

Supplementary Data 3.

Notes on modeling trace element zoning in English Peak amphibole.

Mineral/melt partition coefficients. The values of calcic amphibole/melt partition coefficients (d) vary widely and are functions of T, melt composition, and amphibole composition. These relationships are evaluated in detail in Shimizu et al. (in press) and Supplementary Table 1 provides a summary of such data from experimental studies and natural samples. The study of Nandedkar et al. (2016) provides a systematic example of the variability of d values over a range of temperatures appropriate for this study, and the subset of their data in Table 1 illustrates the increase in d values with decreasing temperature. Nevertheless, it is noteworthy that (1) the experiments of Klein et al. (1997) at 800°C yielded lower d values than the higher-T experiments of Nandedkar et al. (2016), and (2) some d values determined from natural samples range to higher values than were determined in any experimental study. The recent study of Shimizu et al. (in press) permits calculation of d values for calcic amphibole on the basis of amphibole composition and temperature, permitting thorough evaluation of d values derived from experimental and natural samples. Application of the Shimizu et al. algorithms to our data set is on-going and is beyond the scope of this work. At present, we can say that the d_{REE} values reported by Nandedkar et al. (2016) are similar to those calculated using the Shimizu et al. approach. We additionally note that Klein et al. (1997) reported d_{Sr} values from 6.39 to 6.80, whereas all other studies indicated that d_{Sr} is incompatible in Hbl. In our models, Sr was assumed to be incompatible in Hbl (i.e., $d_{\text{Sr}} < 1.0$).

Bulk partition coefficients and effects of crystal accumulation. Typically, calculation or estimation of bulk partition coefficients (D) relies on results of major-element mass balance calculations, modal data, or results from thermodynamic models such as rhyolite-MELTS (refs). These calculations generally assume that bulk-rock compositions are equivalent to melt compositions. However, recent studies of compositional variation in plutonic suites (e.g., Lee and Morton, 2015; Barnes et al., 2016a) indicate that many granitoid rocks are cumulates. The cumulate nature of late-stage rocks of the English Peak pluton is demonstrated here via comparison of the amphibole/bulk-rock Fe-Mg K_D value ($[\text{Fe/Mg}]_{\text{Hbl}}/[\text{Fe/Mg}]_{\text{rock}}$) with the average amphibole/melt K_D of 0.28 ± 0.11 (Putirka, 2016). The amphibole/bulk-rock K_D values range from 0.76 to 0.92, which are more than two standard deviations higher than the average

value. This discrepancy is explained if the bulk-rock compositions reflect accumulation of Mg-rich minerals such as Hbl.

Because bulk-rock compositions cannot be treated as melt compositions, estimation of bulk partition coefficients cannot be simply modeled using mass balance calculations. Instead, we developed a sequence of steps that allow for estimation of D , as follows.

Let:

c_l = concentration of trace element in the melt,

c_{mineral} = concentration of trace element in a mineral,

c_l^0 = concentration of trace element in the melt as the mineral of interest begins to crystallize,

d = mineral/melt partition coefficient = c_{mineral}/c_l ,

D = bulk partition coefficient,

F = fraction of melt remaining.

Then, for fractional crystallization, $c_l/c_l^0 = F^{(D-1)}$ (Greenland, 1970).

Melt compositions can be expressed in terms of mineral compositions and d :

$$c_l = c_{\text{mineral}}/d \quad \text{and} \quad c_l^0 = c_{(\text{mineral})}^0/d^0$$

where $c_{(\text{mineral})}^0$ = initial trace element concentration in the mineral (presumably the crystal core in a closed-system model), and d^0 = the initial mineral/melt partition coefficient.

Substituting into the equation for fractional crystallization:

$$[c_{\text{mineral}}/d]/[c_{(\text{mineral})}^0/d^0] = F^{(D-1)}$$

If we assume that over small ranges of F the value of $d \approx d^0$, then these two terms cancel and we get:

$$c_{\text{mineral}}/c_{(\text{mineral})}^0 = F^{(D-1)}$$

In other words, in this simplification, individual d values need not be known.

