INTRODUCTION

There is a long-standing debate on what controls the oxidized nature of arc magmas, particularly those formed in continental arcs (1, 2). This debate has profound implications for Earth’s evolution because oxidized arc magmas, manifested in the form of iron-depleted magmas, are the primary building blocks of the continental crust (3). The debate is centered on whether the oxidized signatures of arc magmas are inherited from the mantle source or developed during magmatic differentiation, crustal interaction, or degassing. Iron and sulfur oxidation states in melt inclusions have been used to suggest that fluids released from the subducted slab pervasively oxidize the sub-arc mantle, producing oxidized arc magmas from the onset (1, 4, 5), but redox-sensitive trace element ratios and Fe isotope signatures of basalts, which have been used to see through eruptive and differentiation processes, suggest that primitive arc magmas are not as oxidized as widely thought (6–8). None of the above studies, however, represent direct constraints on the oxidation state of primitive, pre-erupted magmas.

Here, we examine the Eu systematics of deep-seated (>45 to 80 km) garnet pyroxenite continental arc cumulates to provide the most direct constraint so far on arc magmas before they rise into the crust or erupt. Europium is a rare earth element (REE), but unlike most other REEs, which are exclusively trivalent under typical terrestrial conditions, Eu occurs in both divalent and trivalent states, so the ratio of Eu2+/Eu3+ is sensitive to variations in oxygen fugacity (fO2). Although Eu2+ strongly partitions into plagioclase, in all other magmatic minerals, Eu3+ is more incompatible than Eu2+ and neighboring REEs, making the total partitioning of Eu sensitive to fO2. Eu2+/Eu3+ may be a more robust redox-sensitive index than element pairs, such as V/Sc (9) and Zn/Fe (7), because the geochemical behavior of both Eu2+ and Eu3+ can be well constrained throughout magmatic differentiation. Eu systematics in plagioclase-free rocks can thus be used to constrain the Eu valence state, which in turn can be used to estimate oxygen fugacity using experimentally calibrated Eu oxybarometers (10).

RESULTS

We sampled garnet-bearing pyroxenite xenoliths from Miocene trachyandesitic volcanic centers on the margin of the Colorado Plateau in Arizona (11, 12). They have major element compositions complementary to typical continental arc plutonic rocks and are thus interpreted to represent arc cumulates (11). These deep cumulates do not contain any evidence of plagioclase. Titanite U/Pb systematics suggest crystallization in the Late Cretaceous or Early Paleogene (11). Their mineralogies and trace and major element signatures are identical to arc cumulates associated with the Cretaceous Sierra Nevada batholith toward the west (11, 13, 14). The Arizona garnet pyroxenites are thus interpreted to represent cumulates from hydrous arc magmas associated with Mesozoic to Early Cenozoic arc magmatism in western North America (11). They have Mg#s [atomic Mg/(Mg+Fe), where Fe represents total Fe] ranging from 0.5 to 0.82, the latter representing early formed cumulates from primitive arc magmas and the former representing cumulates from more evolved magmas (see the Supplementary Materials and Methods).

The deep petrogenetic origins of the garnet pyroxenites and the lack of any visible evidence for plagioclase make these pyroxenites ideal for applying Eu systematics as an oxybarometer of arc magmas before eruption. To avoid potential contamination of the whole-rock xenolith by recent injection of Miocene host lavas onto grain boundaries, we performed in situ laser ablation ICP-MS (inductively coupled plasma mass spectrometry) analyses of garnets and clinopyroxenes in thin sections (see the Supplementary Materials and Methods). Longer dwell times on Sm, Gd, and Eu were applied to increase the precision and accuracy of the analyses.

