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Elizabeth Cottrell

Katherine A. Kelley
University of Rhode Island, kelley@uri.edu

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Authors: Elizabeth Cottrell[1]* & Katherine A. Kelley[2]*

Affiliations:

[1]*National Museum of Natural History, Smithsonian Institution, Washington, DC, 20560 USA; (202) 633-1859; cottrelle@si.edu.

[2]Graduate School of Oceanography, University of Rhode Island, Narragansett, RI, 02882 USA.

Abstract: The oxidation state of Earth's upper mantle both influences and records mantle evolution, but systematic fine-scale variations in upper mantle oxidation state have not previously been recognized in mantle-derived lavas from mid-ocean ridges. Through a global survey of mid-ocean ridge basalt glasses, we show that mantle oxidation state varies systematically as a function of mantle source composition. Negative correlations between $Fe^{3+}/\Sigma Fe$ ratios and indices of mantle enrichment such as $^{87}Sr/^{86}Sr$, $^{208}Pb/^{204}Pb$, Ba/La, and Nb/Zr ratios reveal that enriched mantle is more reduced than depleted mantle. Because upper mantle carbon may act to simultaneously reduce iron and generate melts that share geochemical traits with our reduced samples, we propose that carbon creates magmas at ridges that are reduced and enriched.

Main Text: The bulk composition and geophysical properties of Earth's mantle have evolved in response to oxygen fugacity (fO$_2$), a measure of the chemical potential of oxygen in solid systems (*1, 2*). Mantle-derived mid-ocean ridge basalts (MORB) record fO$_2$ through the ratio of oxidized to total iron ($Fe^{3+}/\Sigma Fe$) (*3*), and because MORB also record geochemically distinct mantle reservoirs, the potential exists to discover the existence and evolution of heterogeneities in the oxidation state of mantle reservoirs.

Two previous large (n >75) global surveys of Fe oxidation state in MORB pillow glass (*4, 5*) found no correlation between $Fe^{3+}/\Sigma Fe$ ratios and mantle source composition, establishing the paradigm that oceanic upper mantle oxidation state is relatively uniform, buffered, and not linked to plate tectonic-scale processes. Other work (*6*) has proposed that enriched mantle domains may be more oxidized than normal MORB. We determined high precision (± 0.005) $Fe^{3+}/\Sigma Fe$ ratios by micro XANES (*7*) (*8*) and trace element concentrations on 19 glasses (from 7 geographical locations) that have experienced neither substantial fractionation (i.e., primitive MORB with MgO > 8.5 wt.%), nor plume influence ((*9*), Table S1). A partially overlapping set of 22 glasses (from 10 geographical locations) from ridge segments without plume influence, irrespective of MgO content, additionally have previously published Sr $\pm$ Pb $\pm$ Nd isotope ratios (Table S1). The primitive dataset spans 50% of the global range in $Fe^{3+}/\Sigma Fe$ ratios, while the isotope dataset spans the entire global range (Fig. S1). Globally, the $Fe^{3+}/\Sigma Fe$ ratio in MORB negatively correlates with MgO concentration, whereby the $Fe^{3+}/\Sigma Fe$ ratio increases by ~ 0.03 as MgO decreases from 10 to 5 wt.% (*8*) as Fe^{2+} preferentially partitions into fractionating mafic phases. In order to account for the effect of fractionation, the $Fe^{3+}/\Sigma Fe$ ratios have been recalculated to an arbitrary reference value at MgO = 10 wt.%, $Fe^{3+}/\Sigma Fe_{(10)}$, analogous to $Fe_2O_{3(8)}$ in (*4, 8*). This correction is ~2% relative for the 19 primitive samples and is up to 11% (average 7%) relative for the samples with isotopic data, but correlations between $Fe^{3+}/\Sigma Fe$ ratios, trace elements, and isotopes are also evident in the uncorrected data (*9*) (Fig. S1).

The glasses form sub-parallel arrays in $^{208}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ space as a function of $Fe^{3+}/\Sigma Fe$ ratio, with $^{208}Pb/^{204}Pb$ ratios increasing as a strong function of decreasing Fe

