

Letter

Reevaluating the oxidation effect of garnet crystallization

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ABSTRACT

Garnet has been proposed to be an important fractionating phase during magmatic differentiation in thick volcanic arcs because garnet fractionation can reproduce the hallmarks of continental crust by driving residual magmas to higher silica, lower total iron, and higher iron oxidation states. Recently, Holycross and Cottrell (2023b) have measured the partition coefficients for Fe^{2+} and Fe^{3+} between garnet and melt, which allow for more precise modeling of the oxidation effect of garnet fractionation. Using their new experimental results combined with fractional crystallization modeling, Holycross and Cottrell (2023a, 2023b) concluded that garnet crystallization has little influence on arc magma oxidation. However, these conclusions are based on conceptual errors in modeling the effects of garnet. Firstly, they ignored garnet fractionation beyond 50% crystallization which would cause substantial Fe^{3+} enrichment. Limiting garnet fractionation to the initial 50% crystallization of arc basalts is inconsistent with existing experiments including their own experiments. Secondly, Fe^{2+} partitioning was indirectly and incorrectly parameterized using Fe–Mg exchange coefficients, inconsistent with experimental partition coefficients. Application of these recent models leads to unrealistic Fe^{2+} partitioning behavior with progressive fractionation. When these models are corrected with proper mass balance and partitioning relationships, garnet as a driver of oxidation remains a viable and testable hypothesis.

1. The hypothesis of garnet-driven oxidation

The redox evolution of arc magmas in differentiation exerts critical influences on volcanic degassing, ore deposit formation, and continent evolution. One recent hypothesis suggests that garnet fractionation may preferentially deplete Fe^{2+} over Fe^{3+} in the melt, thus driving oxidation in arcs built on thick crust where garnet can be stabilized (Tang et al., 2018). The garnet-driven oxidation is a type of endogenic oxidation mechanism and causes magma oxidation without incorporating oxidized crustal materials from Earth's surface.

2. Observations

Over the last five years, several observations have been made and found to be consistent with the hypothesis of garnet-driven oxidation.

First of all, Tang et al. (2019) determined the $\text{Fe}^{3+}/\sum\text{Fe}$ in cumulate garnets and found the ratios to be in the range of 0.04–0.08, much lower than the $\text{Fe}^{3+}/\sum\text{Fe}$ of mid-ocean ridge basalts and arc basalts (e.g., Bézous and Humler, 2005; Kelley and Cottrell, 2009). Tang et al. (2019) further showed that Fe^{3+} -rich oxides such as magnetite cannot saturate at the high-pressure conditions relevant to garnet crystallization. Therefore, fractionation of garnet-bearing cumulates will increase $\text{Fe}^{3+}/\sum\text{Fe}$ of the derivative melt.

Secondly, Tang et al. (2020) showed that sulfur (S) content in apatite correlates with whole-rock Dy/Yb in felsic rocks in southern Tibet. Because S^{6+} is compatible in apatite whereas S^{2-} is not, the S content in apatite serves as a reflection of both S and magma oxidation states. On the other hand, garnet fractionation leads to a characteristic high Dy/Yb in the derivative magmas. Therefore, the positive correlation between S content in apatite and whole-rock Dy/Yb indicates that garnet

fractionation plays a critical role in determining the oxidation state of felsic magmas.

Another line of evidence comes from Fe isotopes. Du et al. (2022) found that the oxidized, strongly calc-alkaline arc magmas in the central Andes have systematically heavier Fe isotopes than the moderately calc-alkaline arc magmas in the same region and tholeiitic arc magmas in Mariana. The heavy Fe isotopes seen in the strongly calc-alkaline central Andean arc magmas are best explained by garnet fractionation. Similar conclusions were also reached by Li et al. (2021).

The garnet hypothesis also explains the preferential occurrence of calc-alkaline magmas in arcs built on thick crusts (Chen et al., 2023; Tang, 2021; Tang et al., 2018; Tang et al., 2023). As the crust thickens, garnet becomes an important crystallizing phase in arc magma differentiation, and because these garnets are Fe-rich, their fractionation causes Fe depletion in the magma. The pressure dependence of garnet vs. magnetite fractionation translates into pressure dependence of magma redox evolution, which has important implications for how tectonic processes modulate magmatic volatile degassing (Sun and Lee, 2022).

