Intercrystalline stable isotope diffusion: a fast grain boundary model

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Abstract. We formulated a numerical model for stable isotope interdiffusion which predicts the temperatures recorded between two or more minerals, and the intra-granular distribution of stable isotopes in each mineral, as functions of mineral grain sizes and shapes, diffusivities, modes, equilibrium isotopic fractionations, and the cooling rate of a rock. One of the principal assumptions of the model is that grain boundaries are regions of rapid transport of stable isotopes. This Fast Grain Boundary (FGB) model describes interdiffusion between any number of mineral grains, assuming that local equilibrium and mass balance restrictions apply on the grain boundaries throughout the volume modeled. The model can be used for a rock containing any number of minerals, any number of grain sizes of each mineral, several grain shapes, and any thermal history or domain size desired. Previous models describing stable isotope interdiffusion upon cooling have been based on Dodson's equation or an equivalent numerical analogue. The closure temperature of Dodson is the average, bulk temperature recorded between a mineral and an infinite reservoir. By using Dodson's equation, these models have treated the closure temperature as an innate characteristic of a given mineral, independent of the amounts and diffusion rates of other minerals. Such models do not accurately describe the mass balance of many stable isotope interdiffusion problems. Existing models for cation interdiffusion could be applied to stable isotopes with some modifications, but only describe exchange between two minerals under specific conditions. The results of FGB calculations differ considerably from the predictions of Dodson's equation in many rock types of interest. Actual calculations using the FGB model indicate that closure temperature and diffusion profiles are as strongly functions of modal abundance and relative differences in diffusion coefficient as they are functions of grain size and cooling rate. Closure temperatures recorded between two minerals which exchanged stable isotopes by diffusion are a function of modal abundance and differences in diffusion coefficient, and may differ from that predicted by Dodson's equation by

hundreds of degrees C. Either or both of two minerals may preserve detectable zonation, which may in some instances be larger in the faster diffusing mineral. Rocks containing three or more minerals can record a large span of fractionations resulting from closed system processes alone. The results of FGB diffusion modeling indicate that the effects of diffusive exchange must be evaluated before interpreting mineral fractionations, concordant or discordant, recorded within any rock in which diffusion could have acted over observable scales. The predictions of this model are applicable to thermometry, evaluation of open or closed system retrogression, and determination of cooling rates or diffusion coefficients.

Introduction

One or more of the elements oxygen, carbon, sulfur and hydrogen are major constituents of virtually all minerals. The stable isotopes of these elements potentially provide a large number of geologic thermometers. Fractionations of stable isotopes between coexisting minerals are routinely determined, strongly temperature dependent, and independent of lithostatic pressure. Some of the most common mineral pairs to which stable isotope thermometry can be applied have large enough temperature dependence that, if analytical errors are the only source of uncertainty, precision of a few tens of degrees C or less is possible. In addition, because most rocks are composed of silicates, carbonates and/or oxides, oxygen isotope fractionations between n minerals in any given rock will yield $n-1$ independent thermometers, allowing internal tests for consistency of the temperature determination.

One of the most often observed characteristics of stable isotope thermometers, however, is their failure to record accurately and consistently the peak temperatures experienced by slowly cooled igneous and high grade metamorphic rocks (Deines 1977; Javoy 1977; Valley 1986; Cole and Ohmoto 1986). Although stable isotope fractionation between some common mineral pairs is too insensitive to temperature to yield good temperature estimates (e.g. oxygen isotopes between quartz and feldspar;

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Chiba et al. 1989), many others have well-calibrated frac-tionations that are highly sensitive to temperature (e.g. oxygen isotopes in any of the pairs involving quartz, feldspar or calcite vs magnetite, rutile, garnet, pyroxene, olivine or possibly micas or amphiboles; Bottinga and Javoy 1975; Clayton et al. 1989; Chiba et al. 1989). This observed failure of such potentially useful thermometers has led many petrologists and geochemists to postulate that retrogression leads to resetting of isotope fraction-ations. Where no evidence for significant retrogressive recrystallization is found, interdiffusion between minerals on cooling is suggested as the agent of resetting.

The diffusion of isotopes between coexisting minerals during cooling results from the temperature dependence of stable isotope fractionations. When the bulk isotopic compositions of coexisting minerals are not in equilibrium for a rock's temperature, diffusion will occur. As a rock cools from the peak of a thermal event, the equilibrium fractionations of stable isotopes between the rock's consti-tuent minerals will generally increase. Unless a rock undergoes significant recrystallization, the rate at which the coexisting minerals can approach the lower temper-ature equilibrium is limited by volume diffusion rates within the minerals. Rates of stable isotope diffusion in all minerals are such that re-equilibration on cooling will be only partial, and fractionations representing temperatures between the peak and the final temperatures should be recorded in the integrated isotopic compositions of the minerals obtained by conventional bulk analysis. In addi-tion, diffusion limited exchange during cooling will lead to isotopic zonation within minerals (e.g. cores may more nearly preserve peak temperatures than rims in many cooling pairs). Our objectives in constructing the Fast Grain Boundary (FGB) model are to describe these pro-cesses of exchange and to provide a tool for interpreting stable isotope analyses of bulk mineral separates and zonation obtainable by the newly emerging micro-analytical techniques of stable isotope ratio measure-ment (Eldridge et al. 1987; Wada 1988; Sharp 1990; Crowe et al. 1990; Valley and Graham 1991). Because stable isotope data currently come from both conventional bulk analysis and from *in-situ* micro-analysis, we will consider the effects of diffusion on both volume integrated com-positions and on profiles.

Previous attempts to describe quantitatively the effects of stable isotope diffusion between coexisting minerals have considered retrogressive exchange to be rate limited exclusively by the diffusional characteristics of the slower diffusing mineral of any given pair (Dodson 1973, 1986; Javoy 1977; Giletti 1986). The results of diffusion modeling (predicted integrated compositions and profiles) are strongly dependent on the variables and assumptions one includes in a given model. The FGB model is based on the assumption of grain boundary equilibrium between all minerals undergoing interdiffusion, and considers the characteristics in every different mineral grain in a rock in describing the kinetics and mass balance of diffusive exchange. Our model, which allows for more complex description of the diffusion process, including the size, shape, diffusion coefficient and modal abundance of every mineral in a rock, makes predictions which are dramat-ically different from those of previous models.

Models for interdiffusion

Several models for diffusive transport in and among min-erals have been proposed: (1) Dodson's analytical equa-tion for the closure temperature (Dodson 1973), (2) Lasaga's analytical equations for zonation resulting from cation interdiffusion (Lasaga et al. 1977), and (3) nu-merical solutions for cation interdiffusion (Wilson and Smith 1985; Spear 1990). These models have proven to be useful tools for interpreting the results of diffusion on geochronology and cation thermometry. However, none addresses the unique problems of stable isotope inter-diffusion in a polygranular rock, a process in which every mineral in the rock could play an important role, and mass balance may be as important as diffusion coefficients and cooling rates in dictating the results of diffusive mass transport.

Model rock

Consider models for a hornblende granite primarily com-posed of quartz, feldspar, and hornblende (Fig. 1a). Grains are anhedral to subhedral in shape, but generally equant. A variety of grain sizes occur for each mineral, and grain boundaries of every possible type can be found (i.e. quartz-feldspar, quartz-hornblende, and feldspar-horn-blende, each in all crystallographic orientations). A rigor-ous description of interdiffusion between these minerals as the rock cooled from high temperature would be highly specific to the exact three dimensional geometry, and would need to include accurate knowledge of diffusion rates within each mineral in all directions, as well as the diffusion coefficient and size and shape of each type of grain boundary. Such a model would be difficult to con-struct, and would be applicable only to one specific rock. At present such complexity would not be justified given our incomplete knowledge of transport rates on grain boundaries, and imprecise determinations of diffusional anisotropy in many minerals. Below we review the as-sumptions by which existing models have described such rocks, as a means of placing the FGB model in the context of previous work.

