volatile species proportions for each of these cases are shown in Fig. 5A and B, respectively. The corresponding sink in O_2 was then determined by assuming that only the reduced species can consume O_2 (e.g., CO, CH_4 , H_2S , H_2 , S_2). Fig. 5C shows the O_2 sink corresponding to continental and oceanic volcanic emissions. We have also plotted an intermediate O_2 sink (referred to here as the “average” O_2 sink) corresponding to an arbitrary average of continental (0.4) and oceanic volcanoes (0.6). Regardless of which curve is chosen, it can be seen that, at low fO_2 , the proportion of reduced species is greater; hence, the total O_2 sink is greater.

The volcanic sink calculated above can be compared directly to estimates of modern O_2 inputs. The burial of organic carbon yields a net O_2 input of $(10.0 \pm 3.3) \times 10^{12}$ mol/year, the burial

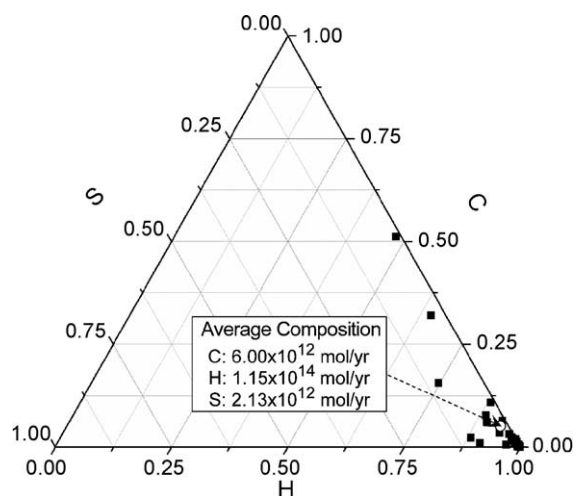


Fig. 4. Volcanic volatile composition ternary diagram based on a compilation of 34 observed volcanic gas systems. Solid squares represent different observed volcanic volatile systems. Open circle represents the average composition.

of pyrite yields an input of $(7.8 \pm 4.0) \times 10^{12}$ mol/year and the burial of ferrous iron yields an input of $(0.9 \pm 0.4) \times 10^{12}$ mol/year [36]. Summing these fluxes, the total O_2 production today is $(18.7 \pm 7.7) \times 10^{12}$ mol/year. Taking the present day O_2 input at face value (bold horizontal line in Fig. 5C), we see that at the present fO_2 of the mantle (~FMQ), the volcanic sink is lower than the input of O_2 regardless of which O_2 sink curve is taken. This indicates that neither oceanic or continental volcanoes are presently a significant sink for O_2 ; there must instead be other sinks, such as oxidative weathering processes as pointed out by others, such as Holland [36]. It can also be seen that the crossover between the possible volcanic sinks (oceanic, continental or a combination of the two) and the average O_2 input occurs roughly between FMQ–1.4 and FMQ–1.8, which means that at fO_2 s less than this range, the volcanic sink is greater than the O_2 input, ultimately leading to the depletion of atmospheric O_2 .

We now examine the above box model in the context of our new constraints on mantle fO_2 in the Archean and the present. There are four ways to change the balance between O_2 production and consumption in order to explain the GOE (Fig. 5C). Prior to 2.3 Ga, the Earth could have been characterized by (1) a mantle with lower fO_2 , (2)

higher total volcanic emissions, (3) lower O_2 production and/or (4) the presence of additional O_2 sinks, which are not present today. Our observations from V/Sc systematics indicate that

the fO_2 s of Archean and modern convecting mantles differ by no more than 0.3 log unit. Assuming that the O_2 inputs and volcanic degassing rates in our box models are constant and that there are no unaccounted O_2 sinks in the Archean, it can be seen from Fig. 5C that an increase in fO_2 by 0.3 log unit cannot explain the transition from an oxygen-poor to -rich atmosphere. If, on the other hand, the uncertainty in the O_2 inputs or volcanic degassing rates is considered, it can be seen from Fig. 5C that it is easy to come up with a particular combination of O_2 inputs and volcanic degassing rates that allows for the crossover to occur at 0.3 log unit below the present day fO_2 of the mantle. However, based on the range of V/Sc data in MORBs and thermobarometrically determined fO_2 s of abyssal peridotites and MORB glasses, the fO_2 of the modern upper mantle probably varies at least between FMQ and FMQ-1. If only a 0.3 log unit difference in mantle fO_2 is required to switch the atmosphere from O_2 -poor to O_2 -rich, the present day mantle would straddle this transition point, possibly making atmospheric O_2 levels extremely sensitive to small perturbations in mantle fO_2 . Other than the 2.3 Gy GOE, changes of similar magnitude in atmospheric O_2 levels have not been observed. We thus conclude that the near constancy of upper mantle fO_2 since 3.5 Gy ago indicates that mantle fO_2 was probably not the dominant influence on atmospheric O_2 levels, consistent with the conclusions of Delano [4].

