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 authors have measured the partition coefficients for Fe^{2+} and Fe^{3+} between garnet and melt and 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. First, their models intentionally limited the extent of fractionation to minimize the effect of garnet fractionation, inconsistent with existing experiments, including their own experiments. Second, 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 Introduction

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 preferentially depletes Fe^{2+} over Fe^{3+} in the melt, thus driving oxidation in arcs built on thick crusts [*Tang et al.*, 2018]. This hypothesis is supported by the extremely low $Fe^{3+}/\sum Fe$ in magmatic garnets in deep arc cumulates, the correlation between sulfur oxidation and crustal thickness [*Tang et al.*, 2020], and arc magma Fe isotopes [*Du et al.*, 2022; *Li et al.*, 2021]. The garnet hypothesis also offers an explanation for the preferential occurrence of calc-alkaline magmas in arcs built on thick crusts [*Chen et al.*, 2023; *Tang et al.*, 2023; *Tang et al.*, 2018] and has implications for the role of orogenesis in modulating magmatic volatile degassing [*Sun and Lee*, 2022].

Recently, *Holycross and Cottrell* [2023b] ran a series of experiments to determine the partition coefficients for Fe^{2+} ($D_{Fe^{2+}}^{grt/melt}$) and Fe^{3+} ($D_{Fe^{3+}}^{grt/melt}$) 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 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).

2 The extent of garnet-pyroxenite fractionation

The argument that garnet-pyroxenite fractionation cannot exceed 50% 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 °C and 1.4 GPa, but the crystallization assemblage in these conditions is dominated by garnet and clinopyroxene (± amphibole) (Fig. 1B). In fact, garnet continues to crystalize 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 evaluated the extent of garnet-pyroxenite fractionation using rhyolite-MELTS simulation Modeling details are available in supplementary materials. Garnet and clinopyroxene remain as the dominant crystalizing 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).
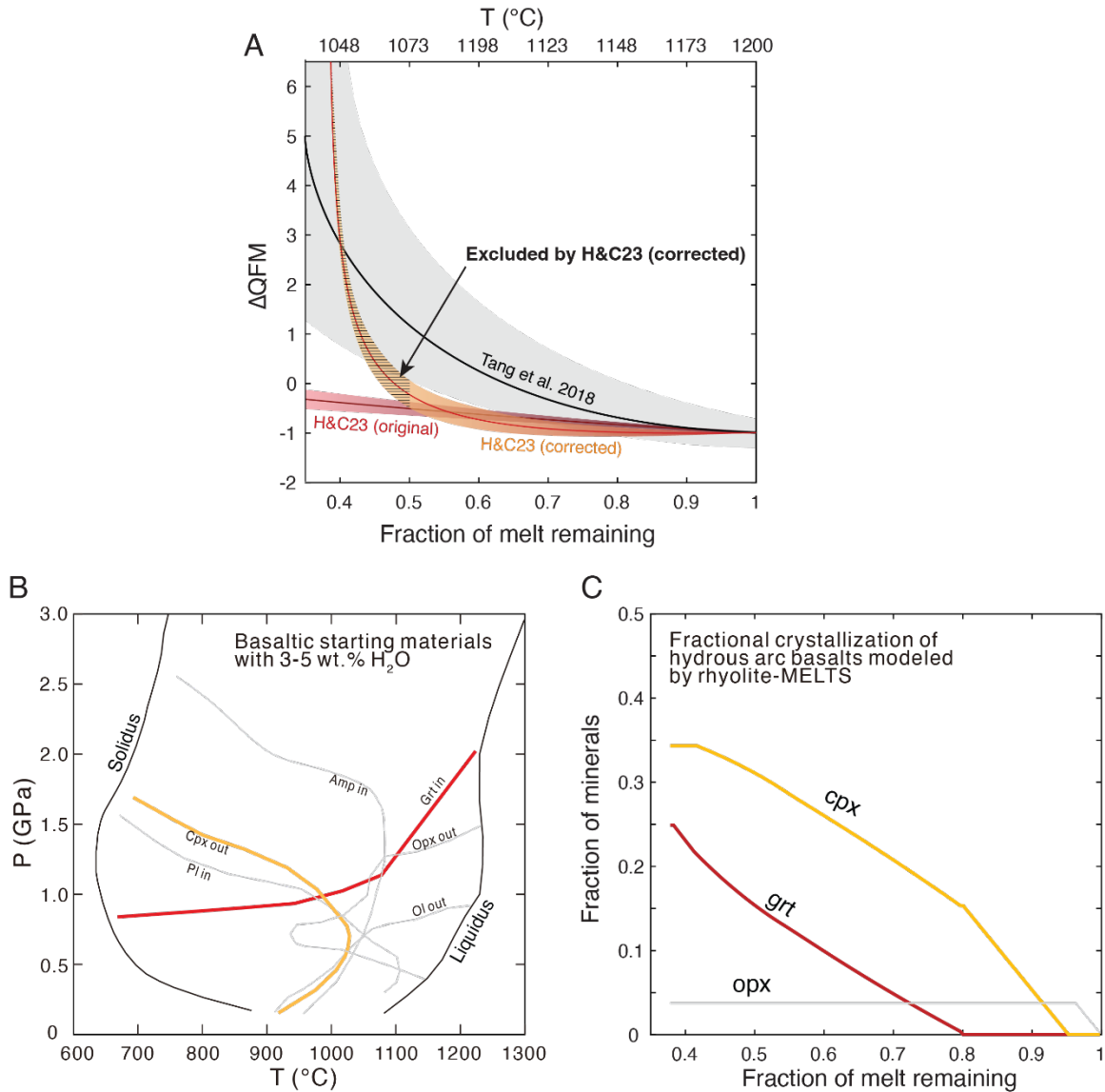