Diffusional closure and the Dodson equation

The closure of a mineral with respect to diffusion may be generally described as the progressive isolation of that mineral from coexisting phases as the diffusion coefficient of that mineral decreases with decreasing temperature (Armstrong 1966; Dodson 1973, 1979). Estimates (for geochronology) and/or interpretations (for geothermo-metry) of closure temperatures of minerals have frequently been based on Dodson's equation (Dodson 1973):

$$T_c = \cfrac{Q/R}{\left[\ln\left(\cfrac{-A*R*T_c^2*(D_0/a^2)}{Q*(\partial T/\partial t)}\right)\right]} \tag{1}$$
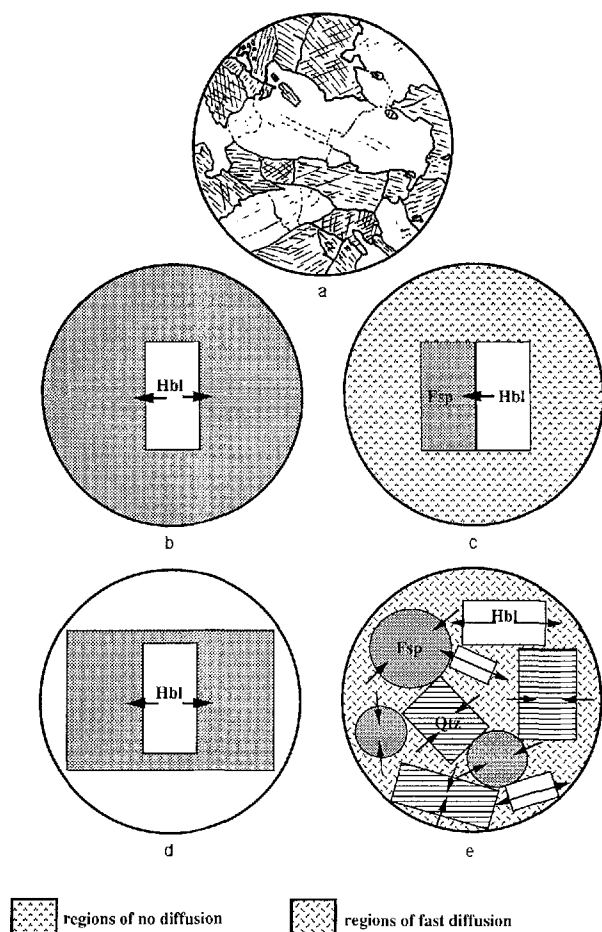
Fig. 1a–e. Schematic illustration of a natural hornblende granite in thin section **a** (after Williams et al. 1954), and that same rock as described by the diffusion models of Dodson (1973) **b**, Lasaga et al. (1977) **c**, Spear (1990) **d** and the FGB model **e**. _Arrows_ represent fluxes of ^{18}O on cooling, while _rectangles_ represent hornblende, _stippled circles_ feldspar and _striped rectangles_ quartz. _Stippled regions_ in **b** and **d** represent both quartz and feldspar at high temperature. See text for discussion

where T_c is the closure temperature, Q the activation energy of diffusion, R the gas constant, "A" a geometric parameter, "a" the diffusion radius or half-thickness, $\partial T/\partial t$ the cooling rate and D_0 the diffusional pre-exponential factor. Dodson's equation is an analytical solution for the closure temperature recorded by the bulk composition of a mineral grain that has undergone diffusional exchange on cooling (such that $1/T$ increases linearly with time) with an infinite reservoir. The infinite reservoir is a source or sink for the element or isotope in question whose composition is unaffected by diffusional exchange with the mineral.

In the case of closed system, cation or stable isotope exchange mass balance restrictions require that diffusional gain or loss by one mineral be balanced by a compositional change of its coexisting phases. Any phase in a rock which can take part in diffusional exchange must be included in the mass balance of the diffusion problem. For the case of oxygen isotopes this can be every mineral in the rock.

The infinite reservoir for mineral-mineral interdiffusion of stable isotopes in a rock that is a closed system (with no advective transport by fluids) is assumed to be the mineral or minerals which have a lower closure temperature defined by Dodson's equation (e.g. Dodson 1973; Giletti 1986; Sharp 1991). This description of the diffusion process for the case of the simplified hornblende granite appears in Fig. 1b. At any given moment during the cooling history, all minerals which are still "open" to diffusion, other than the one with the highest closure temperature, are considered to be part of the infinite reservoir. Fig. 1b represents a time early in the rock's cooling history when quartz and feldspar are considered the infinite reservoir surrounding hornblende. Diffusion coefficients for the faster diffusing minerals and the grain boundary are quantitatively irrelevant. Application of this model was most fully stated by Giletti (1986), who calculated the closure temperature of each mineral by Dodson's equation (i.e. with respect to an infinite reservoir). The values of closure temperature are then used as the temperatures at which each closing mineral is effectively removed from a system of otherwise continuously equilibrating minerals.

The effects of the process are shown in Fig. 2, a schematic plot of the volume-integrated isotopic compositions of quartz, feldspar and hornblende in a rock throughout its cooling history. As the rock cools, the minerals all freely equilibrate their oxygen isotopic compositions until hornblende closes (Period I). At this point hornblende's compositions is fixed for the remainder of the cooling history. Isotopic exchange continues in quartz and feldspar (Period II) until quartz closes, and all exchange ceases (Period III).
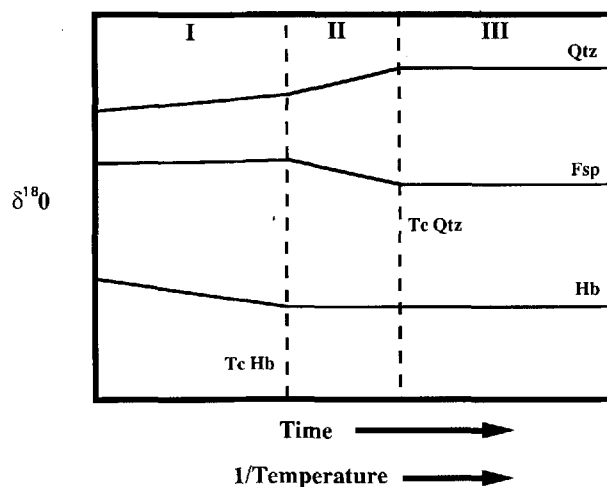

Fig. 2. Schematic illustration of the oxygen isotopic composition of quartz, feldspar and hornblende in a rock undergoing diffusive exchange while cooling, as described by the model of Giletti (1986). Early in the cooling history (period I) all three minerals freely exchange oxygen isotopes, maintaining equilibrium. Later (period II) hornblende has "closed" with respect to oxygen diffusion, and therefore only quartz and feldspar undergo exchange. Note that in period II the feldspar-hornblende fractionation decreases, although no feldspar-hornblende exchange takes place. Finally (period III), after quartz "closes" no further exchange takes place, and the final fractionations are preserved

The insight this model provides is that measured fractionations between mineral pairs need not record the closure temperature of that pair. In this model, only the fractionation between the last two minerals to close should record a true closure temperature. All other mineral pairs will be disturbed from the closure temperature of the first mineral of the pair to close; the extent of this disturbance will be a function of the modal abundance of "open" minerals.

The simplification made by Giletti (1986) is that mass balance is decoupled from diffusion. Dodson's equation is only applicable to describing diffusional exchange with a reservoir that maintains a fixed concentration of the diffusing species throughout the diffusion process. Therefore using the Dodson closure temperature as the temperature at which one fixes integrated compositions of two finite mineral populations undergoing exchange is not strictly correct. Mass balance requires that no closed system stable isotope interdiffusion problem will be rigorously described by exchange with an infinite reservoir. The FGB model considers mass balance among all coexisting minerals throughout the diffusion process, therefore coupling mass balance and diffusion.

