Gao, Y., et al., 2023, Garnet versus amphibole: Implications for magmatic differentiation and slab melting: Geology, https://doi.org/10.1130/G51637.1

Supplemental Material

Methods.

Table S1 (partial melting models and REE partition coefficients used in the calculations).

Table S2 (adakite database).

Supplementary Materials 1

METHODS

REE shape coefficients and petrogenetic process vectors (PPVs)

Chondrite-normalized REE abundances in magmatic rocks are observed to be smooth polynomial functions of REE atomic number except for Eu and occasionally Ce (O'Neill 2016). The smoothness has been tested by the analytical precision now routinely obtainable with modern methods such as those based on Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which show that the REE concentrations of most igneous rocks can be fitted to polynomials to 2 to 4 % relative, one standard deviation, with four or rarely five terms in the polynomial - that is, to λ_3 or rarely λ_4 (O'Neill 2016). Data from less precise analytical methods such as XRF or INAA/RNAA, which were formerly used, often cannot be fit within this error, but can still be used, if the possibility of real non-smoothness due to alteration or unknown effects processes is recognized (e.g., Anenburg and Williams 2021). Although not as precise, shape coefficients adequate for comparative purposes can be obtained from analyses reporting less than the full complement of REEs (O'Neill 2016).

The shape coefficients (λ) have the following significance: λ_0 is the average of the logarithms of the CI-normalized REE abundances (excluding Eu); λ_1 describes the linear slope of the pattern (light REE (LREE)-enriched patterns have positive λ_1); λ_2 describes the quadratic curvature, and λ_3 the sigmoidal deviation from this curvature; λ_4 reflects a W or M shape, but one displaced from the W-shaped deviations of the tetrad effect, which produces non-smooth patterns (O'Neill 2016). Any smooth chondrite - normalized REE pattern can be referred to using the convention $\Lambda\{\lambda_0, \lambda_1, \lambda_2, \ldots\}$, with as many terms as necessary.

Insofar as mineral/melt partition coefficients of the REEs ($D_{REE}^{min/melt}$) are also smooth functions of r_{REE}^{VII}, any petrogenetic process that depends on $D_{REE}^{min/melt}$ will also be, and may be

parameterized using the same orthogonal polynomials, summarized as $\Psi\{\psi_0, \psi_1, \psi_2, \ldots\}$, called petrogenetic process vectors (PPVs). The shape of a REE patter after such a petrogenetic process is given by $\Lambda = \Lambda^o + \Psi$, where Λ^o is the pattern in the initial material (e.g., in the source if the process is partial melting, or in the parental melt for crystallization). The orthogonal polynomials separate the effects on the slopes of the REE patters ($\lambda_1 = \lambda_1^0 + \psi_1$) from the quadratic curvature ($\lambda_2 = \lambda_2^0 + \psi_2$), which may be displayed on a diagram of λ_2 versus λ_1. The great advantage of the PPVs is that, once plotted on this diagram, they may then be conceptually moved around to find the connections between the REE pattern shapes observed in rocks with any postulated source. Somewhat like the the vectors from elementary geometry, they have lengths and directions, but they should not be thought of as having fixed positions.

Trace-element modeling

1. Batch melting equation with constant crystal/melt partition coefficients (Shaw, 2006):

$$\ln([\mathrm{M}]/[\mathrm{M}]_0 = -\ln(\sum D_M^{X/melt} m_X^o - F_b \mathrm{P} + F_b) \quad (2)$$

Here F_b is the mass fraction of melt produced, m_X^o is the mass fraction of crystalline phase X in the source (i.e., the mineral mode) at zero F_b, $D_M^{X/melt}$ is the crystal/melt partition coefficient, and the summation is over all crystalline phases. The parameter P accounts for the change in modal proportions of the crystalline phases with F, and is given by $\sum p_X \times D_M^{X/melt}$, where p_X is the proportion of phase X entering the melt. Parameterizations of experimental melting studies[29,30,31] are listed in Supplementary Material Table 1. For representative REE source composition, we choose the upper oceanic crust (UOC) composition[32] Λ = {3.14, 1.59, -17.4, -170, -811}), and the lower continental crust (LCC) composition[33] Λ = {2.74, 7.16, 7, -96, -729}. The individual REE crystal/melt partition coefficients may also be parameterized with the same orthogonal functions used to describe the chondrite-normalized REE patterns:

$$D_M^{X/melt} = \delta_0 + \delta_1 f_1^{orth} + \delta_2 f_2^{orth} + \delta_3 f_3^{orth} + \ldots \quad (3)$$

2. Simple fractional crystallization (SFX), as described by the Rayleigh equation (Shaw, 2006):

$$\ln([M]/[M]_0 = \ln(F_{SFX}) \left(\sum D_M^{X/melt} m_X - 1\right) \quad (4)$$

where F_{SFX} is the fraction of melt remaining and is the mass fraction of crystalline phase X on the cotectic (m_X = 1 for single-phase crystallization). The effects are easily visualized on a λ_2 vs. λ_1 diagram (O'Neill, 2016), with vectors given by: ψ_0 = ln(F) ($\sum \delta_0 m_X$-1), ψ_1 = ln(F) $\sum \delta_1 m_X$, ψ_2 = ln(F) $\delta_2 m_X$, etc. The PPVs plot as straight lines if, as usually assumed, partition coefficients and, m_X are constant with F_{SFX}.

Data selection

Bulk rock analyses of volcanic samples were downloaded from the GEOROC database on 3 August 2023, using the following parameters: rock name = adakite. The data were filtered by excluding analyses with less than 4 REEs or without HREE, or with unexplained single element anomalies. Most published REE patterns of adakites are smooth except for occasional apparent Er anomalies caused by low contents of Tm and Yb. A smoothness filter was also applied, removing samples with s(ln[REE]) within 5%, leaving 404 Cenozoic (including Quaternary) samples for discussing (Supplementary Material Table 2). The goodness of fit to the polynomials is an indicator of analytical quality, although this is ambiguous as a poor fit could highlight low-temperature alteration, or a hitherto unknown process that fractionates the REEs unsmoothly with atomic number. An example would be a process in which the properties of the REEs were influenced by the tetrad effect.