3. Reevaluating the garnet hypothesis

Recently, Holycross and Cottrell (2023b) ran a series of experiments to determine the partition coefficients for Fe^{2+} ($D_{\text{Fe}^{2+}}^{\text{grt/melt}}$) and Fe^{3+} ($D_{\text{Fe}^{3+}}^{\text{grt/melt}}$) between garnet and silicate melts under various pressure, temperature, and redox conditions. Based on their experiments, Holycross and Cottrell (2023b) calculated the redox effect caused by garnet crystallization and concluded that garnet-pyroxenites can only remove 20% of the total Fe and cause negligible oxidation (~ 0.7 logarithmic

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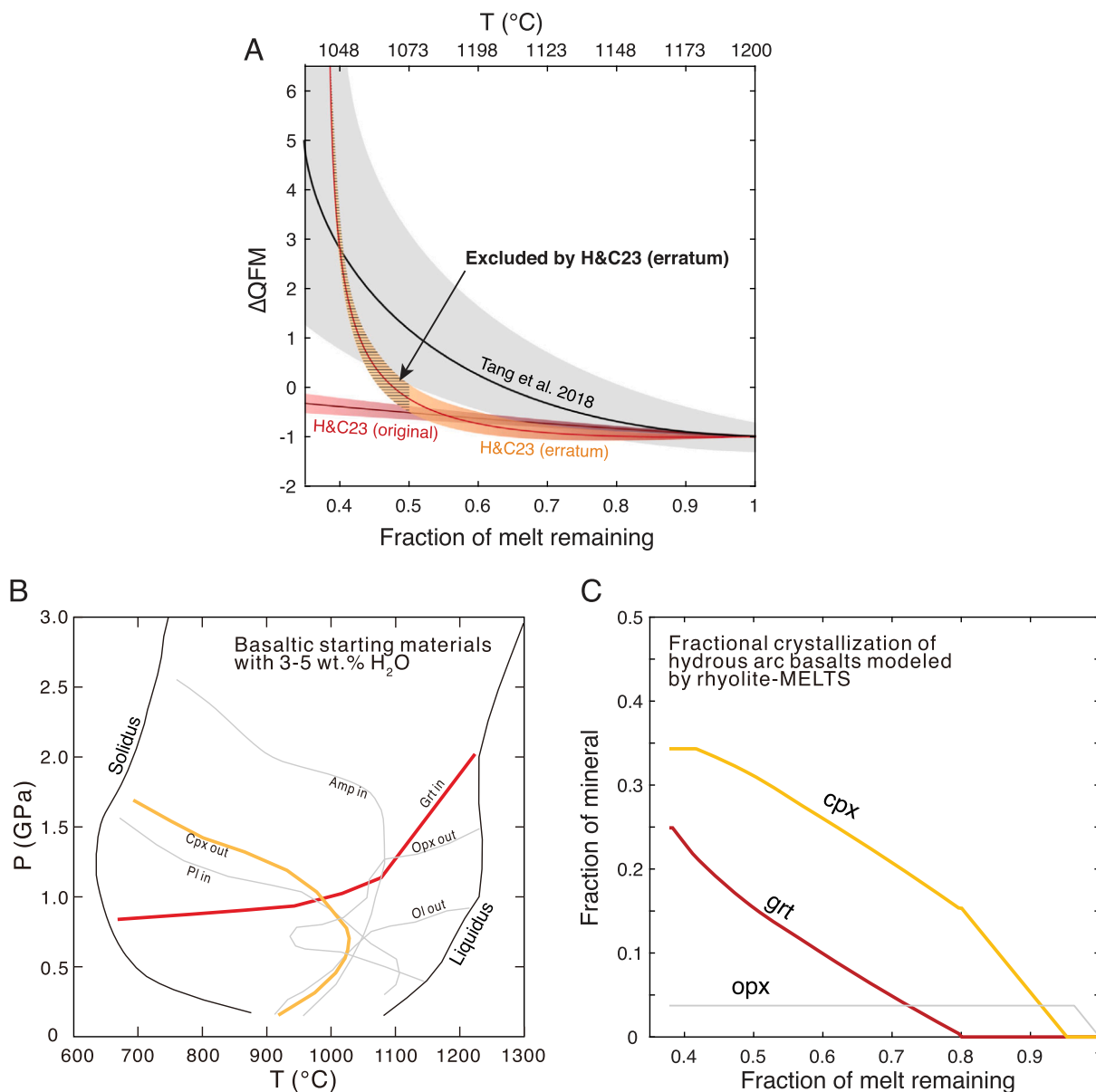