Figure 1. Garnet-pyroxenite fractionation in hydous arc magma differentiation. (A) Arc magma oxidation due to garnet-pyroxenite fractionation calculated by Holycross and Cottrell (original and after correction) and *Tang et al.* [2018]. (B) Phase diagram showing crystallization of hydrous arc basalts. 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. Garnet-pyroxenite continues to crystallize as the dominant assemblage when fractional crystallization exceeds 50%.

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

Holycross and Cottrell's argument of < 50% garnet-pyroxenite fractionation is based on their fractional crystallization model. They found that "[..] after 50% fractional crystallization [..], the Fe/Mg ratios of modeled garnet and clinopyroxene exceed reported compositions of experimental garnet pyroxenites [..] and [..] natural garnet pyroxenites [..]". The extreme Fe/Mg of their modeled garnet and clinopyroxene results from their incorrect use of Fe/Mg exchange coefficient K_D Fe/Mg in their fractional crystallization model.

Although *Holycross and Cottrell* [2023b] explicitly stated that they "[..] evaluate how our new calculated values for $D_{Fe^{2+}}^{grt/melt}$ and $D_{Fe^{3+}}^{grt/melt}$ affect this finding (garnet-driven oxidation)", Fe^{2+} partitioning was not modeled accordingly—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 [*Holycross and Cottrell*, 2023b]. For pyroxene, there are more elements to consider. Because none of these values are known or modeled, *Holycross and Cottrell* [2023b] assumed constant CaO, Al_2O_3 and SiO_2 molar contents in garnet and clinopyroxene. 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, the amount of Fe^{2+} plus Mg entering garnet becomes fixed, even though the melt Fe^{2+} and Mg contents decrease substantially with differentiation. Because of this erroneous assumption, the apparent $D_{Fe^{2+}}^{grt/melt}$ and $D_{Mg}^{grt/melt}$ in Holycross 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 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 Holycross 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.
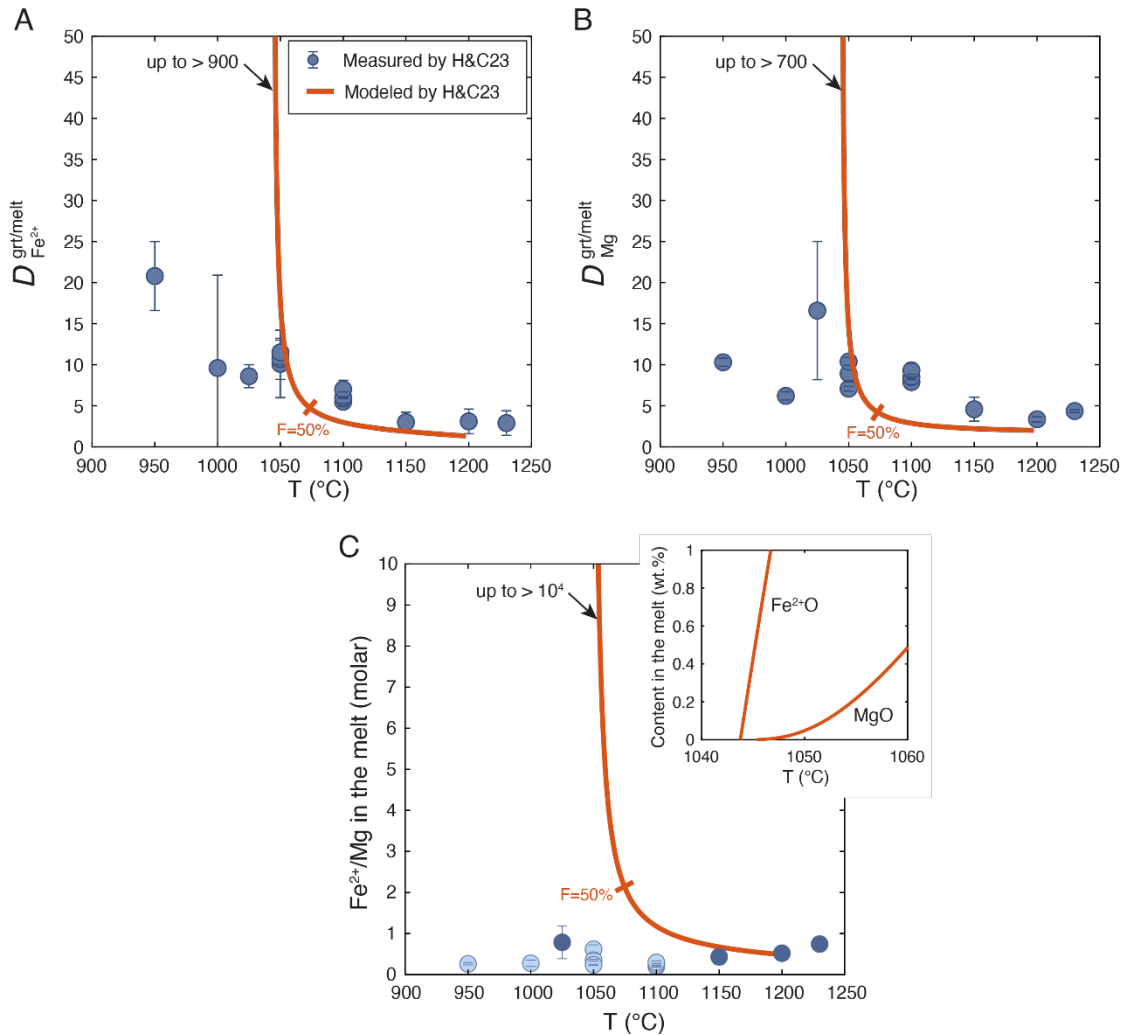
Figure 2. Runaway artifact in Holycross and Cottrell's model. (A, B) Comparison of apparent $D_{Fe^{2+}}^{grt/melt}$ and $D_{Mg}^{grt/melt}$ calculated from Holycross and Cottrell's fractional crystallization model with their experimental results. (C) Comparison of melt Fe^{2+}/Mg between Holycross and 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.