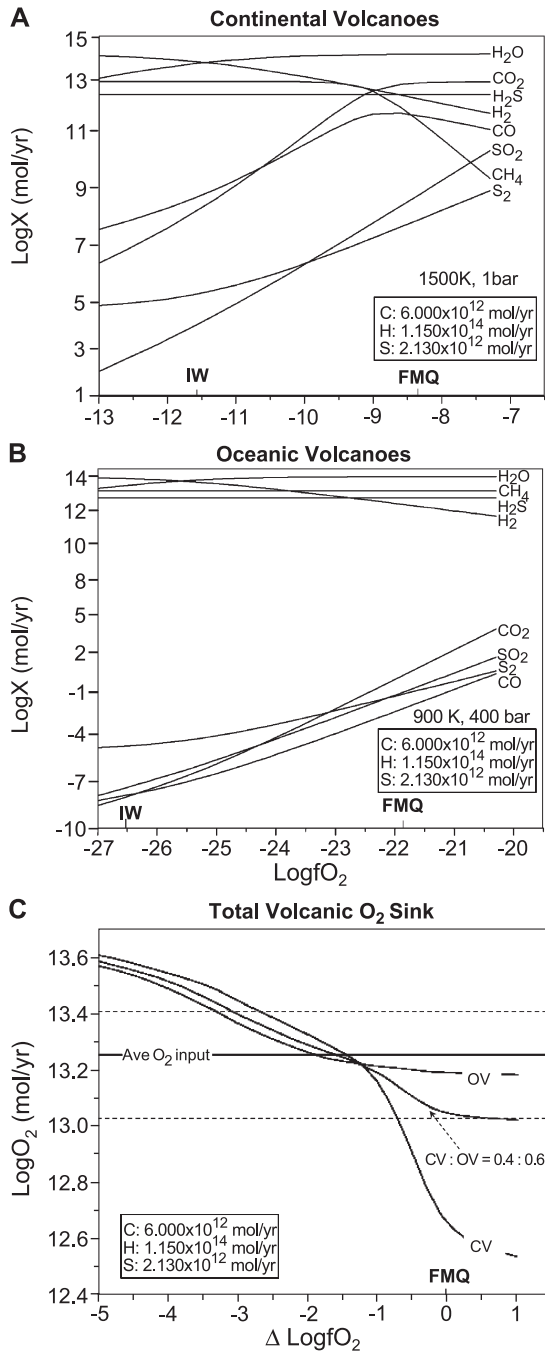


Fig. 5. The volcanic oxygen sink calculated assuming modern volcanic gas fluxes and compositions (e.g., Fig. 3). (A) Gas speciation in continental volcanic systems as a function of fO_2 . (B) Gas speciation in oceanic volcanic systems. (C) Oxygen sinks due to continental and oceanic volcanoes. The C, H, S fluxes used here are 6.00×10^{12} , 1.15×10^{14} and 2.13×10^{12} mol/year, respectively. The IW and FMQ stand for the oxygen fugacity at the iron-wustite (IW) and FMQ buffers, where $\log fO_{2-IW}(1 \text{ bar}, 1500k) = -11.666$, $\log fO_{2-IW}(400 \text{ bar}, 900k) = -26.536$, $\log fO_{2-FMQ}(1 \text{ bar}, 1500k) = -8.306$ and $\log fO_{2-FMQ}(400 \text{ bar}, 900k) = -21.846$. Upper dashed line represents the upper limit of the estimated oxygen input value; dark solid line represents the average value of the estimated oxygen input; lower dashed line represents the lower limit of the estimated oxygen input; CV denotes the oxygen sink from continental volcanoes; and OV denotes the oxygen sink from oceanic volcanoes. An oxygen sink controlled by both continental and oceanic volcanoes is denoted by the intermediate curve (CV/OV=0.4:0.6), which arbitrarily assumes that continental and oceanic volcanic systems account for 40% and 60% of the global volcanic degassing rate.