Slow grain boundary diffusion model for cations

Lasaga et al. (1977) proposed an analytical model for calculating the cation zonation that should result from exchange of iron and magnesium between coexisting silicates. This model explicitly links the mass balance constraints imposed by closed system exchange of an element or elements between two finite reservoirs (coexisting minerals) with the equations describing the diffusional rates of that exchange. Diffusion rates within both minerals undergoing exchange are included. The most significant assumption made in this model is that diffusion along grain boundaries is slow enough that no exchange takes place between non-touching grains. Although formulated for cation exchange, this model can be conceptually applied to stable isotope diffusion. (Fig. 1c). Diffusional exchange takes place on cooling between all touching crystal faces, but the effects should be dependent on local geometry. Conventional bulk mineral analysis of stable isotope ratios in mineral separates would be difficult to interpret using such a model. For the case of oxygen isotope exchange in the model hornblende granite each face of each grain is undergoing exchange, and the results depend largely on the local environment.

The model of Lasaga et al. (1977) and the FGB model are two endmembers in the treatment of grain boundary diffusion. Lasaga (1983) provides equations for variables which dictate the results of interdiffusion between two minerals with no grain boundary diffusion. We have reformulated these variables to include the effect of mass balance over multiple faces of non-touching grains, compatible with the formalisms describing stable isotope fractionation (appendix). These reformulated variables can be used to determine whether or not the mass balance terms used in the FGB model will result in very different profiles from the model of Lasaga for a given mineral pair.

Fast grain boundary model for cations

Numerical models for Fe-Mg interdiffusion between garnet and olivine or biotite (Wilson and Smith 1985; Medaris and Wang 1986; Spear 1990) are also conceptually applicable to stable isotopes, but are a special case of the FGB stable isotope model. The model of Spear (1990) serves as an example of their principal assumptions, although the various models differ in detail. Diffusion in the faster of two minerals is infinitely fast, and the fast mineral is modeled as a single large grain. Mass balance is coupled with diffusion between two finite reservoirs, one with finite diffusion rates and one with infinite diffusion rates (Fig. 1d). For the specific diffusion problems considered by Spear (1990), this is an adequate description due to the very slow diffusion rates with garnet. If mineral diffusivities are within 3–4 orders of magnitude of each other (depending upon their absolute values and relative abundance), such models will differ significantly from the FGB model for even the simple two mineral interdiffusion process.

The FGB model

Our FGB model differs from the models described above in that it considers the characteristics of every grain or different set of grains, and links these grains by assuming that equilibrium is maintained along grain boundaries over the distance and time considered. Mass balance and diffusion are fully linked, and include as many unique mineral grains as are in the rock (Eiler et al. 1991). Figure 1e schematically illustrates the way in which this model describes a rock. Mineral grains have idealized shapes, but any number of grains of different size and mode can be included, for all the minerals in the rock. We will show that the closure temperatures recorded in the bulk compositions or in the isotope zonations of coexisting minerals are as much a function of the environment of those minerals as of their cooling history or diffusional properties.

Fast grain boundary interdiffusion

Model description

The FGB model describes minerals in a portion of rock (e.g. of hand sample or thin section size). Within this domain, grain boundaries continuously maintain mutual isotopic equilibrium over the temperature/time interval described. As temperature changes with time, the shift toward equilibrium of the interior of the minerals is described in terms of volume diffusion toward or away from equilibrated grain boundaries. The equations used to describe diffusion are either that for a sphere (for isotropic minerals),

$$\frac{\partial C_j^i}{\partial t} = D_j^i * \left(\frac{2}{x} * \frac{\partial C_j^i}{\partial x} + \frac{\partial^2 C_j^i}{\partial x^2} \right) \qquad (2)$$

where C_j^i is the concentration of species i in phase j, D_j^i is the diffusion coefficient of species i in phase j, assumed to be independent of r, t is time, and x is distance; or for a semi-infinite plane (for anisotropic minerals)

$$\frac{\partial C_j^i}{\partial t} = D_j^i * \frac{\partial^2 C_j^i}{\partial x^2} \qquad (3)$$

Hereafter, values of δ for the stable isotope of interest (i.e. $\delta^{18}O$) are treated as concentrations in the diffusion equations within each mineral, with elemental concentrations being included in the mass balance equation (Eq. 5, below). This substitution does not introduce a significant error in the diffusion modeling of oxygen or carbon isotopes (Craig 1953), but modeling of sulfur isotopes should instead use actual isotopic concentrations in FGB model calculations. The boundary conditions imposed are:

(i) Grain boundary isotopic equilibrium

$$\delta^j_{boundary} = \delta^r_{boundary} + \Delta \qquad (4)$$

where $\delta^r_{boundary}$ is the composition of a reference mineral at its grain boundary, $\delta^j_{boundary}$ is the composition of a given mineral j at its grain boundary, and Δ is the temperature dependent fractionation between the reference and j. For n minerals, n-1 equations of this form are needed. Equation 4 is based on the approximation that Δ is equal to $1000\ln\alpha$. This will hold for values of Δ less than approximately 20 per mil, if either $\delta^r_{boundary}$ or $\delta^j_{boundary}$ is near 0 (Friedman and O'Neil 1977). A rigorous equation relating $\delta^r_{boundary}$ to $\delta^j_{boundary}$ can be easily substituted into the FGB model if needed.

(ii) Mass balance

$$\sum_j \left(\frac{v_j}{V_j}\right) * Xg_j * A_j * J_j = 0 \qquad (5)$$

where J_j is the isotopic flux per unit area at constant elemental concentration, v_j is the stoichiometric coefficient of the element whose isotopes are diffusing in mineral j, V_j is the molar volume of mineral j, Xg_j is the fraction of the total number of grains which are mineral j, and A_j is the surface area through which isotopes diffuse in mineral j, summed over all minerals j. Note that when δ values are being treated as concentrations, J_j has units of $cm^{-2} sec^{-1}$.

Diffusion within each mineral is calclulated for by a fully implicit finite difference numerical method, based on the Crank-Nicholson analogues of the diffusion equations. The tri-diagonal matrix of Crank-Nicholson equations is solved independently for each mineral using the Thomas algorithm (e.g. Wang and Anderson 1982). A unique solution for polyphase interdiffusion of a temperature/time step is found by iterating over values of $\delta^r_{boundary}$ towards a value such that Eq. 5 and all equations of form 4 are satisfied.

The FGB model is more flexible than other models for interdiffusion. A rock composed of any number of minerals, each having any set of grain sizes can be considered for any thermal history without the compromising assumptions about homogeneity or constant bulk composition for any of the minerals.

Assumptions

There are several assumptions which have been made in constructing this model. The most significant of these concern the process of diffusion, the grain geometry and size, and grain boundary mobility.
(i) *Diffusion controlled exchange.* Isotopic exchange can result from diffusion or recrystallization. Always implicit in any calculation using a diffusion model is that diffusion was the dominant process. This assumption is not trivial in application. Diffusion must be a ubiquitous process in rocks whose minerals are not in equilibrium, but this does not guarantee that the effects of diffusion will be perceptible. Calculation of the effects of diffusion in a rock's history provide us with an endmember case. If processes of recrystallization and/or mass transfer reactions were also operative, the effects of diffusional exchange may be small in some cases.
(ii) *Grain shape and size.* Mineral shapes are approximated by two end-member geometries; spheres and semi-infinite sheets. Minerals that are isotropic with respect to stable isotope diffusion (e.g. oxygen in garnet, magnetite or possibly calcite) are calculated using the equation for diffusion in a sphere (Eq. 2). Minerals that are anisotropic with respect to stable isotope diffusion (e.g. oxygen in quartz, diopside or olivine) are described as rectangular tablets, with a defined width perpendicular to the fast diffusion direction and a

defined half-thickness parallel to the fast diffusion direction. Anisotropic grains are calculated using the one dimensional equation for diffusion in a plane (Eq. 3) and integrated in three dimensions for a given cross sectional area (width squared), assuming bilateral symmetry of compositions about the half-thickness plane. This treatment assumes no diffusion along slow diffusion directions. The tabular approximation may also be appropriate for some minerals which are isotropic with respect to diffusion coefficient, but highly anisotropic in shape.

