Beyond Equilibrium: Kinetic Isotope Fractionation in High-Temperature Environments

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I gneous and metamorphic rocks exhibit greater isotopic heterogeneity than expected from equilibrium. Large nonequilibrium isotope effects can arise from diffusion and chemical reactions, such as crystal growth and dissolution. The effects are time-dependent and can, therefore, be used to probe timescales of igneous and metamorphic processes that are inaccessible to direct observation. New discoveries of isotopic variability in nature, informed by diffusion and reaction modeling, can provide unique insights into the formation of rocks in the interiors of planetary bodies.

KEYWORDS: kinetics; reactions; diffusion; crystal growth; timescales

DISEQUILIBRIUM IS EVERYWHERE

Igneous and metamorphic rocks form at high temperatures. As minerals crystallize, they often do so out of equilibrium with their surrounding fluid or solid phases. Even when crystals grow slowly, in a near-equilibrium regime, subsequent changes in temperature, pressure, and the host melt or fluid composition can render them out of equilibrium. Reestablishing equilibrium requires mobilization of chemical elements by diffusion, sometimes slowly through solid phases, as well as chemical reactions that often do not go to completion as the rocks pass through a sequence of transient nonequilibrium states. The "freezing in" of incomplete reactions and diffusion gradients enables geochemists to access not only the temperatures and pressures those rocks experienced but also the timescales over which the rocks passed through pressure–temperature space. Stable metal isotopes can help discriminate between competing models of rock and mineral formation. They can also be used to decipher fundamental diffusion and reaction mechanisms.

KINETICS: DIFFUSION AND REACTION

It has long been known that equilibrium isotope fractionation between two phases decreases with increasing temperature, leading to the widespread view that there should not be much isotopic variability in igneous and high-*T* metamorphic systems. The discovery that diffusion is capable of generating measurable to large isotope fractionations in silicate melts and minerals changed this perspective and catalyzed the search for isotopic variability in natural rocks. The search has been fruitful. Geochemists are finding isotopic variations far beyond those expected from equilibrium, making it an exciting time of discovery and interpretation.

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Along with diffusive isotope effects, which are described by a mass dependence on diffusion coefficients, there is another class of kinetic isotope effects that arise from chemical reactions (FIG. 1). These are described by a mass dependence of reaction rate constants. The two processes, reaction and diffusion, are often lumped together under the umbrella of "kinetic" even though they are as distinct from one another as "equilibrium" is from "kinetic." In this article, we first discuss the mass-dependent reaction and diffusion parameters themselves—what they mean and how they are measured. We then highlight some recent approaches for using these parameters to model geologic processes at length scales ranging from individual crystals to larger scale reservoirs within the Earth's crust and upper mantle.

ISOTOPE DIFFUSION AND β FACTORS

Diffusion is often thought of as an agent of homogenization. For stable isotopes, however, diffusion can create heterogeneity from an initially homogeneous reservoir. Richter et al. (2003) demonstrated this for diffusion in silicate melts by conducting experiments where a basalt and rhyolite with similar isotopic composition were pressed together in a capsule and subjected to elevated temperatures and pressures. Their experiments showed that light isotopes diffuse notably faster than their heavier counterparts in silicate melts, leading to light isotope enrichment on the low-concentration side of a compositional interface and light isotope depletion on the high-concentration side (FIGS. 2A and 2B). Richter et al. (2003) discussed how the magnitude of isotope fractionation induced by diffusion depends not only on the ratio of isotopic diffusion coefficients but also on the ratio of the elemental concentrations in the two melts. Using a diffusion model to fit their measured isotope ratio profiles, Richter and colleagues determined the ratio of isotopic diffusivities:

$$\frac{D_H}{D_L} = \left(\frac{m_L}{m_H} \right)^{\beta} \quad (0 < \beta < 0.5) \tag{1}$$

where m_H is the heavy isotope mass, m_L is the light isotope mass, and the β factor is a dimensionless empirical parameter. The greater the β value, the greater the diffusivity difference between the two isotopes and the larger the diffusive isotope effects. In ideal gases, β = 0.5. In geological liquids and solids, β is invariably less than 0.5.