4 Fractionation modeling using internally consistent partition coefficients

Finally, we provide an internally consistent fractional crystallization model using the $D_{Fe^{2+}}^{grt/melt}$ and $D_{Fe^{3+}}^{grt/melt}$ parameterized by *Holycross and Cottrell* [2023b]. Even with a $D_{Fe^{2+}}^{cpx/melt}$ of zero, we find that garnet-pyroxenite removes > 80% of total Fe and increases fO_2 by > 2 orders of magnitude, after > 60% crystallization (Fig. 3). Although Fe^{3+} could be moderately compatible in garnet as shown by Holycross and Cottrell's experiments ($D_{Fe^{3+}}^{grt/melt}$ up to 2) [*Holycross and Cottrell*, 2023b], it is the strong compatibility of Fe^{2+} in garnet that dominates melt Fe depletion and thus oxidation.
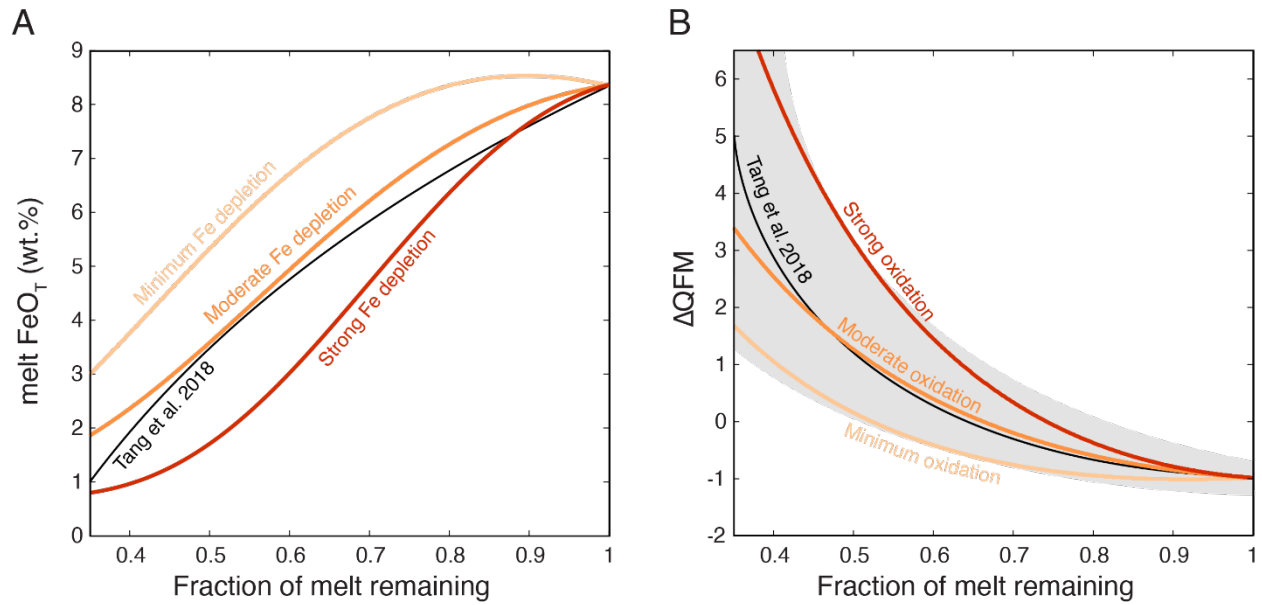
Figure 3. Impact of garnet pyroxenite crystallization on Fe depletion (A) and fO₂ (B) of arc magmas. We modeled Fe depletion and oxidation during garnet pyroxenite fractionation using the $D_{Fe^{2+}}^{grt/melt}$ and $D_{Fe^{3+}}^{grt/melt}$ determined by *Holycross and Cottrell* [2023b]. The results of *Tang et al.* [2018] are shown for comparison. We considered three scenarios by varying Fe partition coefficient for cpx $D_{Fe^{2+}}^{cpx/melt}$ and grt/cpx modal ratio. Minimum scenario: Fe 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.