These approximations are simplified descriptions of highly irregular grains, or minerals with diffusion coefficients that are neither sub-equal in all directions nor highly anisotropic. However, these shapes should be good general descriptions for populations of equant and tabular minerals in many igneous and metamorphic rocks. In any case, diffusion coefficients determined for the slow directions in anisotropic minerals are typically poorly constrained and/or described simply as several orders of magnitude lower than diffusion coefficients in the fast direction (e.g. Farver and Giletti 1985, 1989; Farver 1989). Therefore a more sophisticated treatment of diffusion in anisotropic minerals (e.g. two or three dimensional numerical modeling) does not appear to be warranted at this time.

In the examples provided in this paper, the diffusion domain, or effective grain size, is considered to be equal to the physical grain size. This assumption should hold in minerals containing low densities of planar structural defects and/or exsolution lamellae. Studies of argon, cation and stable isotope diffusion have not given a clear indication of the validity of this assumption. Argon loss from hornblende and feldspar has generally been found to fit a model of diffusional loss from domains smaller than grains (e.g. Harrison 1981; Baldwin et al. 1990; Lovera et al. 1991), and the diffusion coefficient for oxygen isotopes in perthite is found to be several orders of magnitude higher along lamellae than in the bulk (Nagy and Giletti 1986). However, Giletti (1974) and Foland (1974) found that the diffusion domain corresponded to the physical grain size for diffusion of argon in phlogopite and alkalis in orthoclase, respectively. Jenkin and Fallick (1989) found similar results for hydrogen diffusion in hornblende up to 5 mm long. In any application of diffusion modeling, a careful examination of the sample is necessary by optical and/or electron microscopy. The absence of sub-domains greatly strengthens this assumption, but care must be taken in samples with lamellae, inclusions or unusual numbers of crystal defects.
(iii) *Grain boundary mobility.* The FGB model assumes that grain boundaries of coexisting minerals maintain isotopic equilibrium. This assumption is also implicit when applying existing stable isotope diffusion models to hand samples (Dodson 1973; Giletti 1986). The physical requirement which must be met is that the transport rate on the grain boundaries is much greater than that within the minerals, and large enough in absolute value that transport over the dimensions of the domain being modeled occurs rapidly relative to the time over which the rock cools.

The length scale over which this assumption will hold will depend on the geologic setting of the diffusion problem of interest. This distance could be a function of the conditions on the grain boundaries (e.g. wet vs dry; strained vs annealed; thick vs thin) (Joesten 1991), as well as the mineral pair forming a particular grain boundary, grain distributions, the mineral diffusivities, the grain boundary diffusivities, and the mineral modes and grain sizes (Brady 1983; Joesten 1991). A model could be constructed to describe finite grain boundary transport by using diffusional penetration calculations (Fisher 1951; Joesten 1991) or double porosity models from the hydrologic literature (e.g. Wang 1992). However, this level of complexity is not currently justified due to the lack of experimental data on grain boundary transport mechanisms and rates. We are attempting to provide a general model for mineral interdiffusion in which grain boundary mobilities fit the end-member case of continuous equilibration for the scale being sampled. We therefore recommend careful selection of the scale and geometry of a domain being modeled and analyzed. One of the applications of this model will be in determining the scales over which its assumptions hold in natural rocks, and therefore the scales and settings over

which minerals "see" one another in metamorphic and slowly cooled plutonic rocks.

There are several lines of evidence that suggest that the scale over which the assumption of grain boundary equilibrium should hold is on the order of centimeters (i.e. thin section to hand sample scale) in many slowly cooled regional metamorphic rocks. Although cation volume diffusion rates are frequently observed to be greater than those for stable isotopes within a given mineral, grain boundary diffusivities of cations and oxygen are often comparable (Joesten 1991). Therefore the large number of studies of cation diffusion in metamorphic rocks may indicate the behavior of stable isotope transport along grain boundaries. Studies of cation exchange thermometry which have considered the role of diffusional resetting report concentric zonation of cations within slow diffusing minerals (e.g. garnets) and a uniform concentration in the relatively fast diffusing minerals (e.g. biotite or olivine) within and between grains (Tracy 1982; Medaris et al. 1990). Both observations suggest that the assumption of grain boundary equilibrium on the scale of a thin section holds during the retrogression of at least some regional metamorphic rocks. Observations of the apparent rates of transport of cations on grain boundaries should provide a minimum estimate for stable isotopes due to the much greater solubility of the common stable isotopes in a C–O–H fluid relative to cations, coupled with the observation that grain boundary diffusivities of stable isotopes and cations are approximately equal.

Cation zonation within garnet on occasion shows only localized interdiffusion with touching grains of other minerals (Tracy 1982). If similar observations are made for stable isotope diffusion profiles, one should use either a modified version of the slow grain boundary cation diffusion model of Lasaga et al. (1977), or link the mode, grain sizes and relative widths of the minerals undergoing exchange such that the FGB model we propose can be used.

Another estimate of the grain boundary mobility of stable isotopes comes from the analysis of the diffusional penetration of a chemical or isotopic species into a monomineralic matrix (Fisher 1951; Joesten 1991). Experimental determinations of w^*D^{Gb} (where w is the grain boundary width, and D^{Gb} is the diffusion coefficient of the species of interest on the grain boundary) show that grain boundary diffusivities are generally 4 to 6 orders of magnitude greater than volume diffusion coefficients of stable isotopes in minerals (Nagy and Giletti 1986; Coghlan 1990; Joesten 1991; Farver and Yund 1991). These differences may actually be larger in real rocks where grain boundaries are between dissimilar minerals and/or contain fluid, as opposed to the dry, monomineralic aggregates used for many experimental determinations (Joesten 1991). Calculations based on the diffusional penetration model indicate that oxygen isotope diffusion along grain boundaries is much faster than volume diffusion, and that transport distances for time scales used in our numerical time steps should be on the order of millimeters to centimeters (Joesten 1991). The observed values of w^*D^{Gb} therefore appear to be sufficiently large to justify our assumption over a centimeter scale for slow cooling.

Results

Calculations using the FGB model have shown that both the isotope zonation and bulk fractionations between minerals are a strong function of modes and relative diffusion coefficients (variables not considered in Dodson's equation), as well as cooling history, and the magnitude of the diffusion coefficient, grain size and shape of any one mineral. These results differ considerably from predictions based on Dodson's equation in many rock types of interest. We will first consider these effects in terms of rocks composed of two minerals, and then examine rocks with three or more minerals and/or heterogeneous grain size distributions.

Closure temperature in the two mineral system

The results of interdiffusion are simplest and most easily understood in the case of two minerals undergoing interdiffusion. With a change in temperature, isotopic exchange takes place because there is a temperature dependence to the fractionation. The end result of this exchange, as seen in the bulk compositions and profiles preserved in these minerals, is a function of the cooling rate, diffusion coefficients of the two minerals, the grain sizes and shapes (e.g. spherical vs tabular), and the relative abundances of the minerals. The effects of the cooling rate, and the grain size, shape and diffusion coefficient of a slower diffuser in an infinite reservoir are already qualitatively understood through the analysis of Dodson (1973). We therefore focus on the effects of mode and relative diffusion coefficient described for interdiffusion by the FGB model.