Over the past 20 years, β factors for a variety of elements in silicate melts have been determined by experiment as well as by computer simulation, as summarized in FIGURE 2C. Some important lessons learned include: (1) β varies for a given cation depending on liquid composition; (2) there is a covariation between β and element diffusivity relative to that of the solvent molecules (e.g., D_i/D_{Si} or D_i/D_{H_2O}), implying that β should be greater in silicate melts than in aqueous fluids and also greater in felsic melts than in mafic melts (Watkins et al. 2011); (3) the current upper limit to β in silicate melts is around 0.25–0.30.

The β factors have also been determined for several elements (Li, Mg, and Fe) in major rock-forming minerals such as olivine (Richter et al. 2016), clinopyroxene (Richter et al. 2014), and periclase (Van Orman and Krawczynski 2015), as well as for Fe and Ni in metals or alloys relevant to meteorites (Watson et al. 2016). The β factors in solids are generally higher than in silicate melts and likely depend on the direction of diffusion along different crystallographic axes. Given the limited number of previously studied isotopic systems and the complex dependence of β factors on the nature of the host medium, there are opportunities to expand the data set to include more elements, minerals, and melt compositions.

ISOTOPE REACTIONS AND KINETIC FRACTIONATION

Because chemical reactions involve the breaking and making of chemical bonds, kinetic isotope effects attending reactions are expected to be comparable in magnitude, but not necessarily sign, to equilibrium isotope effects (FIG. 1). This makes them nonnegligible, and yet, it is fair to say that they have been largely overlooked in igneous and metamorphic petrology. Moving forward, there are three key questions to be answered. (1) Where are reaction-controlled effects likely to be important? (2)

Do they amplify or dampen equilibrium effects? (3) How do we distinguish these effects from diffusion-related kinetic effects?

To begin addressing these questions, consider a chemical reaction that describes plagioclase crystallization from dissolved melt components:

$$CaO + Al_2O_3 + 2SiO_2 \underset{k_b}{\overset{k_f}{\rightleftarrows}} CaAl_2Si_2O_8 \qquad (2)$$
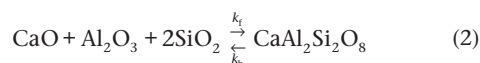
where the k's are reaction rate coefficients that can depend on temperature, pressure, and melt composition. The subscript 'f' stands for the forward (growth) reaction and 'b' stands for the backward (dissolution) reaction. The k's also have a slight dependence on mass, meaning that plagioclase can become isotopically fractionated from the melt in which it crystallizes. The sign and magnitude of isotopic fractionation is described by an expression that includes a growth-rate dependence on the isotopic composition of a crystal (DePaolo 2011):

$$\alpha_p = \frac{\alpha_f}{1 + \dfrac{R_b}{R_p + R_b}\left(\dfrac{\alpha_f}{\alpha_{eq}} - 1\right)} \qquad (3)$$

where α_p is the isotopic fractionation between the precipitating crystal and the fluid at the crystal–liquid interface; α_f is the kinetic fractionation factor (KFF) attending the forward reaction (note that it is equal to the ratio of forward rate constants, $k_{f,heavy}/k_{f,light}$); α_b is the KFF attending the backward reaction (equal to the ratio of backward rate constants, $k_{b,heavy}/k_{b,light}$); R_b is the dissolution rate (moles $m^{-2} s^{-1}$); $R_p = R_f - R_b > 0$ is the net precipitation rate (same units).