Understanding the consequences of this assumption is critical and must be justified on a case-by-case basis. In this study, it is noteworthy that the trace element d values measured by

Nandedkar et al. (2016) vary slightly from 890–830°C (Supplemental Data 4). In such cases, because the mineral/melt partition coefficient varies only slightly over a range of F , it is possible to model variation of trace element concentrations in the mineral as a function of F and D , the bulk partition coefficient. Moreover, if values of d are available, it is possible to calculate the trace element abundances in melts in equilibrium with the crystallizing phase. An additional caveat is that at low but super-solidus temperatures, d values can increase to substantially higher values than measured in experimental studies. Use of the Shimizu et al. (in press) algorithms on green rims and embayments in English Peak Hbl results in computed d_{REE} values as high as 16 at 750°C.

Modeling. This discussion refers to models presented in Figure 8.

Fractional crystallization. Our models begin with elements that are incompatible or very weakly compatible in Hbl. Nandedkar et al. (2016) showed that Sr and Ba are incompatible in Hbl and that Zr ranges from incompatible to weakly compatible as T decreases from 890–830°C. Because abundances of all three elements decrease from Hbl cores to rims, we conclude that D values for each element are greater than 1.0. In Figure 8A, decreasing Sr and Zr in Hbl are ascribed to plagioclase and zircon fractionation, respectively. Moreover, the linear trend of these two elements indicates that the *ratio* $D_{\text{Sr}}/D_{\text{Zr}}$ must be constant. This relationship is illustrated in two models (Fig. 8A), one with $D_{\text{Zr}} = 3.0$ and one with $D_{\text{Zr}} = 2.0$. The trend calculated for both models tracks core-to-rim zonation. However, the former model results in a calculated F value of ca. 0.4 at the end of Hbl crystallization. This melt fraction lies within the range in which crystal-liquid separation can occur (e.g., Lee refs). In contrast, if $D_{\text{Zr}} = 2$ is used, the equivalent value of F at the end of crystallization is ca. 0.1, a value suggestive of crystal lock-up and the inability melt to segregate from a highly mushy magma..

It is not necessary that D_{Sr} and D_{Zr} are constant during crystallization, only that their ratio is constant. Thus, one could generate models in which D for both elements increased, so long as their ratio remained the same. In contrast, gradual increase of D for just one element results in a curved trend, as illustrated in Figure 8A. This approach, changing D of one element during crystallization, is used in Figure 8B to model the S-shaped trend in the Ba vs. Zr plot. The illustrated model assumes that D_{Ba} increases linearly from 1.0 to 9.0, reflecting crystallization of biotite and its increasing importance as a fractionating phase with decreasing T .

Figures 8C–8E address modeling of compatible element variations, and in particular the unusual feature seen in these amphiboles in which the core-to-rim abundances of 3^+ cations initially decrease, then remain constant, and then increase. A simple-minded explanation would lead to the idea that D values for the 3^+ cations decrease with decreasing T . Figure 8C illustrates a *model* in which D_Y decreases from 5 to 0.1. Although this model fits the data, we do not view it as realistic in that it contradicts all that is known about the relationship between d_Y and T . Instead, a more sophisticated (?) explanation is needed.

In each of the illustrated cases (Figs. 8C–8E), Sc, Y, and Sm initially decrease approximately linearly with decreasing Zr, an indication that all three elements are compatible in the system, as well as in Hbl (Table 1). However, abundances of each of these three elements (1) ‘level off’ and then (2) increase toward crystal rims. One explanation for (1) is that Hbl d_Y , d_{Sc} , and d_{Sm} values all decrease with decreasing T . This explanation is contrary to published data on d values (Table 1). Magma mixing could provide an alternative explanation and would require that the magma from which Hbl cores crystallized was mixed with a highly evolved (low Zr) magma that was also enriched in 3^+ cations. Such magmas are uncommon at best and no examples of felsic rocks with such trace element compositions exist in the Klamath Mountain province. Moreover, such mixing would be expected to affect virtually all of the trace elements, rather than primarily the 3^+ elements. A third explanation is that the bulk D values of 3^+ cations decreased as biotite replaced Hbl as the principal fractionating phase. Abundances of the 3^+ cations in biotite are low ($Sc \leq 10$ ppm; $Y < 0.5$ ppm; $Sm < 0.13$ ppm; Table). Thus, as the proportion of fractionating biotite relative to Hbl increased, it is possible that D values decreased to ca. 1.0. This interpretation is consistent with the abrupt decrease in Ba in Hbl at ca. 90 ppm Zr, as discussed above and in the text (Fig. 8B).