5 Summary

To conclude, the difference between $D_{Fe^{2+}}^{grt/melt}$ and $D_{Fe^{3+}}^{grt/melt}$ 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 is the path forward towards testing current hypotheses and identifying new ones.

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Additional Supporting Information (available upon request)

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Introduction

In this Supporting Information file, we provide details of our Rhyolite-MELTS simulations, fractional crystallization modeling, two additional figures, and a dataset that contains the modeling results.

Text S1.

Rhyolite-MELTS simulation

We simulated hydrous arc basalt fractional crystallization using rhyolite-MELTS [Gualda et al., 2012]. 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 °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 Data Set S1.

Fractional crystallization modeling

We followed Holycross and Cottrell [2023] 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:

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

The assumption regarding the grt/cpx modal ratio adopted by *Holycross and Cottrell* [2023] 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 *Holycross 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* [2023] in the treatment of Fe^{2+} partitioning:

1. Fe^{2+} partitioning in garnet was calculated based on the experimentally determined partition coefficients from *Holycross and Cottrell* [2023], as was done for Fe^{3+}:

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

2. Because we do not have an independent or internally consistent constraint on clinopyroxene partitioning from their experiments, we assume clinopyroxene to have a $D_{Fe^{2+}}^{cpx/melt}$ of 0. This means that clinopyroxene removes only Fe^{3+} from the melt. This is obviously unrealistic, but a $D_{Fe^{2+}}^{cpx/melt}$ of 0 provides a strict minimum bound on the amount of Fe^{2+} and total Fe that can be removed from the system by garnet pyroxenite fractionation (Fig. 3). Note that by assuming a $D_{Fe^{2+}}^{cpx/melt}$ of 0, one tends to get an artifact of high Fe^{2+} contents in garnet (~26 wt.% on average) because melt Fe^{2+} content is higher than it should be. By assuming more realistic $D_{Fe^{2+}}^{cpx/melt}$ and/or higher grt/cpx modal ratios, stronger oxidation effects will result (Fig. 3, Data Set S1), and Fe^{2+} contents in garnet in our model will be reduced to the levels comparable those seen in natural garnet pyroxenites from Arizona (~16 wt.% on average [*Tang et al.*, 2019]). Detailed results of our fractional crystallization models can be found in Data Set S1.