This expression applies whether crystal growth is "reaction-limited" or "diffusion-limited." When growth is reaction-limited, diffusion in the host liquid is sufficiently fast that
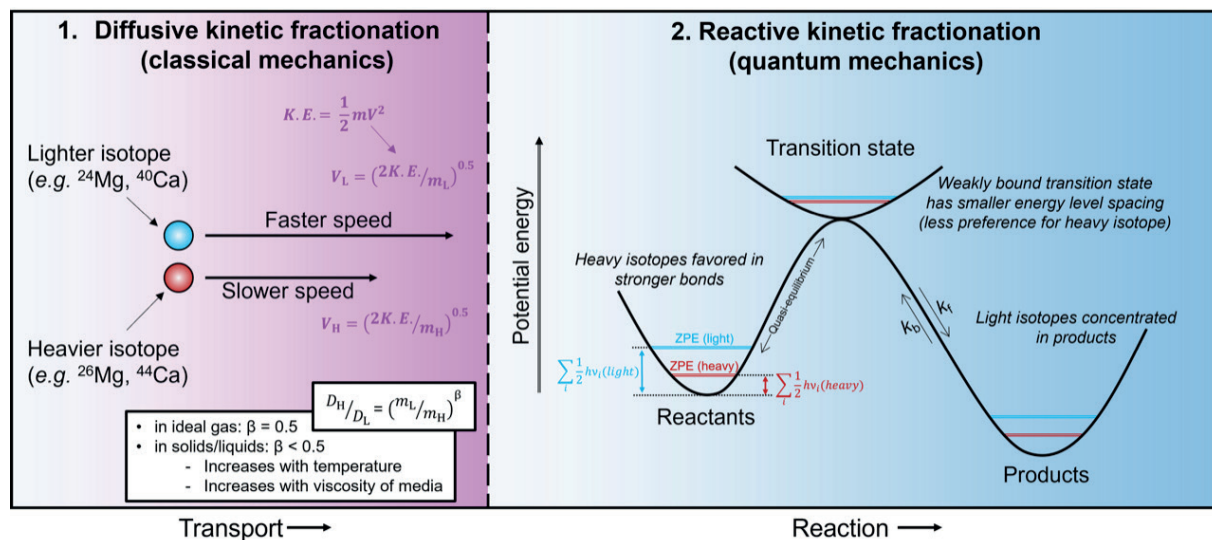

1. Diffusive kinetic fractionation (classical mechanics)

Lighter isotope (e.g. ^{24}Mg, ^{40}Ca)
$K.E. = \frac{1}{2}mV^2$
$V_L = \left(2K.E./m_L\right)^{0.5}$
Faster speed
Slower speed
$V_H = \left(2K.E./m_H\right)^{0.5}$
Heavier isotope (e.g. ^{26}Mg, ^{44}Ca)

$D_H/D_L = \left(m_L/m_H\right)^\beta$
- in ideal gas: β = 0.5
- in solids/liquids: β < 0.5
  - Increases with temperature
  - Increases with viscosity of media

Transport →

2. Reactive kinetic fractionation (quantum mechanics)

Transition state
Weakly bound transition state has smaller energy level spacing (less preference for heavy isotope)
Potential energy
Heavy isotopes favored in stronger bonds
Quasi-equilibrium
k_b k_f
Light isotopes concentrated in products
ZPE (light)
ZPE (heavy)
$\sum_i \frac{1}{2} h\nu_i(light)$
$\sum_i \frac{1}{2} h\nu_i(heavy)$
Reactants
Products

Reaction →

FIGURE 1 Diagram illustrating the differences between diffusion-based and reaction-based kinetic isotope effects. (**LEFT**) Diffusion effects are the result of higher speeds for lighter isotopes at a given kinetic energy. These effects tend to increase with increasing temperature and fluid viscosity. Abbreviations: K.E. = kinetic energy; m = mass; V = velocity; L = light isotope; H = heavy isotope; D = diffusivity; β = empirical parameter. (**RIGHT**) Reactive effects are the result of quantized vibrational energy differences between bonds with heavy versus light isotopes, where tighter bonds are preferentially stabilized through the substitution of a heavier isotope. Assuming equilibrium between the reactants and the more weakly bound transition-state (as opposed to between the reactants and the products, in the case of