Oxygen fugacity of primitive arc magmas constrained by mineral Eu anomalies

Europium valence can be quantified from the relative difference (the Eu anomaly) in geochemical behavior between Eu2+ and neighboring REEs. Eu anomalies are expressed as Eu/Eu*, where Eu* represents the hypothetical concentration of Eu if it behaved solely like a trivalent REE and is calculated by polynomial interpolation of REE systematics in the order of their ionic radii (see the Supplementary Materials and Methods).
Eq. 1 assumes that the mineral is in equilibrium with the melt (subsolidus reequilibration in garnet- pyroxenites has minimal effect on mineral Eu/Eu* because Eu2+ is highly incompatible in garnet). $D_{\text{min-melt}}^{\text{Eu}}$ is estimated from the behavior of trivalent REEs, whereas $D_{\text{melt}}^{\text{Eu}}$ can be estimated from the behavior of geochemically similar Sr2+. In clinopyroxene, $D_{\text{cpx-melt}}^{\text{Eu}}$ can be equated to $D_{\text{Sr}} / D_{\text{Gd}}$, which ranges between 0.03 and 1.53 with a median value of 0.22 ($n = 89$, excluding kimberlites and carbonatites) based on published partition coefficients (16). Additional constraints come from clinopyroxenes in ureilite meteorites, wherein most of the Eu is divalent due to the highly reducing conditions of ureilites (17). Ureilite clinopyroxenes have Eu/Eu* ranging from 0.18 to 0.63 with a median value of 0.29 ($n = 49$), and assuming that parental magmas begin with Eu/Eu* = 1, the measured Eu/Eu* values in ureilites provide an upper bound of ~0.2 on $D_{\text{cpx-melt}}^{\text{Eu}} / D_{\text{Eu}}^{\text{III}}$. In garnet, Sr is highly incompatible, which is consistent with the pyroxenite garnets having Sr barely above detection limits (0.1 to 1 parts per million); $D_{\text{garnet}}^{\text{Sr}} / D_{\text{Eu}}^{\text{III}}$ is thus effectively zero in garnet, simplifying Eq. 1. In the extreme case, in which $D_{\text{min-melt}}^{\text{Eu}} = 0$ for all minerals, Eq. 1 simplifies such that the ratio of the Eu anomaly in the pyroxenite versus that in the melt provides a maximum bound on the Eu3+/ΣEu ratio.

We use both clinopyroxene and garnet in the most primitive cumulates to estimate the Eu valence state of the primitive magma. As noted above, the primitive magma is assumed to have Eu/Eu* = 1. We can use experimentally calibrated Eu2+/Eu3+–fO2 relationships in silicate melts (10) to obtain fO2. Details of the calculation are provided in the Supplementary Materials. Garnets and clinopyroxenes in CC-ME1 give
Redox evolution of arc magmas during differentiation

We now turn to the increase of Eu/Eu* with decreasing Mg#. This trend reflects the enrichment of more incompatible Eu** in the melt and/or rising fO2 with differentiation. Progressive crystal fractionation leads to a predictable decrease in the Mg# of the melt and cumulate (see the Supplementary Materials and Methods). Using a semiempirical relationship between Mg# of the cumulate and residual melt fraction relative to a primitive mantle-derived magma to estimate the residual melt fraction corresponding to each cumulate, we can estimate the mineral/melt partition coefficient at any given Mg# of the cumulate and residual melt fraction. This inverse approach allows us to identify how the cumulate/melt bulk Eu partition coefficient, calculated as $D_{Eu^{**}}$ relative to $D_{Eu^{**}}$ (Fig. 2B), varies with crystallization in the cumulates. The $D_{Eu^{**}}$ values are higher than those used here, which seems unlikely, even lower fO2 values were estimated (Fig. 2A).

Sample SB1-ME9 has too few garnets to investigate while clinopyroxenes show significant scatter in Eu/Eu* (Fig. 1A) due to uncertainties associated with extremely low REE concentrations (tens of parts per billion Eu). Nevertheless, the mean Eu/Eu* of SB1-ME9 clinopyroxenes is identical to those of CC-ME1 (Fig. 1C). We thus use CC-ME1 to constrain the maximum fO2 in primitive arc magmas.

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magma \( f_{O_2} \) rises more rapidly with differentiation, so our estimates of \( f_{O_2} \) during differentiation are minimum bounds. On the basis of this analysis, we find that \( f_{O_2} \) increased from FMQ–1 to at least FMQ+1 with crystal fractionation of these garnet pyroxenite cumulates (Fig. 2C). Our observations suggest that the \( f_{O_2} \) of the sub-arc mantle may not be significantly different from that beneath mid-ocean ridges and that the oxidized signature of arc magmas may be acquired during ascent and differentiation.