Figure 3 is a plot of the difference between the Dodson closure temperature for the mineral with the lower diffusion coefficient and the temperature that the FGB model predicts to be recorded in the bulk fractionations between the two minerals, as a function of the relative volume fraction of the fast and slow diffusers. These sample calculations are for rocks composed exclusively of quartz and feldspar, quartz and hornblende, or feldspar and hornblende. By varying the modal abundance of the two minerals in each of these three model rocks, the effects of mode and of the difference in diffusion coefficient are shown. In these calculations cooling rate was approximately 10 °C per million years at the Dodson closure temperatures of quartz and hornblende (cooling from 750 °C
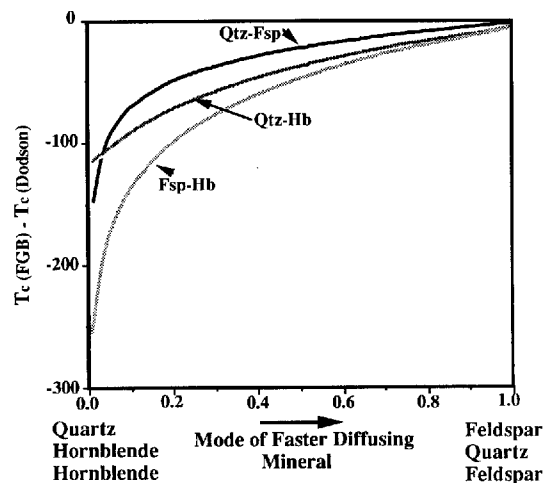

Fig. 3. Plot of the difference between the closure temperature predicted by the FGB model and the Dodson closure temperature of the slower diffuser of a given mineral pair, as a function of modal abundance. When the faster diffuser is modally dominant, the closure temperature approaches that calculated by Dodson's equation because the fast diffuser is behaving approximately as an infinite reservoir. As the modal abundance of the fast diffuser decreases, the temperature recorded between the pair decreases, to a minimum which approaches the Dodson closure temperature of the fast diffuser. The difference between Qtz-Fsp and Hb-Fsp curves illustrate the influence of relative diffusion coefficients. When the minerals have nearly equal diffusion coefficients and size, the "mode effect" is smaller at sub-equal modal abundances than pairs which have widely differing diffusion coefficients
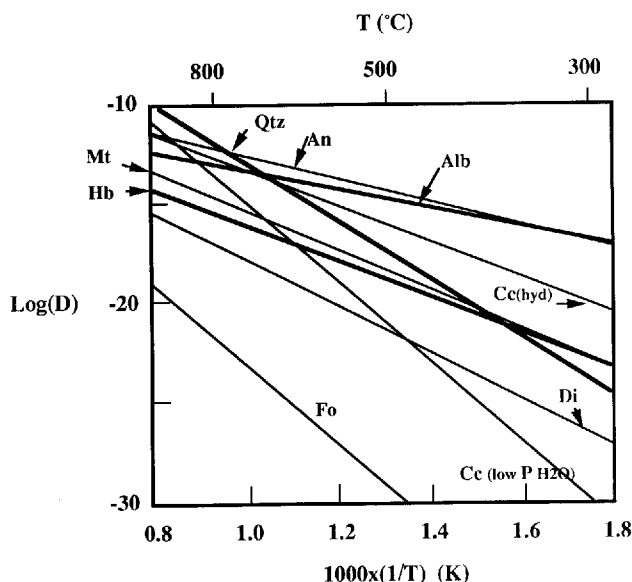
Fig. 4. Arrhenius plot showing diffusion coefficient data for minerals used in this paper (*bold lines*), as well as representative data for several other minerals of interest. References: albite and anorthite, Giletti et al. (1978); quartz, Giletti and Yund (1984); calcite (hydrothermal), Farver (1990); calcite (low P_{H_2O}), Kronenberg et al. (1984); magnetite, Giletti and Hess (1988); hornblende, Farver and Giletti (1985); diopside, Farver (1989); forsterite, Hallwig et al. (1982)

to 25 °C in 181 my with $1/T$ in degrees K increasing linearly with time). Feldspar was treated as spheres with a 1 mm radius; quartz and hornblende as prisms 1 mm wide with a 1 mm half-thickness. The diffusion coefficients used are those in Fig. 4, which also represents oxygen diffusion in some other common minerals. Diffusion coefficients used for quartz, feldspar and hornblende are the same as those used by Giletti (1986). They were chosen in order to simplify comparison of the two models in the calculations for rocks composed of three minerals described below. The largest difference in diffusion coefficient (for the high temperatures at which most diffusional exchange on cooling takes place) for the three minerals calculated is between hornblende and feldspar, the smallest difference is between quartz and feldspar.

The closure temperature which should be recorded between two minerals, as predicted by the FGB model, diverges dramatically from the Dodson closure temperature as the modal abundance of the fast diffusing mineral decreases (i.e. as the system diverges from the infinite reservoir approximation). We have termed this the "mode effect". Previous workers who have made use of the Dodson equation or a numerical analogue have recognized that the infinite reservoir approximation should hold when significant quantities of the fast diffusing mineral are present (Javoy 1977; Giletti 1986). However, no limits are specified for application. The FGB model indicates that even a rock which has a modal majority of the fast diffusing mineral could record a temperature which deviates from the Dodson closure temperature by 50 °C or more. As the modal abundance of the fast diffusing mineral decreases this difference rapidly increases, reaching a maximum equal to the difference between the Dodson

closure temperatures of the two minerals (most clearly seen in Fig. 3 for the quartz-hornblende curve).

The magnitude of the mode effect on closure temperature is a function of the difference in diffusion coefficients of the two minerals undergoing interdiffusion. This is also seen in Fig. 3 by comparison of the curves for the three mineral pairs. If rates of stable isotope diffusion in the two minerals are identical at all temperatures, then for minerals of the same size and shape, the blocking temperatures of the two minerals are the same as the Dodson closure temperature of either of the two minerals (not shown). As the diffusion coefficients diverge, the closure temperature of the pair calculated by the FGB model decreases below the Dodson closure temperature of the slow diffusing mineral. The mode effect is sensitive enough to differences in diffusion coefficient between minerals that it will be important with any two minerals of the same size whose diffusion coefficients are different by more than an order of magnitude. When differences in diffusion coefficient are large and a slow diffusing mineral is modally dominant, systematic errors of hundreds of degrees could be engendered by using a method that does not consider mass balance.

Profiles in the two mineral system

Modal abundance and relative diffusion coefficient have also strong effects on the compositional profiles preserved in minerals undergoing interdiffusion. The use of Dodson's equation is based on the assumption that little if any compositional profile should be preserved within the more rapidly diffusing of two minerals. This assumption seems reasonable if one considers the equation relating flux to instantaneous compositional gradient. If mass balance is controlled only by diffusion across a plane between two minerals, and the concentration of oxygen is equal in them, then the instantaneous gradients at the grain boundary can be described by the steady state approximation:

$$- D_a * \frac{\partial \delta_a}{\partial x} = D_b * \frac{\partial \delta_b}{\partial x} \tag{6}$$

where $\partial \delta_j / \partial X$ is the isotopic gradient in mineral j, evaluated at the boundary of the mineral, and D_j is the diffusion coefficient in mineral j. If D_b is orders of magnitude greater than D_a, it is clear by inspection of Eq. 6 that no gradient should be found within mineral b ($\partial \delta_b / \partial X \Rightarrow 0$). However, if mass balance is applied over parts or all of the surfaces of multiple grains, and/or if concentrations of oxygen are not equal in the two minerals, several other terms must be included:

$$- \left(\frac{v_a}{V_a}\right) * Xg_a * A_a * D_a * \frac{\partial \delta_a}{\partial x} = \left(\frac{v_b}{V_b}\right) * Xg_b * A_b * D_b * \frac{\partial \delta_b}{\partial x} \tag{7}$$

where Xg_j is the fraction of total number of grains which are mineral j, A_j is the surface area across which species i may diffuse in mineral j, v_j is the stoichiometric coefficient of the element whose isotopes are diffusing in mineral j, and V_j is the molar volume of mineral j. This leads to the breakdown of the validity of the assumption that no gradient will be found in the fast diffusing mineral. In

considering these additional terms it is clear that unless the diffusion coefficients of the two minerals are many orders of magnitude apart, there will be cases of relative size, mode and elemental concentration that lead to appreciable profiles in the fast diffuser. It is, in fact, possible that the fast diffusing mineral could preserve a greater profile than that of the slow diffusing mineral. The results of calculations using the FGB model demonstrate this possibility. Figures 5a–c illustrates the effect of mode alone (for equal grain sizes and shapes, using diffusion coefficients shown in Fig. 4) on profiles which should be preserved within quartz (fast) and hornblende (slow) on cooling along the same T-t path described above. When the fast diffusing mineral is modally dominant (Fig. 5a), the assumption based on Eq. 6 holds; the slow mineral preserves a steep and deeply penetrating profile, while the fast mineral is homogeneous over the scale of mm). With equal amounts of fast and slow diffuser (Fig. 5b) the profile in the slow diffuser is smaller, and a profile has been developed in the rim of quartz. Finally, for the case of a modally dominant slow diffuser (Fig. 5c), there develops a complete reversal of the behavior predicted from Eq. 6. Quartz has developed a steep and deeply penetrating

diffusion profile, and the profile within hornblende, the slower diffusing mineral, has become relatively insignificant.