Fig. 1. Garnet-pyroxenite fractionation in hydrous arc magma differentiation. (A) Arc magma oxidation due to garnet-pyroxenite fractionation calculated by Holycross and Cottrell (original and after correction) and Tang et al. (2018). (B) Phase diagram showing crystallization of hydrous arc basalts. This phase diagram was modified from Chen et al. (2023) and was constructed based on published experimental results. (C) Rhyolite-MELTS simulation of hydrous arc basalt fractional crystallization in conditions similar to those of Holycross and Cottrell's model. The starting basalt composition is the same as that used in Holycross and Cottrell's model. The simulation was carried out in a temperature range from liquidus to 950 $^{\circ}C$ and a pressure range from 2.0 GPa to 1.3 GPa. Initial water content was set to 4 wt%. fO_2 was maintained at FMQ. The simulation results are provided in Supplementary Material 2. Garnet-pyroxenite continues to crystallize as the dominant assemblage when fractional crystallization exceeds 50%. In Supplementary Material 1, we also plotted the simulation results for fractional crystallization over a broader P-T range (temperature ranging from liquidus to 700 $^{\circ}C$ and a pressure from 2.0 GPa to 1.0 GPa).

units increase in the fO_2) after >60% crystallization.

Their original model had calculation errors which led to mass conservation issues. We informed the authors of these issues, resulting in publication of an Erratum (Holycross and Cottrell, 2023a). Their corrected model now shows a strong oxidation effect after >50% crystallization, consistent with the results of Tang et al. (2018) (Fig. 1A). However, in their Erratum, Holycross and Cottrell (2023a) decided to cut off the modeling trends at 50% crystallization and continue to conclude that garnet crystallization does not oxidize arc magmas significantly (Fig. 1A).

Holycross and Cottrell's conclusion of negligible oxidation after correction (Holycross and Cottrell, 2023a) is based on their argument that garnet-pyroxenite fractionation cannot exceed 50%. We first

evaluate this argument in the context of existing experiments, and then show how this erroneous argument arises from an additional artifact in their model which fails to reproduce their experimental trends for almost all major elements (Fig. S1).

3.1. The extent of garnet-pyroxenite fractionation

The argument that garnet-pyroxenite fractionation cannot proceed after 50% crystallization of arc basalts is inconsistent with the published arc magma crystallization experiments (Fig. 1B), including their own experiments (Fig. S2). In Holycross and Cottrell's model, arc basalts reach 50% crystallization at ~ 1073 $^{\circ}C$ and 1.4 GPa, but the crystallizing/residual assemblage in these conditions is dominated by garnet