oxidation state (Figs. 1a, e). Reduced glasses also possess elevated $^{87}Sr/^{86}Sr$ ratios and tend to have lower $^{143}Nd/^{144}Nd$ ratios (Figs. 1b, f). Oxygen fugacities, calculated from $Fe^{3+}/\Sigma Fe$ ratios and glass compositions (*10*) and referenced to the quartz-fayalite-magnetite buffer (ΔQFM), also correlate with isotopic enrichment (Figs. 1c,d). These observations link the Fe oxidation state of erupted MORB to mantle source heterogeneity, with enriched samples more reduced than depleted ones, because no magmatic process can fractionate these isotopes. Moreover, because these signatures require ancient fractionation of radiogenic parent-daughter pairs, these data also require preservation of the factors that lead to heterogeneity in $Fe^{3+}/\Sigma Fe$ ratios on plate tectonic time scales. For the primitive samples, $Fe^{3+}/\Sigma Fe_{(10)}$ ratios correlate strongly with enrichment in highly incompatible elements (e.g. Ba, Th, Nb) (Fig. 2) such that the most enriched samples are also the most reduced. Moderate correlations are also evident between $Fe^{3+}/\Sigma Fe_{(10)}$ ratios and depletions of the high field strength elements Hf and Zr (Fig. 2e, f). We define a Hf anomaly, Hf/Hf*, relative to elements with similar compatibility during mantle melting, such as Sm and Nd ($Hf/Hf^* = Hf_N/\sqrt{(Sm_N^* Nd_N)}$) and observe that reduced samples also tend to have more negative Hf anomalies (Fig. S3). By contrast, oxidation state does not correlate with ratios of mid- to heavy-REE such as Sm/Yb or Dy/Yb; the heavy rare earth element (HREE) patterns in these samples are flat (Fig. S4).

These data require a process that links source enrichment to a reduced oxidation state. This is contrary to the relationship expected if redox heterogeneities simply reflected a difference in partitioning between the two Fe species (i.e., $D^{Fe3+} < D^{Fe2+}$) (*4, 5*), or if enriched MORB derived from graphite-buffered melting at greater depth (*6, 11*),

both of which would predict MORB enriched in incompatible elements to be more

oxidized. Garnet-bearing lithologies previously implicated in the generation of enriched

MORB [e.g. (*12*)] might hold back Fe^{3+} during melting; however, a silicate melt of a

garnet-bearing source is inconsistent with the trace and major element characteristics of

our reduced samples (SM text, Figs. S4, S5). Here we hypothesize that control over the

Fe oxidation state of MORBs is exercised by another incompatible element: carbon.

Carbon concentration has the potential to control the eruptive $Fe^{3+}/\sum Fe$ ratios of

MORBs such that the most reduced basalts derive from sources with greater carbon

concentrations (*13*). This is because reduced carbon, stabilized at depth by lower f_{O2} (*2*),

must fully oxidize upon ascent to be consistent with the oxidation state of the erupted

basalts (*8*). Ferric iron becomes reduced in the process in proportion to the initial carbon

content (*13, 14*). To generate the observed range of $Fe^{3+}/\sum Fe$ ratios in either the primitive

or isotope data sets solely through reduction of Fe_2O_3 by carbon requires variations in

mantle C on the order of 80 to 170 ppm. Independent estimates of mantle C

concentration, which co-vary with enrichment (*15*), range from ~ 16 (depleted mantle) to

> 300 ppm (enriched mantle) (*16*). Thus carbon may exert a primary influence on MORB

oxidation state even if the erupted melts are too oxidized to be in equilibrium with

graphite (*8*).

We cannot directly assess the relationship between carbon and oxidation state in

our samples because CO_2 is partially degassed from most, if not all, MORB (*17*). Mantle

carbon is constrained in two locations, however, and we note that trace element and

carbon-enriched sample 2πD43 ('popping rock') suggests a mantle source with ~159 ppm

CO_2 (*18*) and is more than two standard deviations more reduced than the global mean,

whereas the trace element-depleted Siqueiros fracture zone basalts indicate ~72 ppm CO_2 in the source (*19*) and are among the most oxidized in our suite (Figs. 2, S1). Critically, some of the geochemical signatures most highly correlated with oxidation state (e.g., isotopes tending toward the EM-1 ('enriched mantle') end-member (*20*), elevated Ba/La, Th/La, Nd/Hf, Ba/Rb, Nb/Ta, Nb/La ratios and negative Hf anomalies are not easily generated by silicate melting but are a natural consequence of melting in the presence of carbon (SM text and Fig. S3). Low-degree carbonatitic or kimberlitic melts may extract the highly incompatible elements to the melt phase while leaving Hf and Zr in the residue (*21-23*). Carbonatitic melts also fractionate radiogenic parent-daughter pairs, such that carbonatitic melts evolve more radiogenic Sr, Pb, and less radiogenic Nd isotopic ratios over time, toward the EM-1 mantle component (*22*). Our samples are geographically distributed (Fig. S2) and are not genetically related. Thus it is not sensible to develop a petrogenetic model that accounts for each sample's full major, trace, and radiogenic element signature. We do show in Figs. 1 and 2, however, that addition of a few tenths of a percent of low-degree carbonatitic melt of subducted material to depleted silicate melt generates trace element and isotopic arrays that reproduce the most salient geochemical signatures associated with low $Fe^{3+}/\sum Fe$ ratio (SM text).