The increase in 3^+ cations in the outer parts of Hbl crystals is also difficult to explain solely by increasing D values, because dramatic increases in Hbl d values will lead to an initial slight increase in abundance of 3^+ cations in the crystal, but the cumulative effect is to deplete the element in the *melt* to such an extent that its abundance in the crystal will decrease, no matter how large the Hbl d value.

Thus it appears that in order for 3^+ cation abundances to increase continuously in the outer zones of Hbl crystals, it is necessary for the Hbl d values to increase **and** for a source for these elements to be available. As discussed above, such a source could be a mixed magma, but we are

unaware of evolved, calc-alkaline magmas with high abundances of Sc, Y, and REE. The alternative discussed in the paper and illustrated in Figures 8D and 8E calls on resorption of early-formed (olive-brown) Hbl, with releases 3^+ cations to the local melt, and by precipitation of a lower-T Hbl: the green rims and embayments. The effects of such resorption/precipitation are modeled using the Shaw's (2006) equation 5.26:

$$c_l = (c_a * P) / (D + P - 1) + (c_o - (c_a * P) / (D + P - 1)) * F^{((D + P - 1) / (1 - P))}$$

where:

c_l = concentration in melt

c_o = initial concentration in melt as resorption begins

c_a = concentration in resorbed mineral

P = mass ratio resorbed/crystallized

F = melt fraction remaining after resorption begins

D = bulk partition coefficient

The value of c_a can be estimated using measured Hbl compositions. The value of c_o must be calculated. In our models, c_o was determined using an appropriate d value for low temperatures (Table 1) such that $c_o = [c_{\text{mineral}} (\text{at beginning of resorption}) / d]$. The value of P is not readily calculated, so in these examples we estimated P on the basis of typical proportions of green rims and embayments to olive-brown cores (ca. 0.3). In these models, variation in 3^+ cation abundances are compared to Zr contents, because Hbl has scant effect on Zr concentrations relative to zircon fractionation.

Values of $d^{(\text{Hbl/melt})}$ for Zr, Sc, and Sm were obtained from Sisson (1994), Klein et al. (1997), and Bachmann et al. (2005).

Model input.

Model	Sc-Zr		Sm-Zr (1)		Sm-Zr (2)	
	Zr	Sc	Zr	Sm	Zr	Sm
c_i = conc. in Hbl as resorption begins	52.5	82.7	52.5	16.5	52.6	16.5
c_a	90	110	100	30	90	28
c_o	65.6	10.3	65.6	2.7	65.6	4.2
D	3	2	2.5	0.5	3	1.5
$d^{(Hbl/melt)}$	0.8	8	0.8	6	0.8	4
P	0.3	0.3	0.3	0.3	0.3	0.3

Assessing effects of accessory minerals. Any trace element modeling of granitic systems should account for the effects of accessory mineral fractionation. Apatite, zircon, and ilmenite are accessory minerals in late-stage rocks, and occur as inclusions in Hbl cores and rims. Fractionation of apatite and zircon is evident in decreasing bulk-rock P and Zr (Barnes et al., 2016) and in the core-to-rim decreases of Zr in Hbl.

As noted in the Petrography section, magmatic sphene is virtually absent and allanite was observed only in samples of the interior Chimney Rock unit. Moreover, where allanite is in contact with Hbl, the contact is with green rims, not with olive-brown cores. This textural relationship suggests that effects of allanite fractionation should only be seen in the rim compositions of Chimney Rock Hbl. Table 2 presents allanite analyses from Chimney Rock sample RBEP-022. The average abundances of Y and Sm in this allanite are 437 ppm and 1791 ppm, respectively. Thus, if allanite fractionation were controlling Y and Sm abundances in Hbl rims, one would expect decreasing abundances rather than the increasing concentrations seen in Figures 8D and 8E.

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