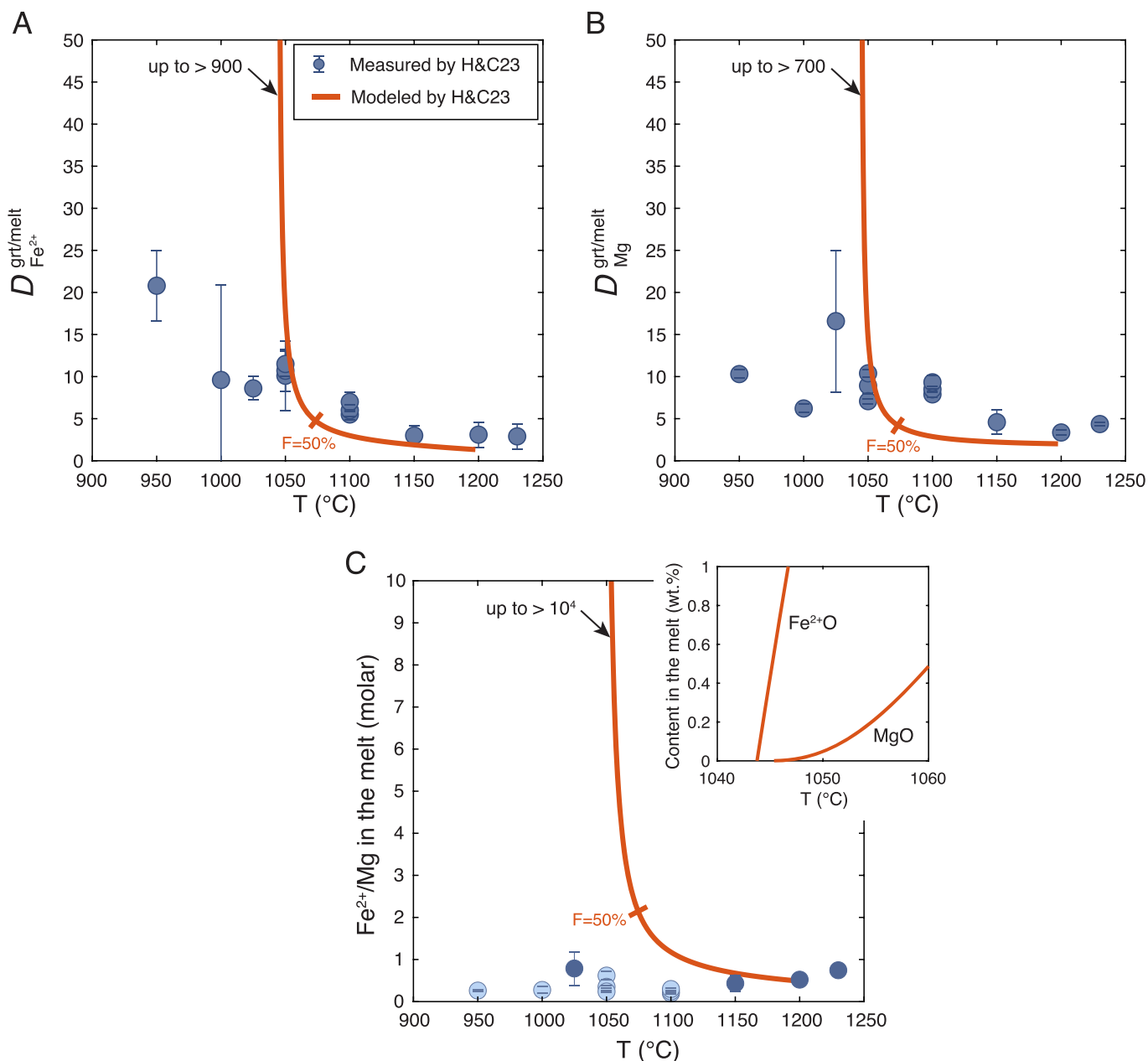


Fig. 2. Runaway artifacts in Holycross and Cottrell's model. (A, B) Comparison of apparent $D_{\text{Fe}^{2+}}^{\text{grt/melt}}$ and $D_{\text{Mg}}^{\text{grt/melt}}$ calculated from Holycross and Cottrell's fractional crystallization model with their experimental results. (C) Comparison of melt Fe^{2+}/Mg between Holycross and Cottrell's model and experiments. Inset shows a zoom-in plot of FeO and MgO contents in the modeled melt after 50% fractionation. Error bars are 1 SE.

and clinopyroxene (\pm amphibole) (Fig. 1B). In fact, garnet continues to crystallize as the melt evolves to highly felsic compositions provided that pressure remains above 1 GPa (Fig. 1B). At low temperatures, amphibole may join garnet and clinopyroxene. The role of amphibole in fractionating Fe^{2+} and Fe^{3+} is similar to that of clinopyroxene—limited fractionation or slightly enriching Fe^{3+} in the residual liquid (King et al., 2000; Zhang et al., 2022).