The relation between relative diffusion coefficient and mode is reversed as it applies to compositional profiles; greater differences in diffusion coefficient lead to progressively shallower profiles within the fast diffuser. The profiles shown in Fig. 5 are less extreme than those calculated for other mineral pairs of geologic interest for which diffusion coefficients are closer together and fractionations are larger (e.g. magnetite with quartz or calcite).

Interdiffusion among three minerals

Interdiffusion involving three or more minerals is not explicitly described by any of the commonly used models. Given the method of calculation used in the FGB model, interdiffusion problems involving more than two phases are similar to the two mineral case; mass balance and equilibrium constraints are simply imposed over the boundaries of more than two minerals within the domain being modeled. In order to understand the results of
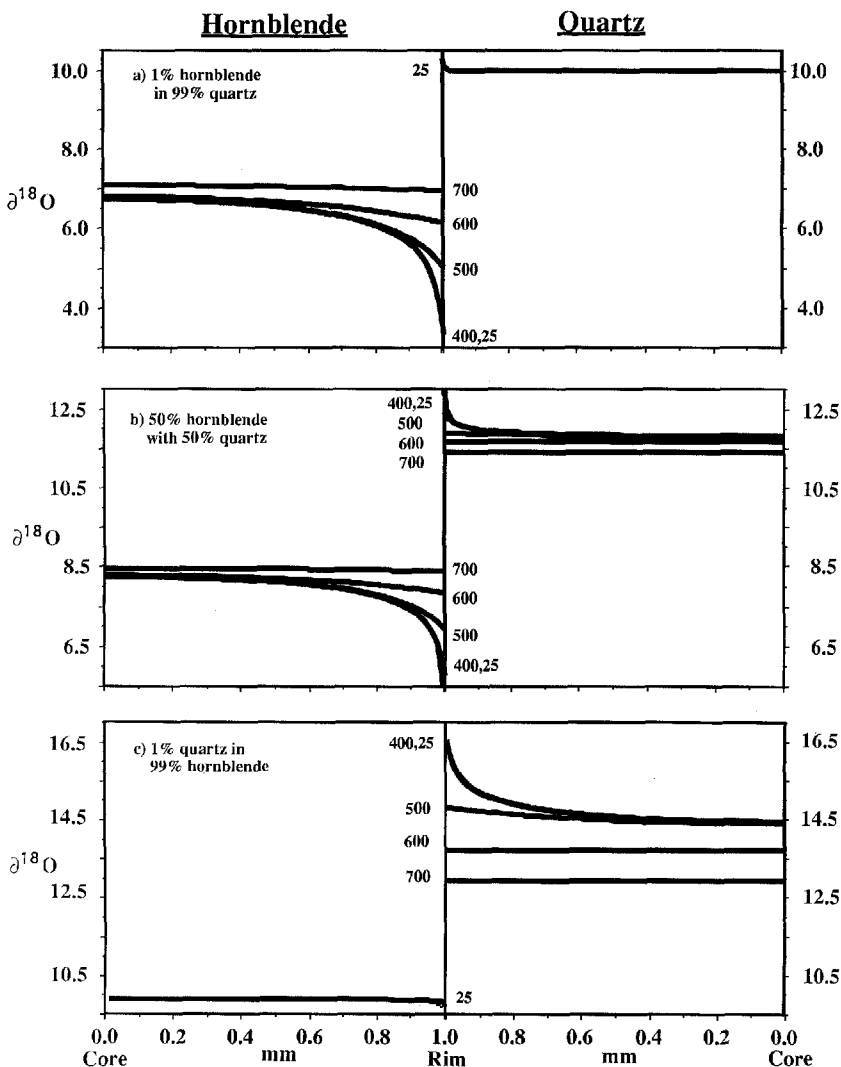

Fig. 5a–c. Isotopic zonation produced by diffusional exchange on cooling between hornblende and quartz as a function of modal abundance. Diffusion profiles are shown at a variety of labeled temperatures (°C), illustrating the development of zonation during cooling. Diffusion profiles do not change significantly between approximately 400 and 25 °C. Note that hornblende preserves a sharp isotopic profile in a while quartz preserves the profile in c. Profile c shows that steep isotopic gradients may be preserved within the faster diffusing mineral

interdiffusion in rocks with three or more minerals we need to consider the effects of competition between mineral pairs on all the final fractionations recorded in a rock.

In the model of Giletti (1986), the final fractionations between coexisting minerals are calculated based on the closure temperature of each mineral and mass balance at the closure temperatures of minerals as the system cools. The model of Giletti does not, however, consider that the closure temperatures should be a function of the relative abundances and diffusivities of the coexisting minerals. The mode effect described by our model will occur simultaneously with the mass balance effect described by Giletti (see Fig. 2), and will dramatically change the predicted results from those found with the Giletti model. We have illustrated the combined results of these two effects by comparing the predictions of Giletti's model with those of our model for the temperatures recorded between pairs in a three-mineral rock (potassium feldspar, quartz and hornblende) as a function of mode.

The results are illustrative rather than general, however, and each system of minerals requires its own set of calculations. In our calculations we have used the same grain sizes, shapes, diffusion coefficients and fractionation factors used in the calculations of Giletti (1986, p. 227). The cooling history used for our calculations was one in which $1/T$ (K) increased linearly with time, and the cooling rate was $10\,°C/my$, the cooling rate used by Giletti, at the Dodson closure temperature of quartz ($513\,°C$). The cooling history we used should approach the path needed for the application of Dodson's equation as closely as possible, therefore maximizing the similarity to Giletti's calculations. The values used for these variables result in a Dodson closure temperature of $624\,°C$ for hornblende, $513\,°C$ for quartz, and $274\,°C$ for feldspar. The Dodson equation describes hornblende as "closing" first, allowing quartz and feldspar to exchange down to the closure temperature of quartz. Below this temperature ($513\,°C$) no further isotopic modifications should occur. The predicted results of this process are quartz-feldspar tempereatures of $513\,°C$, independent of modes, and quartz-hornblende and feldspar-hornblende temperatures which have been reset to higher and lower temperatures respectively as a function of the relative modes of quartz and feldspar only (Figs. 6a–c).