5. Conclusions

We conclude that V/Sc ratio systematics in basalts may represent a sensitive tool in constraining the fO_2 of mantle source regions. V/Sc systematics are more precise and sensitive than V and/or Cr systematics alone. By comparing V/Sc systematics in Archean and mid-ocean ridge basalts, we show that the fO_2 s of their respective mantle source regions differ by no more than 0.3 log unit. These results independently confirm the results of earlier studies by Canil [3], Delano [4], Canil [6] and Lee et al. [7] but place even tighter constraints on the fO_2 s of magma source regions. If the Archean basalts are representative of the entire Archean mantle, it follows that there has been very little change (<0.3 log unit) in upper mantle fO_2 since ~3.5 Gy. If so, the transition from a reducing to an oxidizing atmosphere at ~2.3 Gy probably had nothing to do with changes in mantle fO_2 . The possibility that the Earth's upper mantle has been oxidized since the early Archean (cf. [3,4,6,7]) has previously been argued to be inconsistent with the fact that the mantle must have at some point been in equilibrium with the metallic core and hence should be characterized by low fO_2 s. However, it has been recently suggested that disproportionation of FeO to Fe⁰ and Fe³⁺ at high pressures followed by segregation of the metal phase to the core could lead to a net increase in the amount of oxygen, and hence fO_2 , of the mantle early in Earth's history [37].

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References

- [1] J.F. Kasting, Earth's early atmosphere, *Science* 259 (1993) 920–926.
- [2] L.R. Kump, J.F. Kasting, M.E. Barley, Rise of atmospheric oxygen and the “upside-down” Archean mantle, *Geochem. Geophys. Geosyst.* 2 (2001) DOI:10.1029/2000GC000114.
- [3] D. Canil, Vanadium partitioning and the oxidation state of Archean komatiite magmas, *Nature* 389 (1997) 842–845.
- [4] J.W. Delano, Redox history of the Earth's interior since ~3900 Ma: implications for prebiotic molecules, *Orig. Life Evol. Biosph.* 31 (2001) 311–341.
- [5] H.D. Holland, Volcanic gases, black smokers, and the Great Oxidation Event, *Geochim. Cosmochim. Acta* 66 (2002) 3811–3826.
- [6] D. Canil, Vanadium in peridotites, mantle redox and tectonic environments: Archean to present, *Earth Planet. Sci. Lett.* 195 (2002) 75–90.
- [7] C.-T.A. Lee, A.D. Brandon, M.D. Norman, Vanadium in peridotites as a proxy for paleo- fO_2 during partial melting: prospects, limitations, and implications, *Geochim. Cosmochim. Acta* 67 (16) (2003) 3045–3064.
- [8] M.J. Toplis, A. Corgne, An experimental study of element partitioning between magnetite, clinopyroxene and iron-bearing silicate liquids with particular emphasis on vanadium, *Contrib. Mineral. Petrol.* 144 (2002) 22–37.
- [9] C.-T.A. Lee, W.P. Leeman, D. Canil, Z.-X.A. Li, Similar oxygen fugacities in arc and MORB mantle source regions: evidence from V/Sc systematics, *J. Petrol.* (2004) (submitted for publication).
- [10] B.J. Wood, L.T. Bryndzia, K.E. Johnson, Mantle oxidation state and its relationship to tectonic environment and fluid speciation, *Science* 248 (1990) 337–345.
- [11] D.M. Christie, I.S.E. Carmichael, C.H. Langmuir, Oxidation states of mid-ocean ridge basalt glasses, *Earth Planet. Sci. Lett.* 79 (1986) 397–411.
- [12] E.A. Mathez, Influence of degassing on oxidation states of basaltic magmas, *Nature* 310 (1984) 371–375.
- [13] I.S.E. Carmichael, The redox states of basic and silicic magmas: a reflection of their source regions? *Contrib. Mineral. Petrol.* 106 (1991) 129–141.
- [14] D. Canil, Vanadium partitioning between orthopyroxene, spinel and silicate melt and the redox states of mantle source regions for primary magmas, *Geochim. Cosmochim. Acta* 63 (1999) 557–572.
- [15] D. Canil, Y. Fedortchouk, Clinopyroxene-liquid partitioning for vanadium and the oxygen fugacity during formation of cratonic and oceanic mantle lithosphere, *J. Geophys. Res.* 105 (2000) 26003–26016.
- [16] D. Canil, Y. Fedortchouk, Olivine-liquid partitioning for vanadium and other trace elements with applications to modern and ancient picrites, *Can. Mineral.* 39 (2001) 319–330.
- [17] R.O. Colson, G.A. McKay, L.A. Taylor, Temperature and composition dependencies of trace element partitioning: olivine/melt and low-Ca pyroxene/melt, *Geochim. Cosmochim. Acta* 52 (1988) 539–553.
- [18] T.H. Green, Experimental studies of trace-element partitioning applicable to igneous petrogenesis—Sedona 16 years later, *Chem. Geol.* 117 (1994) 1–36.
- [19] S.R. Hart, T. Dunn, Experimental cpx/melt partitioning of 24 trace elements, *Contrib. Mineral. Petrol.* 113 (1993) 1–8.
- [20] E.H. Hauri, T.P. Wagner, T.L. Grove, Experimental and natural partitioning of Th, U, Pb and other trace elements between