One can further evaluate the extent of garnet-pyroxenite fractionation using rhyolite-MELTS simulation (Gualda et al., 2012). Garnet and clinopyroxene remain as the dominant crystallizing phases as fractionation proceeds to well beyond 50% (crystal fraction >50%) under the conditions similar to those of Holycross and Cottrell's model (Fig. 1C). Substantial garnet fractionation in late-stage differentiation of arc magmas is also supported by the continuously increasing Dy/Yb ratio with differentiation at $\text{MgO} < 4$ wt% (Chen et al., 2023) and heavy Fe

isotopes in thickened continental arcs (Du et al., 2022).

3.2. The argument of <50% garnet-pyroxenite fractionation results from a model artifact

Holycross and Cottrell's argument of <50% garnet-pyroxenite fractionation is not grounded in observational evidence but rather in their modeling outcomes. As they described: "[...] after 50% fractional crystallization [...], the Fe/Mg ratios of modeled garnet and clinopyroxene exceed reported compositions of experimental garnet pyroxenites [...] and [...] natural garnet pyroxenites [...]". We note that their model is plagued by a runaway artifact, and the extreme Fe/Mg of their modeled garnet and clinopyroxene results from their incorrect use of Fe/Mg exchange coefficient $K_D \text{ Fe/Mg}$ in their fractional crystallization model.

Holycross and Cottrell (2023b) explicitly stated that they "[...]

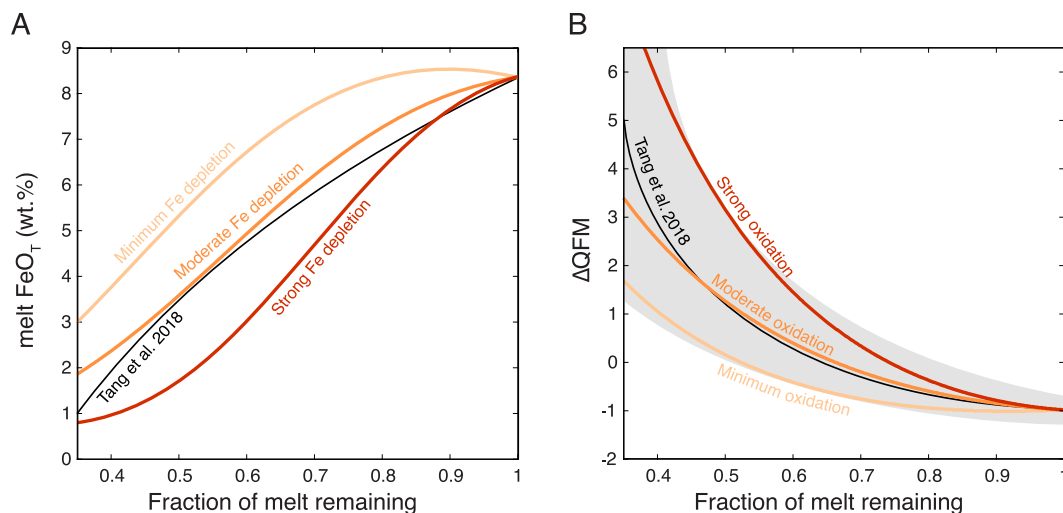


Fig. 3. Impact of garnet pyroxenite crystallization on Fe depletion (A) and fO_2 (B) of arc magmas. We modeled Fe depletion and oxidation during garnet pyroxenite fractionation using the $D_{Fe^{2+}}^{grt/melt}$ and $D_{Fe^{3+}}^{grt/melt}$ determined by [Hollycross and Cottrell \(2023b\)](#). The results of [Tang et al. \(2018\)](#) are shown for comparison. We considered three scenarios by varying Fe^{2+} partition coefficient for cpx $D_{Fe^{2+}}^{cpx/melt}$ and grt/cpx modal ratio. Minimum scenario: Fe^{2+} partition coefficient in cpx $D_{Fe^{2+}}^{cpx/melt} = 0$ and grt/cpx = 0.3/0.7; moderate scenarios: $D_{Fe^{2+}}^{cpx/melt} = 1$ and grt/cpx = 0.3/0.7; strong scenario: $D_{Fe^{2+}}^{cpx/melt} = 1$ and grt/cpx = 0.5/0.5. All other modeling parameters were kept the same.