equilibrium fractionation), heavy isotopes preferentially remain in the reactants and light isotopes are preferentially transferred over to the products during reaction. As higher quantum vibrational levels ($n > 0$) are populated with increasing temperatures, isotope-dependent vibrational frequency shifts become smaller, leading to decreased fractionation at high T. Note: inverse kinetic effects (where heavy isotopes are preferentially concentrated in the transition-state and products) can occur in cases where the transition-state is more strongly bound than the reactants. Abbreviations: KIE = kinetic isotope effects; ZPE = zero-point energy; ν = frequency; h = Planck's constant; k_f = forward reaction rate constant; k_b = backward reaction rate constant.
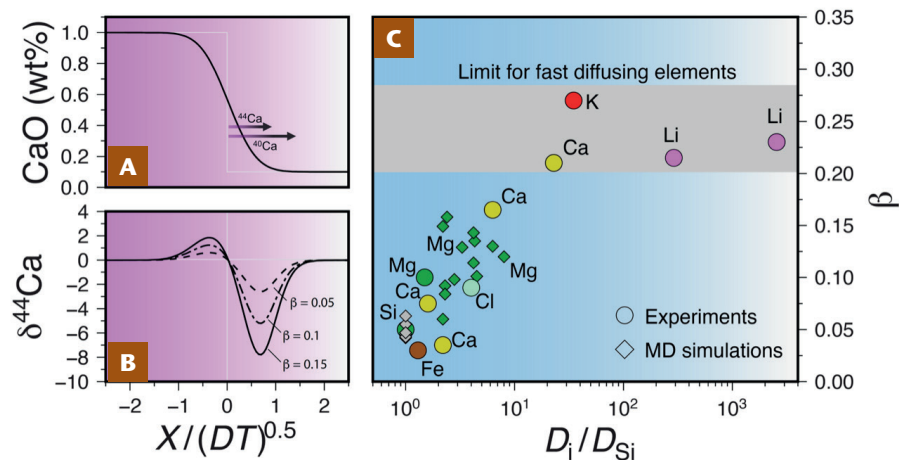
the interface liquid composition matches the bulk liquid composition. On the other hand, when growth is "diffusion-limited," there are chemical gradients (and perhaps also isotopic gradients, depending on the β factor) around the growing crystal and the interface liquid composition does not match the bulk liquid composition.

The behavior of Equation (3) is shown in FIGURE 3. In the limit of slow growth, the crystal is in equilibrium with the adjacent fluid, and in the limit of fast growth ($R_p \gg R_b$), the backward dissolution rate is negligible, and the crystal's isotopic composition differs from the fluid by an amount given by the forward fractionation factor. The crossover between the two regimes occurs at $R_p = R_b$. Hence, another key parameter is the ratio R_p/R_b. The numerator R_p is simply the net or observed growth rate. A minimum value for R_b can be estimated from dissolution studies, with the caveat that R_b may, in fact, be a complicated function of the nanoscale surface topography of the mineral (DePaolo 2011). The next generation of geochemists will need to find creative ways of inferring the parameters of this equation and their functional form.

Reaction-controlled kinetic isotope effects have been reported in isotopic studies of evaporation in the early solar nebula (see Tang and Young 2021 this issue) as well as in crystal growth from aqueous or hydrothermal solutions at $T < 400\,°C$ (Watkins et al. 2017 and references therein; Brown et al. 2020). However, neither the kinetic fractionation factor nor the growth rate parameter R_p/R_b has been estimated for crystals grown from silicate melt or high T metamorphic fluids. This is, in part, because it is difficult to determine growth rates of crystals grown at high-T in experimental capsules but also because larger diffusive isotope effects in silicate melts can obfuscate the kinetic signals from reactive effects.

MASS LAWS FOR DIFFUSION AND REACTION

The mass-laws relating fractionations for multiple isotopes are different for diffusion, which are controlled by molecular translations $[\ln(m_1/m_2)/\ln(m_1/m_3)]$, than for reaction, which are controlled by molecular vibrations similar to equilibrium effects; i.e., $(1/m_1-1/m_2)/(1/m_1-1/m_3)]$ (see Young et al. 2002). This makes it possible in some cases to determine whether kinetic isotope effects are dominated by diffusion or reaction. Triple-isotope measurements (where >3 isotopes are accurately measured) are required for this purpose (Antonelli et al. 2019b and references therein). This approach is still in its infancy but could be extended to any element with three or more stable isotopes (e.g., Fe,

Ca, Mg, Zr, Ti, Cr, Ni, Zn, and others) in order to greatly enhance our understanding of the underlying mechanisms leading to kinetic isotope effects in various settings.