- garnet, clinopyroxene and basaltic melts, *Chem. Geol.* 117 (1994) 149–166.
- [21] C. Langmuir, E.M. Klein, T. Plank, Petrological systematics of mid-ocean ridge basalts: constraints on melt generation beneath ocean ridges, *Geophys. Monograph*, vol. 71, American Geophysical Union, 1992, pp. 183–280.
- [22] K. Lehnert, Y. Su, C.H. Langmuir, B. Sarbas, U. Nohl, A global geochemical database structure for rocks, *Geochem. Geophys. Geosyst.* 1 (2000) DOI:10.1029/1999GC000026.
- [23] T.L. Grove, S.W. Parman, Thermal evolution of the Earth as recorded by komatiites, *Earth Planet. Sci. Lett.* 219 (2004) 173–187.
- [24] B.A. Redman, R.R. Keays, Archean basic volcanism in the Eastern Goldfields Province, Yilgarn Block, western Australia, *Precambrian Res.* 30 (1985) 113–152.
- [25] R.W. Nesbitt, S.-S. Sun, A.C. Purvis, Komatiites: geochemistry and genesis, *Can. Mineral.* 17 (1979) 165–186.
- [26] A.H. Wilson, J.A. Versfeld, D.R. Hunter, Emplacement, crystallization and alteration of spinifex-textured komatiitic basalt flows in the Archaean Nondweni greenstone belt, southern Kaapvaal Craton, South Africa, *Contrib. Mineral. Petrol.* 101 (1989) 301–317.
- [27] N.T. Arndt, N.A. Teixeira, W.M. White, Bizarre geochemistry of komatiites from the Crixas greenstone belt, Brazil, *Contrib. Mineral. Petrol.* 101 (1989) 187–197.
- [28] N.T. Arndt, G.A. Jenner, Crustally contaminated komatiites and basalts from Kambalda, western Australia, *Chem. Geol.* 56 (1986) 229–255.
- [29] A. Cattell, Enriched komatiitic basalts from Newton Township, Ontario: their genesis by crustal contamination of depleted komatiite magma, *Geol. Mag.* 124 (1987) 303–309.
- [30] N.T. Arndt, Komatiites, kimberlites and boninites, *J. Geophys. Res.* 108 (2003) 2293.
- [31] R.L. Rudnick, D.M. Fountain, Nature and composition of the continental crust: a lower crustal perspective, *Rev. Geophys.* 33 (1995) 267–309.
- [32] R.A. Robie, B.S. Hemingway, J.R. Fisher, Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5) pascals pressure and at higher temperatures, U.S. Geol. Surv. Bull., Rep B 1452 (1978) 456.
- [33] B. Marty, I.N. Tolstikhin, CO₂ fluxes from mid-ocean ridges, arcs and plumes, *Chem. Geol.* 145 (1998) 233–248.
- [34] P. Allard, The origin of hydrogen, carbon, sulphur, nitrogen, and rare gases in volcanic exhalations: evidence from isotopic chemistry, in: H. Tazieff, J.-C. Sabroux (Eds.), *Forecasting Volcanic Events*, Elsevier, 1983, pp. 337–386.
- [35] R.B. Symonds, W.I. Rose, G.J.S. Bluth, T.M. Gerlach, Volcanic-gas studies: methods, results, and applications, in: M.R. Carroll, J.R. Holloway (Eds.), *Volatiles in Magmas*, *Rev. Mineral.* 30 (1994) 1–66.
- [36] H.D. Holland, *The Chemistry of the Atmosphere and Oceans*, John Wiley, New York, 1978.
- [37] D.J. Frost, C. Liebske, F. Langenhorst, C.A. McCammon, R.G. Tronnes, D.C. Rubie, Experimental evidence for the existence of iron-rich metal in the Earth's lower mantle, *Nature* 428 (2004) 409–412.