In the FGB model, the mode effect imposes a modal dependence of the closure temperatures of the mineral pairs themselves, which, when combined with the mass balance effects for three mineral systems (Fig. 2) leads to predicted temperatures which can be dramatically different from the predictions of Giletti. The range of possible temperatures recorded by quartz-hornblende (Fig. 7a) and feldspar-hornblende (Fig. 7b) pairs is a factor of five and two greater, respectively, than seen in the Giletti model (Figs. 6a, 6b). In extreme cases the recorded bulk mineral temperatures can be hundreds of degrees above the highest Dodson closure temperature, or over a hundred degrees below the Dodson closure temperature of either quartz or hornblende. The quartz-feldspar temperatures (Fig. 7c), rather than being independent of mode, show a dramatic range of values (over $1500\,°C$), few of them near the Dodson closure temperature of quartz. In some instances these temperatures are far above those
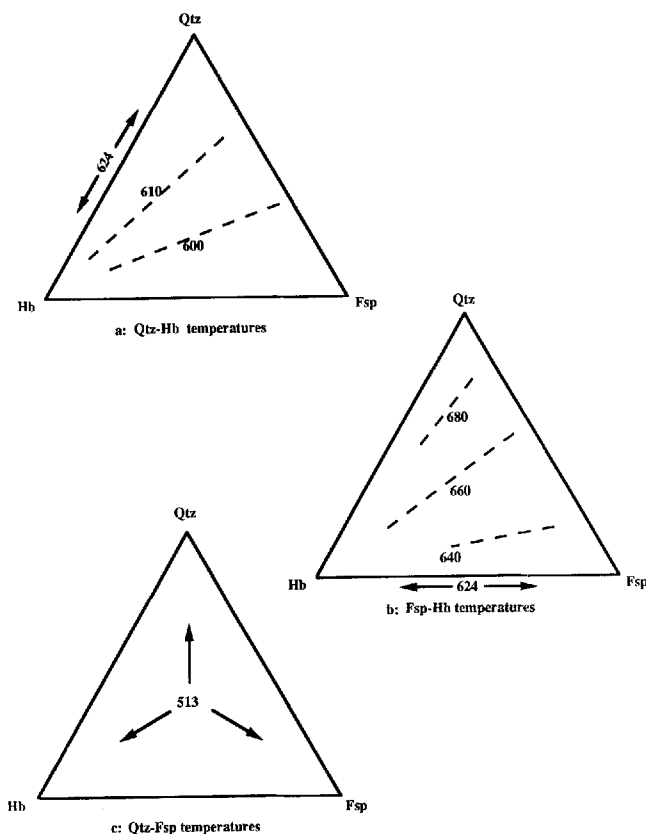

Fig. 6a–c. Contour of the temperatures predicted that would be recorded by the bulk compositions of quartz and hornblende **a**, feldspar and hornblende **b** and quartz and feldspar **c** pairs in Qtz-Fsp-Hb rocks, as calculated by the model of Giletti (1986). Adapted from Figs. 2 and 3 of Giletti (1986). See text for discussion

predicted by Giletti (feldspar-hornblende in quartz rich rocks; quartz-feldspar in hornblende rich rocks); in other cases far below (quartz-feldspar in quartz rich rocks; hornblende-feldspar in hornblende rich rocks). In addition, the FGB model predicts a dramatically different shape to the isotherms of apparent temperatures from that of the model of Giletti. Rather than being straight lines parallel to constant quartz-feldspar ratios (Figs. 6a, b), the FGB model predicts that isotherms will be a complex function of the modal abundance of all three minerals (Figs. 7a–c).

If the results of our calculations are interpreted in terms of the Giletti model, or any model based on Dodson closure temperatures, the rock typically will appear to have experienced an open system history. Feldspars will appear to have been either enriched or depleted by an outside source, depending on whether the rock was hornblende or quartz-rich, respectively. Hornblende-rich rocks will also have quartz $\delta^{18}O$ values that are too high to be consistent with the Dodson closure temperature of quartz.

The greatest differences between Figs. 6 and 7 are due to the mode effect causing the isotopic composition of feldspar to shift by exchange with either hornblende or quartz below the Dodson closure temperature of either or both mineral. In rocks rich in hornblende and poor in both quartz and feldspar, quartz may also have its isotopic composition shifted by exchange with hornblende
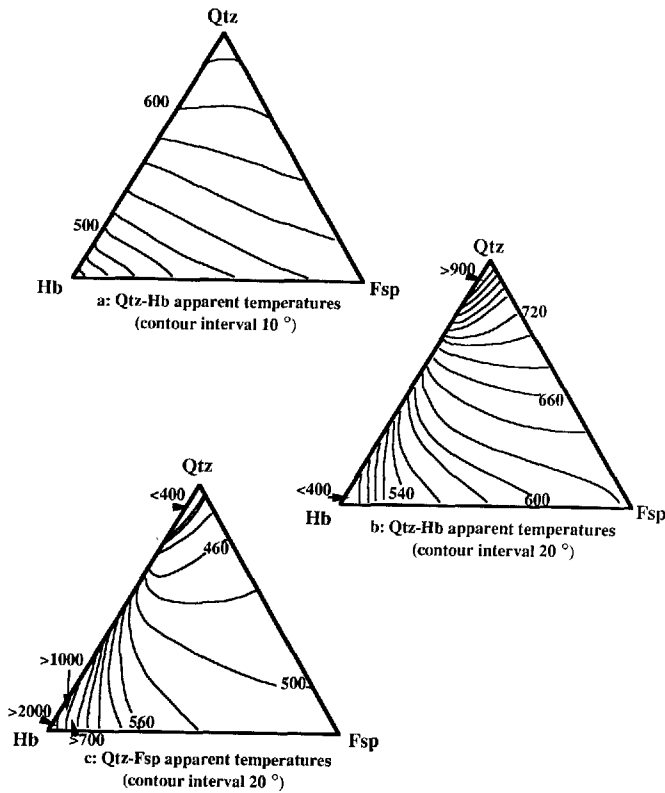
Fig. 7a–c. Contour of the temperatures that would be recorded by the bulk compositions of quartz and hornblende **a**, feldspar and hornblende **b** and quartz and feldspar **c** pairs in Qtz-Fsp-Hb rocks, as calculated by the FGB model. See text for discussion
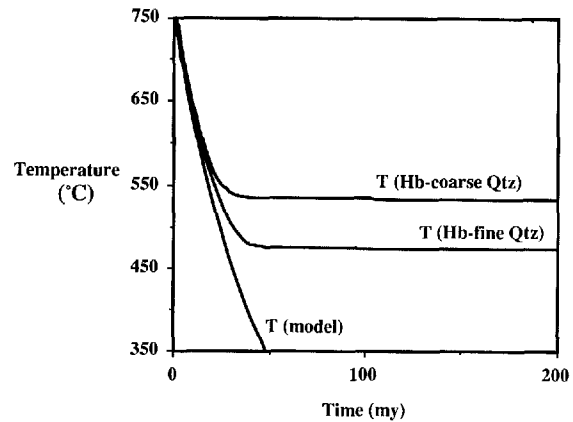

Fig. 8. Plot of the temperatures recorded between fine quartz (0.1 mm half-thickness) and coarse quartz (1.0 mm half-thickness), and coarse hornblende (1.0 mm half-thickness), in a rock composed of 90% hornblende, 9% coarse quartz and 1% fine quartz (by mode), as a function of time as the rock cools. A curve showing the actual temperature as a function of time is shown for comparison (T model). Note that two grain size fractions of the *faster* diffusing mineral (Qtz) take on different isotopic compositions by diffusional exchange with a slower diffusing mineral (Hb). This is contrary to the predictions one would make based on the application of Dodson's equation to stable isotope interdiffusion

below the Dodson closure temperature of hornblende. Results would be different in rocks containing minerals with different relative fractionations and diffusion coefficients, but additional calculations with a variety of minerals have shown that the results shown here are representative. Because of the large number of possible permutations of fractionation factors, diffusion coefficients and modal abundances, rocks containing three or more minerals can conceivably record a large span of fractionations by closed system processes alone. Additional calculations have shown that among the possibilities is a near concordance of mineral thermometers, none of which record the Dodson closure temperature of one of the refractory minerals in a rock. These results indicate that the effects of diffusive exchange must be evaluated before interpreting the mineral fractionations, concordant or discordant, recorded within any rock in which diffusion could have acted over observable scales.