**DISCUSSION**

The initially low \( f_{O_2} \) inferred for primitive arc magmas raises the question of what drives the Fe depletion characterizing calc-alkaline series differentiation. Iron depletion, which distinguishes the calc-alkaline series from the tholeiitic series, is generally attributed to early magnetite saturation in oxidized magmas. However, if primitive arc magmas are reduced, magnetite saturation will be suppressed initially (23) and magmatic differentiation should follow the Fe-enriching tholeiitic series unless the magma becomes oxidized during differentiation.

At low pressure, Fe is moderately incompatible in olivine and clinopyroxene and strongly incompatible in plagioclase, so crystallization leads to Fe enrichment. Although Fe\(^{3+}\) is generally incompatible in Fe-bearing silicates, the low-pressure silicate fractionating phases incorporate limited Fe (Fig. 4A). Furthermore, the combination of crystallizing low Fe\(^{3+}\)/ΣFe silicate phases with high Fe\(^{3+}\)/ΣFe iron oxide phases pushes the redox state of the magma due to crystal fractionation at low pressure to the Fe-rich end.

On the other hand, as pressure increases, the Fe-bearing crystallizing assemblage transitions from olivine + clinopyroxene + spinel/magnetite to garnet + clinopyroxene (Fig. 4A). At high pressure, garnet is the major Fe-bearing phase and removes up to ~50% of the total initial Fe in the melt, consistent with experimental observations (35). The connection...
between calc-alkaline differentiation and garnet fractionation was first proposed by Green and Ringwood (36–38). Here, we show that the effect of garnet fractionation is borne out in global compilations of arc magma data, where Fe depletion clearly correlates with Dy/Yb (Fig. 4B), the latter being a strong tracer of garnet fractionation (39, 40). Garnets in pyroxenites have been shown to have extremely low ferric Fe contents (Fe$_{3+}$/S$_{Fe}$ < 0.01) (41). Eclogite garnets have also been found to contain low ferric Fe (Fe$_{3+}$/S$_{Fe}$ < 0.08) (42, 43). We note that although Fe$_{3+}$ is more compatible in clinopyroxene than in garnet (44), clinopyroxene takes much less Fe than garnet. Collectively, fractionation of garnet-bearing cumulates at high pressure can simultaneously drive Fe depletion and increase Fe$_{3+}$/S$_{Fe}$ in the derivative melt with differentiation.

To quantify the garnet fractionation effect on Fe valence in the derivative melt, we use a simplified crystal fractionation model in which the crystallizing assemblage is represented by garnet, whereas all other phases are treated as a separate nongarnet assemblage. As a minimum bound on the degree of Fe depletion, we designate the nongarnet assemblage to have bulk partition coefficients of 1 and 0.8 for Fe$^{2+}$ and Fe$^{3+}$, respectively. We assume that garnet takes only Fe$^{2+}$ and has a bulk Fe partition coefficient significantly >1. For various differentiation pressures, we explore a range of garnet mode from 0 to 30% in the fractionation assemblage, and a range from 0 to 60% Fe removal via garnet fractionation. When the garnet mode is zero, as would be the case for low-pressure differentiation, magma $f$O$_2$ remains nearly constant (Fig. 5B). When garnet mode increases and its fractionation removes over 40% of the total Fe, the magma can be progressively oxidized to at least FMQ+1, consistent with the terminal magma redox conditions constrained by observed cumulate Eu/Eu* values. Our forward-modeled Eu/Eu* trend during garnet fractionation agrees well with the observed cumulate Eu/Eu* data (Fig. 5C).

We recognize that magma oxidation and Fe depletion paths will also be influenced by Fe oxides and changing Fe partition coefficients with differentiation, which are not accounted for in our simplified model. Nevertheless, we show that garnet fractionation leads to simultaneous Fe depletion (35) and oxidation of the derivative melt, both of which characterize calc-alkaline differentiation. Because the mode of garnet, and thus the amount of Fe removed by garnet, increases with pressure and water content in the melt during crystal fractionation (45), this model explains why calc-alkaline differentiation is associated with thickened crust. Magnetite saturation should only occur after the magma is significantly oxidized by garnet fractionation, and is unlikely to be the main driver of Fe depletion in calc-alkaline series because magnetite removes ferric Fe, which reduces the $f$O$_2$ of the derivative melt and prevents the magma from remaining oxidized. Fe-oxide fractionation is a consequence of increasing $f$O$_2$. Consistent with this conclusion is that Fe oxides only appear in the differentiated cumulates, not the primitive ones. With progressive differentiation, eventual coprecipitation of magnetite and garnet may then buffer the differentiated arc magmas at a certain $f$O$_2$ above FMQ.

