Crustal Assimilation Calculation

We evaluate whether crustal assimilation is a viable explanation for the elevated calculated f_{O2} of mafic enclaves by calculating the amount of felsic crust that can be assimilated by a cooling basaltic magma, the percent of that crust that must be magnetite to oxidize the basaltic magmas to the f_{O2} recorded by amphibole, and the effect of the assimilation on the major element composition of the basaltic melt.

The amount of crustal assimilation possible in a magmatic system is limited by the sensible heat of the assimilating magma and the latent heat of crystallization of the assimilating magma and heat capacity, melting point, and latent heat of fusion of the assimilant. There is no constraint on the composition of the crust underlying Shiveluch; we assume for this calculation that the crust is granitic. We calculate the maximum amount of granitic crust that can be assimilated by 1g of basaltic magma at Shiveluch by assuming that the granite is already at its melting temperature (i.e., no energy needs to be expended to heat it to that temperature). The basalt is assumed to have cooled from 1100°C to 1014°C (ΔT=86°C). The maximum temperature constraint is based on the petrology of the enclaves, which show evidence for co-crystallizing high forsterite olivine and high Mg# amphibole; the co-crystallization of these magnesian phases cannot occur above 1100°C, the approximate upper thermal stability of amphibole (e.g. Helz, 1973; Blatter and Carmichael, 2001; Alonso-Perez et al., 2008; Krawczynski et al., 2012; Blatter et al., 2017). The minimum temperature is the average temperature of high forsterite olivine crystallization minus 1 standard deviation determined by Al-in-olivine thermometry (Goltz et al., 2020). The amount of crystallization associated with that ΔT was calculated using a dF/dT of 0.2558 determined for basalt with 4.5 wt% H_2O from the experimental study of Melekhova et al. (2013). The calculated fraction of basalt crystallized

(0.22) was multiplied by the latent heat of melting of basalt (0.4184 J/kg) and divided by the latent heat of melting of granite (0.2092 J/kg) (Hon and Weill, 1982) to find that a maximum of 0.44g of granite can be assimilated into 1g of hydrous basaltic melt at Shiveluch.

The oxidizing potential of the assimilant is determined by the proportion of materials with high Fe^{3+}/Fe_{total} in the assimilant. We calculate the proportion of oxidizing materials that must be in the 0.44g granite being assimilated into 1g of basalt to oxidize the enclaves to their measured values. The enclaves are assumed to have an initial Fe^{3+}/Fe_{Total} equal to that of the most reduced sample on average, 16B (35.1%), and we make the simplifying assumption that assimilation of magnetite (Fe^{3+}/Fe_{total}=67%) is solely responsible for oxidation of the basaltic magma. The proportion of magnetite needed in the granite (X_{mt}) was calculated using the equation

$$X_{mt} = \frac{(Fe_0^{2+})\left(Fe^{3+}/_{Fe^{2+}}\right)_{measured} - Fe_0^{3+}}{Fe_{mt}^{3+} - \left(Fe^{3+}/_{Fe^{2+}}\right)_{measured}(Fe_{mt}^{2+})}$$

where $(Fe^{3+}/Fe^{2+})_{measured}$ is the ferric-ferrous ratio of the enclaves calculated by multiplying the Fe^{3+}/Fe^{2+} amphibole-melt partition coefficient for basalt and the average Fe^{3+}/Fe^{2+} of amphibole in the sample, $Fe^{2+}{}_0$ and $Fe^{3+}{}_0$ are the ferrous and ferric iron contents respectively of enclaves with 35.1% Fe^{3+}/Fe_{total}, and $Fe^{2+}{}_{mt}$ and $Fe^{3+}{}_{mt}$ are the ferrous and ferric iron contents of magnetite. Calculated X_{mt} ranged from 1% to 63% of the assimilant with an average of 17%.

Assimilating crustal material will likely change the whole rock major element composition of an initially basaltic magma and in order for assimilation to be a viable explanation for the elevated f_{O2} of the enclaves, the enclaves' whole rock major element compositions must be reasonably modeled by mixing. Again assuming the crustal material being assimilated is granitic, we calculated the composition of melts of the 3600 tephra with up to 44%

by weight of a granophyre xenolith erupted from Karymsky volcano in 1997 (Izbekov et al., 2004; Bindeman et al., 2004) added to it. The granophyre xenolith erupted from Karymsky (another active volcano on the Kamchatka peninsula that commonly erupts andesite) is thought to have originated from a plutonic body underneath the volcano that is compositionally related to modern erupted basalts; it is possible that the crust under Shiveluch could contain similarly evolved plutonic material.

The mixed melts do not replicate the compositions of the enclaves. Liquids with more than 18% granite added have SiO_2 higher than the highest SiO_2 enclaves meaning that, to have the necessary oxidizing effect with only this much assimilant, the granite must have on average over 30% magnetite; even with 100% magnetite, this mixture could not replicate the ferric ferrous ratio of the most oxidized enclave sample. If the crust is more mafic than granitic values, then the mixing calculation can approach enclave compositions, but more mafic assimilants are highly unlikely to have enough magnetite to shift the overall f_{O2}. Based on these calculations, we are ruling out that crustal assimilation alone could account for the elevated f_{O2} of the enclaves, and variable degrees of crustal assimilation cannot account for the observed range in f_{O2}.

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