KINETIC ISOTOPE EFFECTS AT THE SMALL SCALE

When crystals grow in a diffusion-limited regime, they deplete the surrounding medium in compatible elements (those that are more concentrated in the crystal than in the fluid) (FIG. 4A) and enrich the medium in incompatible elements (FIG. 4B). This establishes chemical gradients that drive diffusion either towards or away from the growing crystal. Because light isotopes diffuse faster than their heavier counterparts, diffusive isotope fractionations can get imparted on both phases. After crystals form, the initial growth-related isotopic zonations can be modified by diffusion during cooling or entrainment in magmas of different composition. The isotope effects attending crystal growth, subsolidus cooling, and changes in magma composition have been used in clever ways to decipher crystal growth rates, cooling rates, and timescales of volcanic processes.

Crystal Growth Rates

A longstanding challenge is to estimate crystal growth rates in natural high-T settings. Such information is extremely valuable for constraining the timescales of (1) long-term
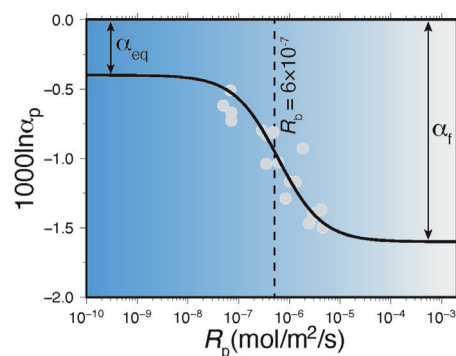
magma residence, (2) magma rejuvenation, (3) magma ascent, (4) magma cooling on the surface, (5) volcanic eruptions, and (6) metamorphic *P–T* paths.

Watson and Müller (2009) derived a useful expression that is the basis for inferring growth rates from diffusive kinetic effects. Their expression represents a different endmember regime than that described by Equation (3) and relates the diffusive kinetic fractionation [Δ_{kin}, in permil (‰)] to the growth rate (*R*, in m s^{-1}) through

$$\Delta_{kin} = 1000 \left(1 - \frac{D_L}{D_H} \right) \left(\frac{R \cdot B}{D_L} \right) (1 - K) \qquad (4)$$

According to this equation, the kinetic fractionation depends on: (1) the ratio of light to heavy isotopic diffusivities in the liquid (D_L/D_H); (2) the crystal growth rate relative to the diffusivity of an element in the liquid (*R/D*), (3) the boundary layer thickness (*B*); (4) the partition coefficient (*K*, which is equal to the equilibrium concentration of the element in the solid versus in the liquid at the interface). Equation (4) describes how the interface liquid composition differs from the bulk liquid composition, and because *K* and *R* are not isotope-specific, it is implied that the crystal directly inherits the isotopic composition of the interface liquid. By contrast, Equation (3) describes a crystal becoming isotopically fractionated from the interface liquid composition due to isotope-specific ion attachment and detachment rates. To our knowledge, diffusive and reactive kinetic isotope effects have not been combined into a general model for kinetic isotope effects attending crystal growth.

The sign of Δ_{kin} (i.e., whether the interface liquid composition is isotopically lighter or heavier than the bulk liquid composition) depends solely on whether *K* is greater than or less than unity. For compatible elements (*K* > 1; e.g., Ca in plagioclase), diffusion through a boundary layer towards a growing crystal leads to an enrichment of light isotopes at the crystal surface that is inherited by the crystal (top right panel of FIG. 4C). By contrast, incompatible elements (*K* < 1; e.g., Ca in olivine) become concentrated in the boundary layer and diffuse away from a growing crystal (bottom right panel of FIG. 4C). For both compatible and incompatible elements, the greater the departure of *K* from unity, the larger the concentration gradients and the larger the isotopic fractionations in the boundary layer.