![Fig. 5. Modeled garnet effect on magma redox evolution with differentiation.](http://advances.sciencemag.org/) (A) Fe depletion curves assuming 0 to 60% Fe removal by garnet fractionation. (B) Magma $f$O$_2$ evolution curves as a function of the amount of Fe removed by garnet fractionation. Magma $f$O$_2$ paths calculated from cumulate Eu/Eu* data (shaded area) are also shown for comparison. (C) Calculated Eu/Eu* in cumulate garnet based on the magma $f$O$_2$ evolution curves in (B). Superimposed are the cumulate garnet Eu/Eu* data from this work.
CONCLUSIONS AND IMPLICATIONS

In summary, the Fe-depleting calc-alkaline differentiation series, which dominates the composition of the continental crust, may not be determined by initial magma redox conditions, but may instead be controlled by the effective pressure of magmatic differentiation in the crust. Our conclusions do not exclude other scenarios for generating calc-alkaline signatures, such as partial melting of eclogitic slabs, crustal contamination, and metasomatic oxidation of the sub-arc mantle (1, 4, 5), and no doubt, calc-alkaline magmas occasionally do occur in island arcs. However, the overall relationship between crustal thickness and degree of calc alkalinity appears to be a general global phenomenon and points to the dominance of upper plate thickening, or orogenic processes, in the formation of calc-alkaline magmas and Earth’s continental crust (46–48). Our study provides an internally consistent mechanism for explaining this connection between oxidation and magmatic differentiation in thick crust.

Important implications follow. Iron depletion driven by garnet fractionation under reduced conditions will lead to sulfide saturation in the magma because sulfide solubility decreases with FeO content in the melt, thereby driving extensive sulfide coprecipitation with the cumulates (47, 49, 50). Deep continental arc cumulates may be an important reservoir for chalcophile elements and unradiogenic Pb isotopes (47, 51, 52). If these cumulates were to founder back into the mantle, owing to their high densities (14, 52–55), then the progressive growth of the continental crust would lead to a flux of reduced materials to the mantle, thereby driving extensive sulfide coprecipitation with the cumulates, which may have influenced Earth’s surface redox evolution by limiting the magmatic output of ferrous Fe and sulfides (56, 57).

MATERIALS AND METHODS

Details about the samples, analytical techniques, and modeling are provided in the Supplementary Materials. Data are provided in data files S1 to S3.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/5/eaar4444/DC1

Supplementary Materials and Methods

Supplementary Text

fig. S2. Long-term (8 months) reproducibility in the analysis of glass standards BIR-1G and BCR-2G.
fig. S3. Chondrite-normalized REE/FeO values for clinopyroxene.
fig. S4. Chondrite-normalized REE/FeO values for garnet.
fig. S5. Mean Eu/Eu* versus MgO in global arc lavas.
fig. S6. Calculated log gCO2 as a function of optical basicity assuming Eu/Eu* = 0.8 in garnet.
fig. S7. Mineral Mg# versus whole-rock Mg# in the cumulates documented in this work.
fig. S8. Melt-cumulate Mg# correlation simulated by MELTS at 2 GPa, 4 wt % H2O, and various oxygen fugacities.
fig. S9. Observed K2O-Mg# correlation in arc magmas, parameterized by an exponential function shown in the figure.
fig. S10. Error propagation by Monte Carlo resampling.
fig. S11. Sensitivity test of calculated DFe3+/DFe2+ and redox paths to the value of DFe2+ used in the crystal fractionation model.
fig. S12. Calculated optical basicity (Λ) as a function of Mg# in arc magmas, data file S1. In-situ mineral composition data and cumulate whole-rock data.
data file S2. Primitive arc magma compositions.
References (59–63)

REFERENCES AND NOTES


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The redox "filter" beneath magmatic orogens and the formation of continental crust
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