evaluate how our new calculated values for $D_{Fe^{2+}}^{grt/melt}$ and $D_{Fe^{3+}}^{grt/melt}$ affect this finding (garnet-driven oxidation)”, they did so for Fe^{3+} but not Fe^{2+} —their experimentally calibrated $D_{Fe^{2+}}^{grt/melt}$ was not used in their subsequent evaluation of the impact of garnet. Unlike Fe^{3+} , Fe^{2+} partitioning was instead modeled via a more complex approach using the Fe/Mg exchange coefficient K_D Fe/Mg.

In some cases, exchange coefficient is preferred over partition coefficient for modeling major elements like Fe. However, to apply an exchange coefficient, a stoichiometry-based mass conservation equation is needed to quantify element partitioning because K_D represents relative rather than absolute partitioning. For major elements, this can be done by setting up mass action laws for all major elements and assuming their contents add up to 100%. Therefore, the K_D approach works best for minerals with simple stoichiometries, such as olivine. However, both garnet and clinopyroxene have complex stoichiometries. For garnet, one would need to establish mass action laws for at least MgO, FeO, CaO, Al_2O_3 , and SiO_2 , which was not done ([Hollycross and Cottrell, 2023b](#)). For pyroxene, there are more elements to consider. Because none of these values are known or modeled, [Hollycross and Cottrell \(2023b\)](#) assumed constant CaO, Al_2O_3 and SiO_2 molar contents in garnet and clinopyroxene throughout the crystallization path. This assumption removes the benefit of using K_D to calculate Fe partitioning.

More problematically, by assuming constant CaO, Al_2O_3 , and SiO_2 contents in garnet leads to an artifact in the calculated Fe/Mg in garnet (and clinopyroxene and melt). This assumption fixes the $(Fe^{2+} + Mg)$ molar content in garnet throughout the crystallization path. This would mean that early-stage garnet will have the same $(Fe^{2+} + Mg)$ molar content as late-stage garnet, even though both $Fe^{2+}O$ and MgO contents in the melt decrease from ~8 wt% to ~0 wt%. Because of this erroneous assumption, the apparent $D_{Fe^{2+}}^{grt/melt}$ and $D_{Mg}^{grt/melt}$ in [Hollycross and Cottrell’s](#) model are initially lower than their own experimental results when melt Fe^{2+} and Mg contents are high, and then follow runaway paths when melt Fe^{2+} and Mg contents become low (Fig. 2A, B). As a consequence, depletions of Fe^{2+} (and hence oxidation) and Mg are initially underestimated, and then dramatically overestimated when crystallization exceeds 50%. Accelerated depletions cause Fe^{2+} and Mg in the modeled remaining melt to approach zero rapidly at >50% crystallization (Fig. S1). And because Mg content reaches zero slightly earlier than Fe

content in their model (Fig. 2C inset), Fe/Mg in the modeled melt and the garnet increase dramatically at >50% crystallization (Fig. 2C). Therefore, the high Fe/Mg in the garnet modeled by [Hollycross and Cottrell](#) is entirely an artifact of errors introduced by their K_D Fe/Mg approach, and cannot be used as a criterion for evaluating garnet-pyroxenite fractionation.

3.3. Fractionation modeling using internally consistent partition coefficients

Finally, we provide an internally consistent fractional crystallization model using the $D_{Fe^{2+}}^{grt/melt}$ and $D_{Fe^{3+}}^{grt/melt}$ obtained by [Hollycross and Cottrell \(2023b\)](#). These partition coefficients were parameterized as functions of temperature, pressure, and redox conditions ([Hollycross and Cottrell, 2023b](#)). Our approach using parameterized partition coefficient is in no way near perfect, but it is consistent with [Hollycross and Cottrell’s](#) experiment data and does not require assumptions of Ca, Al, and Si contents in garnet and clinopyroxene.