To simplify the conversion of melt Fe^{3+}/Fe^{2+} to fO_2, we fixed the melt composition term $\sum diXi$ at a constant value of 0.213, same as the initial $\sum diXi$ value in Holycross and Cottrell's model. $\sum diXi$ changes as melt composition evolves with differentiation, but the change in $\sum diXi$ over the entire modeled crystal fractionation span causes a change of fO_2 of < 0.1 log units [*Holycross and Cottrell*, 2023].
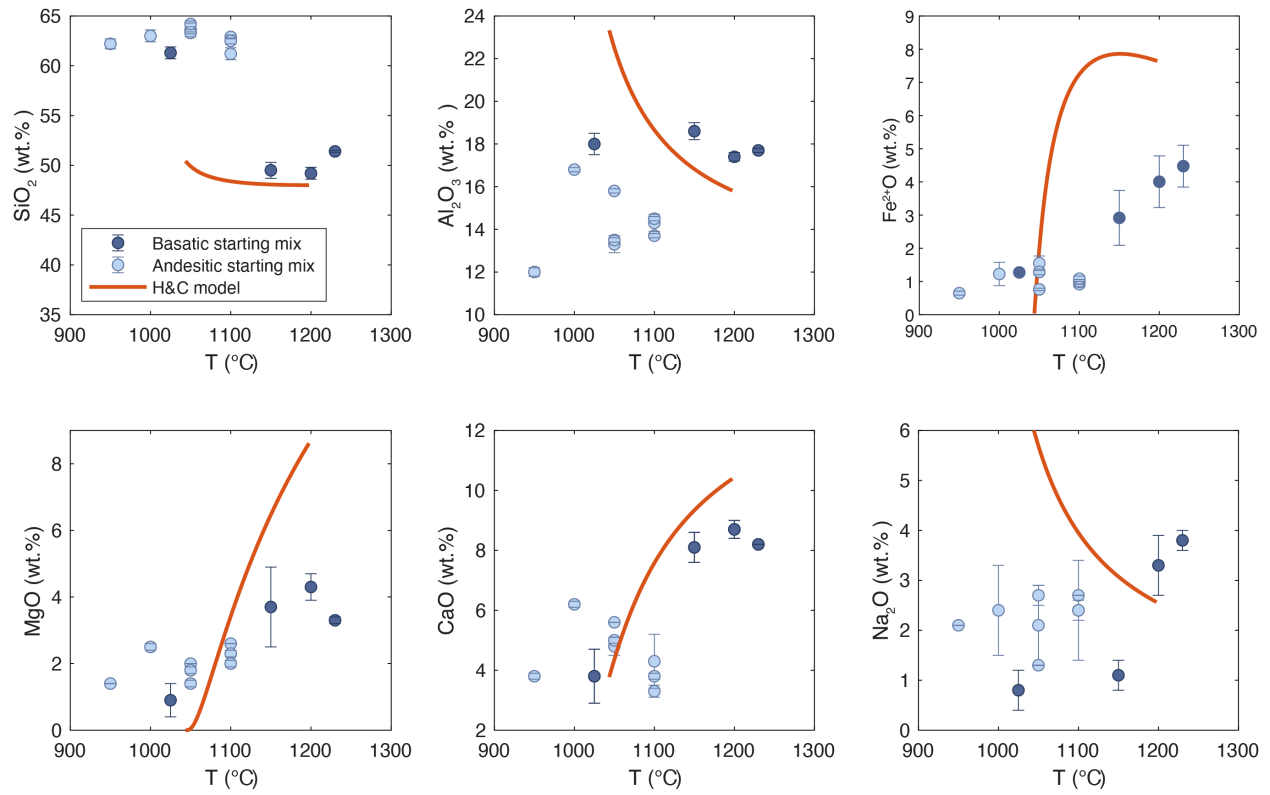
Fig. S3. Liquid compositions modeled by *Holycross and Cottrell* [2023] compared with their experimental liquid compositions.
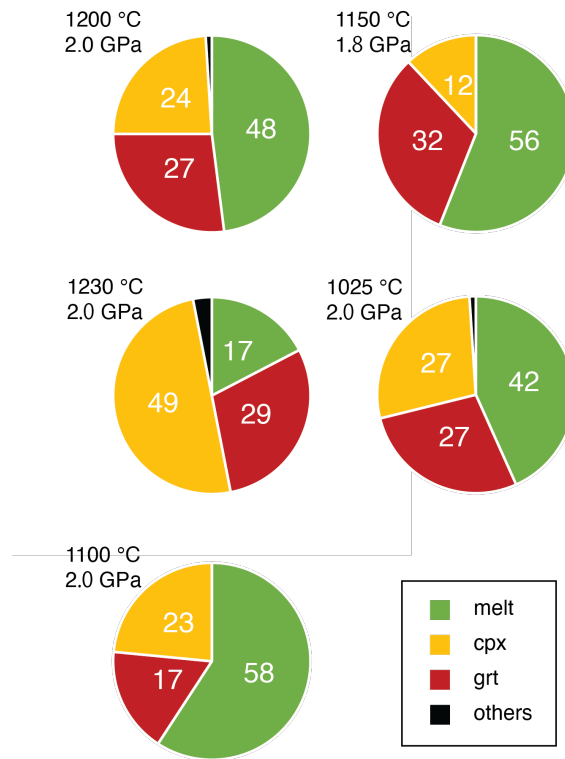
Fig. S2. Modal proportions of run products from *Holycross and Cottrell's* experiments.

Data Set S1 (Separate file)
Rhyolite-MELTS simulation results and garnet pyroxenite fractional crystallization modeling

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