Although there are simplifying assumptions built into Equation (4) (i.e., 1-D, diffusion-limited crystal growth through a fixed-width boundary layer that has reached a steady-state concentration gradient for the element of interest), a major advantage is that it is straightforward to apply. It has been used with appropriate caution in several recent studies to infer: (1) growth rates of plagioclase phenocrysts in volcanic rocks (and eruption timescales) using Ca isotopes (Antonelli et al. 2019a); (2) growth-rates/timescales of orbicular granite formation using Ca isotopes (Antonelli et al. 2019a); (3) growth rates of zircon using Zr isotopes (Méheut et al. 2020); (4) mechanisms responsible for Nd isotope variations among gabbros (McCoy-West et al. 2020).

Subsolidus Cooling Rates

After crystals grow, they can remain above the closure temperature for long enough to undergo chemical and isotopic modification by diffusion. The thermal history of a rock can be complex, but, ultimately, all rocks cool down and lock in any remaining disequilibrium chemical and isotopic gradients. Chemical gradients of slow-diffusing elements can be used to extract the residence time of crystals in magma chambers or metamorphic environments, whereas fast-diffusing elements can be used to estimate cooling rates during magma ascent and emplacement. Isotopes provide additional information that can be used to distinguish elemental gradients caused by crystal growth versus those caused by subsolidus diffusion.

Kinetic isotope effects during cooling can depend on a variety of factors, including the initial temperature, the initial element concentration in each mineral, the closure temperature of the element in each mineral, the grain size, the β factor(s), and the thermal history. If everything but the latter is known, or can be estimated, then the thermal history can be estimated (FIG. 5). This approach has been carried out using kinetic isotope effects in olivine (e.g., Sio and Dauphas 2017; Collinet et al. 2017; Bai et al. 2019), clinopyroxene (Richter et al. 2016; Richter et al. 2020), plagioclase (Neukampf et al. 2020), and between coexisting phases in meteorites (Chernonozhkin et al. 2017) and terrestrial rocks (Tian et al. 2020). The cooling rates that have been modeled span from very slow (~10 °C/ky) (Bai et al. 2019) to very fast (~150 °C/h) (Richter et al. 2016).
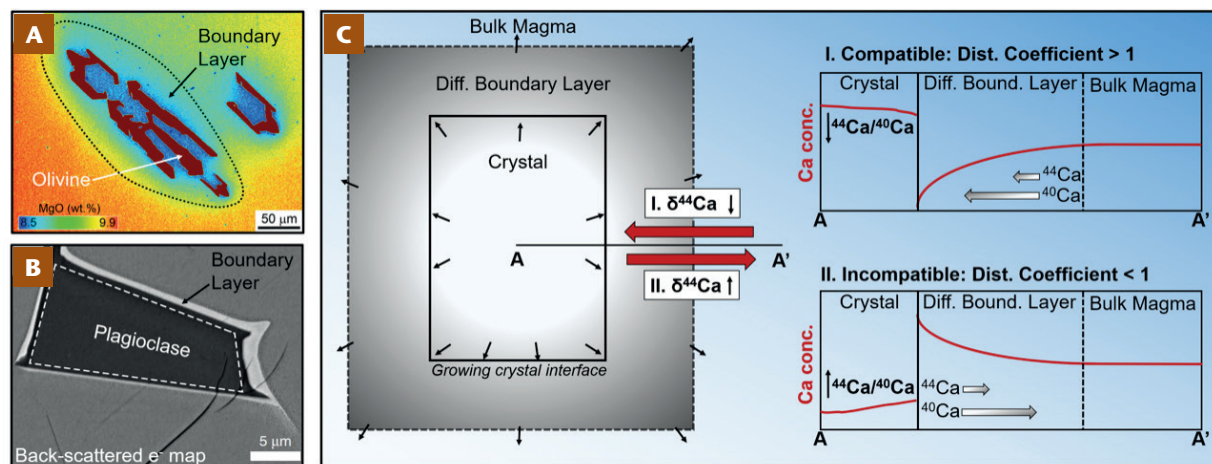