The deep Earth is a large reservoir for carbon, continually replenished by subduction (*24, 25*) and thus the mixtures of low-degree carbonatitic and/or kimberlitic melts and high-degree silicate melts may be widespread depending on the distribution of carbon in the deep Earth (*13, 23, 26*). Prior to 2.3Ga, anoxic conditions at Earth's surface (*27*) would have resulted in subduction of reduced carbon associated with trace- and isotopically-enriched sediment and crust into mantle that was already relatively oxidized

(*28*). Subduction at 2.8 Ga may have created reduced domains in the mantle while enabling carbonate-fluxed melting to fractionate parent-daughter pairs consistent with those observed (Fig. 1). Today, the mantle's descending f_{O_2} gradient should immobilize carbon through redox freezing (*29*); however, the potential of subducted carbonate to generate mobile reduced carbon species (*2*) cannot be ruled out. Any mobilization of reduced carbon may, upon decompression, result in melts that are simultaneously enriched and reduced (SM text, Fig. S6). Additional mechanisms may exist to create geochemically enriched reducing domains in the mantle (*30*), but their geochemical implications for MORB are still unknown.

Our observations have important implications for the persistence of heterogeneities in mantle oxidation state through time. Far from being homogeneous or well-buffered, the mantle appears capable of retaining oxidation state information over plate tectonic time scales. This implies that redox-active elements such as H, C, S and Fe do not buffer the upper mantle at uniform f_{O_2}. Rather, the $Fe^{3+}/\sum Fe$ ratios of MORB, like arcs (*31*), reflect variations in their sources.

Fig. 1. Decrease in $Fe^{3+}/\sum Fe_{(10)}$ ratio as a function of isotopic enrichment. $^{208}Pb/^{204}Pb$ and $^{87}Sr/^{86}Sr$ versus $Fe^{3+}/\sum Fe_{(10)}$ ratio (**A, B**) and calculated 1-atm f_{O2} (**C, D**), with $Fe^{3+}/\sum Fe_{(10)}$ ratio accounting for 50 and 44% of the variance in these isotopic ratios, statistically significant at $P \leq 0.001$ (F Test results, Table S3). **Filled circles** show individual analyses and **open diamonds** show the regional average and 1σ variability for each geographic location. $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ (**E**) and $^{87}Sr/^{86}Sr$ vs $^{143}Nd/^{144}Nd$ (**F**), as a function of $Fe^{3+}/\sum Fe_{(10)}$ ratio, showing a decrease in the oxidation state of Fe in the glasses as a function of isotopic enrichment. **Colorbar** shows the relative Fe oxidation state of each sample. Curve 1 models 0.1% additions of a low-degree carbonatitic melt of subducted material to Depleted-Depleted MORB Mantle (D-DMM; star), generated 2Ga after subduction. Depleted (square) and Enriched (hexagon) MORB mantle shown for reference (*20*). Curve 2 demarcates additions of a low-degree carbonatitic melt of the same subducted source material as 1, but with the carbonatitic melt generated immediately following subduction at 2.8Ga. The difference between these two curves is timing of the parent-daughter fractionation introduced by carbonatitic melting, where curve 1 assumes no fractionation of the subducted material until melting beneath the mid-ocean ridge and curve two assumes carbonatitic melt-induced fractionation immediately following subduction. Model details are in the SM text. Errors in isotopic ratios are as provided by the authors of those studies.

Fig. 2. Decrease in $Fe^{3+}/\sum Fe_{(10)}$ ratios with trace element enrichment in primitive glasses with >8.5wt.% MgO. (A-B) Ba/La and Th/La decreasing as a function of $Fe^{3+}/\sum Fe_{(10)}$ ratio and the f_{O2} of the source mantle at the average pressure and temperature

of melt segregation ($\sim$ 0.7 – 1.3 GPa) relative to the QFM buffer (*8*) **(C-D),** with

$Fe^{3+}/\Sigma Fe_{(10)}$ ratio accounting for 53 and 43% of the variance in these trace element ratios,

statistically significant at P $\leq$ 0.002 (F Test results, Table S3). **Filled circles** show

individual analyses and **open diamonds** show the regional average and 1σ variability for

each geographic location ("popping rock" Ba/La = 13.2, Th/La = 0.11, $Fe^{3+}/\Sigma Fe_{(10)}$ =

0.137). **(E-F)** Co-variation of Ba/La with Nd/Hf ratios and Th/La with Nb/Zr ratios as a

function of $Fe^{3+}/\Sigma Fe_{(10)}$ ratio. Lines model 0.1% additions (+) of a low-degree

carbonatitic melt of subducted material (SM Text) to depleted sample VG5211 from

Siquerios (SM Text). D-DMM (star) shown with silicate melt trajectory to 1% melt

fraction. Errors in trace element ratios are smaller than the symbol size.

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