Specifically, we followed [Hollycross and Cottrell \(2023b\)](#) and adopted the following assumptions in our fractional crystallization model:

1. modal garnet/clinopyroxene (grt/cpx) = 0.3/0.7;
2. 65% fractional crystallization beginning at 1200 °C, 2.0 GPa to 1035 °C, 1.3 GPa;
3. Initial melt $Fe^{3+}/\Sigma Fe = 0.088$ ($fO_2 = QFM-1$);
4. For clinopyroxene, Fe^{3+} partition coefficient $D_{Fe^{3+}}^{cpx/melt} = 0.56$;
5. For Fe^{3+} partitioning in garnet:

$$D_{Fe^{3+}}^{grt/melt} = 6.24 - 0.15 * \log fO_2 - 0.00412 * T(K) \quad (1)$$

The assumption regarding the grt/cpx modal ratio adopted by [Hollycross and Cottrell \(2023b\)](#) was taken from [Tang et al. \(2018\)](#). This was a loosely constrained estimate because Tang et al.’s model served only as a proof of concept in evaluating the plausibility of garnet-driven oxidation, and in particular, provide a conservative minimum bound on the extent of oxidation and Fe depletion. Likely, the grt/cpx modal ratio should increase with progressive differentiation, driving oxidation and Fe depletion further. Indeed, in [Hollycross and Cottrell’s](#) experiments, grt/cpx modal ratio ranges from 0.24/0.76 to 0.73/0.27 with an average

of 0.43/0.57. Nevertheless, to be consistent with Holycross and Cottrell's model and to focus solely on the effects of Fe partitioning, we adopted the same fixed grt/cpx modal ratio of 0.3/0.7 here.

Our modeling differs from that of Holycross and Cottrell (2023b) in the treatment of Fe²⁺ partitioning—Fe²⁺ partitioning in garnet was calculated based on the experimentally determined partition coefficients from Holycross and Cottrell (2023b), as was done for Fe³⁺:

$$D_{\text{Fe}^{2+}}^{\text{grt/melt}} = 81.8 - 0.0542 * T(\text{K}) \quad (2)$$

Because we do not have an independent or internally consistent constraint on clinopyroxene partitioning from their experiments, we may assume clinopyroxene to have a $D_{\text{Fe}^{2+}}^{\text{cpx/melt}}$ of 0. This means that clinopyroxene removes only Fe³⁺ from the melt. This is obviously unrealistic, but a $D_{\text{Fe}^{2+}}^{\text{cpx/melt}}$ of 0 provides a strict minimum bound on the amount of Fe²⁺ and total Fe that can be removed from the system by garnet pyroxenite fractionation (Fig. 3). We find that, even with a $D_{\text{Fe}^{2+}}^{\text{cpx/melt}}$ of zero, garnet-pyroxenite removes >80% of total Fe and increases $f\text{O}_2$ by >2 orders of magnitude, after >60% crystallization (Fig. 3). Although Fe³⁺ could be moderately compatible in garnet as shown by Holycross and Cottrell's experiments ($D_{\text{Fe}^{3+}}^{\text{grt/melt}}$ up to 2) (Holycross and Cottrell, 2023b), it is the strong compatibility of Fe²⁺ in garnet that dominates melt Fe depletion and thus oxidation.

4. Summary

To conclude, the difference between $D_{\text{Fe}^{2+}}^{\text{grt/melt}}$ and $D_{\text{Fe}^{3+}}^{\text{grt/melt}}$ determined by Holycross and Cottrell (2023b) is sufficient to drive substantial oxidation at arcs, consistent with the garnet hypothesis by Tang et al. (2018) and contrary to Holycross and Cottrell's conclusions. The Erratum published by Holycross and Cottrell (2023a) did not resolve all of the critical issues in their model. We emphasize that our analysis here does not prove that the garnet hypothesis is correct, but Holycross and Cottrell's analysis cannot disprove it. Careful partitioning experiments, such as those presented Holycross and Cottrell (2023b), combined with physical insights from the study of natural rocks and well implemented models, is the path forward towards testing current hypotheses and identifying new ones.

Declaration of competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.lithos.2024.107537>.

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