FIGURE 4 Examples of chemical boundary layers formed around crystals. (**A**) A Mg-poor boundary layer formed around skeletal olivine grown experimentally from basalt. MODIFIED FROM MOUREY AND SHEA (2019). (**B**) An Fe-rich (and Ca-poor) boundary layer formed around plagioclase phenocryst from the 1976 Kilauea Iki lava lake (Hawaii, USA). MODIFIED FROM HONOUR ET AL. (2019). (**C**) Schematic of kinetic isotope effects caused by diffusion through a boundary layer. Abbreviations: Bound. = boundary; conc. = concentration; Diff. = diffusive; Dist. = distribution. AFTER ANTONELLI ET AL. (2019A).
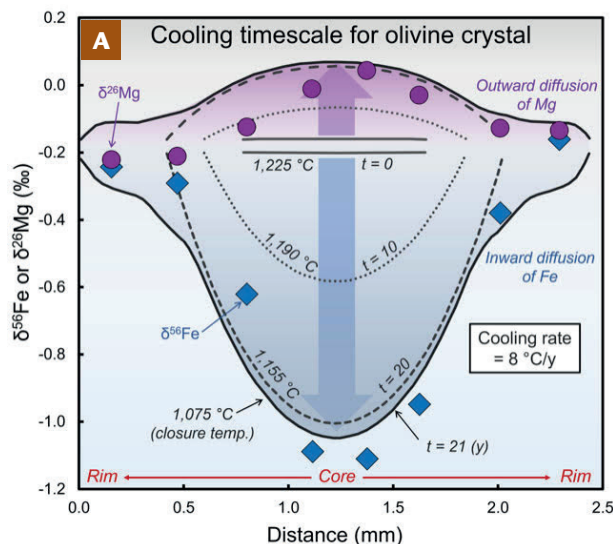
FIGURE 5 Kinetic isotope effects can be used to estimate cooling timescales. (**A**) Example where Mg and Fe counter-diffuse in an olivine crystal and exhibit isotope effects characteristic of diffusion, as opposed to growth-related zoning. Note that all data points are from within the olivine crystal. MODIFIED FROM SIO AND DAUPHAS (2017).

(**B**) Example where bulk isotopic measurements of the trace element Cr in olivine have been used to constrain cooling timescales. The grid shows the effects of initial Cr concentration in olivine (dashed curves) and cooling time (solid curves) on the final bulk $\delta^{53}Cr$ and Cr (ppm) in olivine. MODIFIED FROM BAI ET AL. (2019).

HOW SMALL-SCALE EFFECTS ARE EXPRESSED AT LARGER SCALES

Isotopic effects arising from diffusion and crystal-growth reactions are not limited in spatial extent to the length scales of diffusion profiles and crystal boundary layers. The compositional boundary layers produced by diffusion and reaction can be mobilized/aggregated by a fluid (e.g., Honour et al. 2019), ultimately giving rise to isotopic variations at much larger scales, ranging from differences between whole-rock analyses to differences in the isotopic composition of mantle and crustal reservoirs.

Fractional Crystallization

Fractional crystallization can amplify small isotopic effects by isotopic distillation (Rayleigh fractionation). In any situation where growing crystals have a different isotopic composition than their host melt, due either to equilibrium or kinetic effects described herein, the isotopic composition of the residual melt must change with progressive crystallization, which in turn, affects the composition of the next batch of crystals. The role of fractional crystallization in isotopic fractionation is most clearly manifested by a correlation (or lack thereof) between delta values and an index of differentiation, such as MgO or SiO_2 content among a suite of rock samples. For example, rocks from Kilauea Iki lava lake (Hawaii, USA) have been analyzed for a number of isotope systems and those that exhibit fractionations with MgO include Fe, Zn, Ti, Cr, Sn, and V (Ding et al. 2020 and references therein) whereas those that exhibit little to no fractionation during crystallization of basalt include Ca, Mg, Li, Ga, Sr, and Zr (Inglis et al. 2019 and references therein).

Whether such variations reflect kinetic versus equilibrium isotope effects attending crystal growth is debatable, but in principle, different stable isotope systems should be sensitive to different parts of a crystallization sequence, depending on the mineral assemblage and the growth rates of the individual phases. Stable isotope studies will be key to reconstructing when different phases become saturated in melts across the full compositional spectrum and may also extract unique information from kinetic effects during crystal growth.
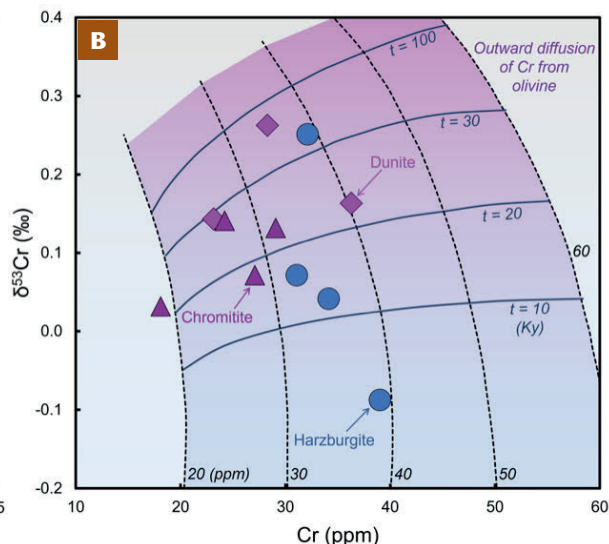
Reactive Transport

It is inevitable that fluids (melts or volatile-rich supercritical fluids) that rise buoyantly through the mantle and crust will pass through country rocks with which they are not in equilibrium. Changes to the host rock caused by interaction with fluids is called "metasomatism," and occurs through a combination of advection, diffusion, and reaction.

Diffusive exchange between percolating or channelized fluids and a solid mineral assemblage is thought to be the main source of kinetic isotopic fractionation during metasomatism. If the diffusive flux of a particular element is from solid to liquid, the reacted host rocks become isotopically heavier while the liquid carries away an isotopically light signature. This signature then gets inherited by later-forming minerals "downstream", and one can imagine how isotopic heterogeneities could arise spanning a range of length scales through cycles of reactive transport.

Stable metal isotope studies of mantle rocks highlight the importance of reactive transport for explaining isotopic heterogeneities of Fe, Cr, and Ca. In the case of Fe isotopes, differences among mantle xenoliths are too large to be due to partial melting alone, so they have been interpreted as arising from kinetic effects during diffusive exchange between fluid-filled veins and host rocks at depth (Poitrasson et al. 2013; Zhao et al. 2017). For Cr isotopes, pyroxenite veins have been found to have extremely light $\delta^{53}Cr$ values attributable to Cr diffusion from the host rocks into adjacent melt channels that subsequently crystallized to pyroxenite (Xia et al. 2017). A similar process was invoked by Zhao et al. (2017) for Ca and Fe isotopes, but in that situation, the Ca and Fe diffusive fluxes went from the percolating melt into the host rock to create altered minerals that were isotopically lighter than those in the unaltered host rock.

Metamorphic rocks are also isotopically heterogeneous, not only at the intermineral scale but also at the bulk-rock scale (Antonelli et al. 2019b). A striking example is a Ca isotope difference of 3 per mil between the center and edge of an ultramafic dike intruded into quartzitic country rock, all metamorphosed to very high temperatures (~900 °C) for

a period of 30–100 My. Antonelli et al. (2019b) found that the β factor needed to explain the Ca isotope variations is the same as predicted for dacitic liquids, suggesting that partial melting (not just dehydration) is responsible for the loss of incompatible elements in granulites. Although nontraditional stable isotope studies of crustal metamorphic rocks are rare, new measurements and modeling of reactive-transport processes will undoubtedly continue to yield important constraints on the mechanisms and durations of high-*T* processes.

OUTLOOK

Over half of the periodic table is now being used in isotope geochemistry for studying transport mechanisms, estimating temperature, estimating timescales of metamorphism and magmatism, and deciphering the history of meteorites. In the coming years, increased precision, as well as sampling resolution, will lead to exciting new discoveries of isotopic heterogeneity beyond that expected from equilibrium. The beauty of kinetic isotope effects is that, unlike equilibrium effects, they depend on reaction pathways and are transient, meaning that the time-dependent equations that describe kinetic isotope effects allow geochemists to probe timescales of natural processes that may otherwise be inaccessible to direct observation. Defensible interpretation of such effects will require command not only of the principles of equilibrium partitioning but also of mass-dependent diffusion and reaction processes.

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