Variable grain size

An additional result of mineral interdiffusion is the potential for isotopic fractionation between different grain sizes of the same mineral in a rock. This effect could be approximated for the mineral with the higher Dodson closure temperature by using Dodson's equation. The analysis predicts that larger grains will record higher temperature fractionations with the "reservoir" than will

smaller grains. This effect provides a potentially useful tool for estimating the value of diffusion coefficients of natural minerals within rocks (e.g. Sharp 1991).

If modal abundances are such that the FGB model predicts a significant "mode effect", differences in grain size may also lead to differences in composition for the fast diffusing mineral as well, even when the Dodson closure temperature of all such grain size populations are below the Dodson closure temperature of a coexisting, slow diffusing mineral. This effect is illustrated by calculations made for a rock which is modally dominated by a single grain size of a mineral with a low diffusion coefficient (90% hornblende with a 1 mm half-thickness), with the remainder being composed of two size fractions of a faster diffusing mineral (9% of 1 mm quartz, and 1% of 0.1 mm quartz). The results are shown in Fig. 8 as a plot of apparent temperature of each size fraction of quartz recorded by its fractionation with hornblende, throughout the cooling history. At high temperature the two grain sizes of the fast diffusing mineral have the same isotopic composition, as would be predicted by an analysis based on Dodson's equation. However, as this rock continues to cool the grain size fractions diverge in isotopic composition as they "close" with respect to the matrix of the slow diffusing mineral at a temperature dependent on their grain sizes.

As was seen in the calculation of isotopic profiles preserved within minerals, the mode effect can lead to a fast diffusing mineral taking on the characteristics normally expected of a slow diffusing mineral (diverging grain size populations). If interpreted in terms of Dodson's equation, the results of these calculations could in fact be used to derive an apparent (and incorrect) set of values for D_0 and Q for the apparently "slow" diffusing mineral, quartz.

Applications

The preceding examples describe calculations that predict a dramatic range of stable isotope profiles and integrated mineral fractionations that will be preserved in rocks. The corollary of these predictions is that the results of inter-diffusion can preserve clear records of the geologic history (temperature; open vs closed system behavior, cooling rate) and kinetic characteristics (D_0; Q; diffusion domains) of natural minerals. The usefulness of the FGB model in applications to study these records can be described in terms of several broad categories.

Thermometry

This model provides a means to evaluate the significance of the temperatures recorded by stable isotope thermo-meters in terms of the geologic history, diffusional charac-teristics, grain sizes, and modes of minerals in a rock. It can also predict the rock types in which meaningful peak temperatures will be most likely to be recorded. In addi-tion, one can now make specific predictions of which minerals within a given rock should be zoned, and which should most nearly preserve peak temperature composi-tions within their cores. This information could be used to guide thermometry based on new microanalytical sampling techniques, as well as with conventional bulk analysis. Application of FGB modeling to many major rock types is treated in detail in Eiler et al. 1993.

Evaluation of open vs closed system behavior

The predictions of the FGB model include a large spec-trum of concordant and discordant fractionations in rocks, produced by closed system processes alone. One potential use for this model is to evaluate whether the fractionations seen among minerals in a given rock are consistent with a closed system behavior, or require ex-change with an external reservoir (i.e. infiltrating fluids). The results of such modeling could potentially be counter-intuitive. Highly discordant thermometers may fit a model of closed system cooling, and conversely, concordant thermometers could indicate open system alteration (e.g. concordant temperatures in a quartz-rich rock from Fig. 7a–c would indicate elevation in feldspar $\delta^{18}O$ from an external source). These are several characteristics of stable isotope systematics which can be taken as a strong indicators of diffusional exchange. Consistent, interpret-able dependence of composition on grain size is a charac-teristic suggested by earlier descriptions of stable isotope diffusion. The FGB model adds the dependence of closure temperature on mode as an indicator of closed system diffusional exchange.

Determination of cooling rate

If a rock has only experienced closed system interdiffu-sion, the observed mineral compositions or profiles are a function of cooling rate. Use of the FGB model yields more accurate cooling rates for rocks which do not con-tain the large amounts of a fast diffusing mineral required by other models (e.g. Dodson 1973, 1986; Javoy 1977; Giletti 1986).

All estimates of cooling rate are subject to con-siderable imprecision. Closure temperatures (both by Dodson's equation and the FGB model) are relatively insensitive to cooling rate, leading to uncertainties in $\partial T/\partial t$ of from a factor of two to ten, based simply on analytical uncertainties in stable isotope ratio mea-surement (Giletti 1986; Jenkin et al. 1990). However, the data required to make such order-of-magnitude estimates from stable isotope data are relatively easy to obtain from most rocks. Therefore this method could be useful for cooling rate determinations in rocks for which geo-chronology is impractical.

Not only are cooling rates determined from oxygen isotope fractionations relatively imprecise, but models based on Dodson's equation will contain large systematic errors in many rock types. This is illustrated in a plot of the cooling rate inferred from Dodson's equation as a function of mode in a rock composed of hornblende and feldspar, whose fractionations were calculated using the FGB model (Fig. 9). The actual cooling rate at the Dodson closure temperature of hornblende was $10\,°C/my$. In a rock composed of two minerals, dominated by a mineral with a high Dodson closure temperature (i.e. large diameter or slow diffusion coefficient), cooling rates will be inferred to be orders of magnitude slower than they actually were. Application of cooling rate estimates for three mineral systems based on Dodson's equation were evaluated using our FGB results (Figs. 7a–c) as input for MacCool, a computer program (Jenkin et al. 1990) which fits cooling rate using the model of Giletti. This model
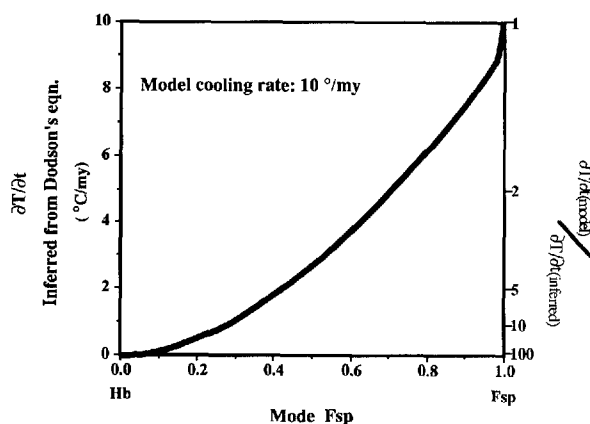

Fig. 9. Dodson's equation can be used to calculate inferred cooling rates recorded in the closure temperature between two minerals, as calculated with the FGB model. The results of such calculations for model rocks containing only feldspar and hornblende are shown. The left hand vertical scale is the cooling rate inferred from Dodson's equation and the right hand vertical scale is the ratio of the inferred cooling rate to the model cooling rate at the Dodson closure temperature of hornblende ($10\,°C/my$ for this example). Systematic errors of up to 4 orders of magnitude difference are made for extreme cases of modal abundance. Note that the cooling rate inferred from Dodson's equation is always lower than the model cooling rate for rocks containing two minerals, but can be greater or less than the model cooling rate for rocks with three or more minerals

erroneously indicated that most rocks experienced open system exchange, and calculated cooling rates that were either too high or too low for all rocks containing a modal minority of feldspar.

Determination of diffusion coefficient

Recent experimental studies have demonstrated that the volume diffusion coefficient in minerals is a function of the composition of coexisting fluid (water fugacity, H_2 fugacity, proton activity) (Yund and Anderson 1978; Giletti and Yund 1984; Elphick et al. 1986; Elphick and Graham 1988; Farver and Yund 1990). Estimation of the diffusion coefficient in a given mineral could therefore serve as a powerful tool for understanding the effects of fluid histories on diffusivity, or interpreting fluid history based on experimentally determined fluid effects. The FGB model could be used to estimate diffusion coefficients of minerals within rocks which have known cooling rates, and are independently known to have undergone closed system retrogression. In such a case, calculation of observed profiles and/or integrated fractionations could be made for a variety of values of D_0 and Q for the mineral of interest. These calculations could provide estimates of mineral diffusivities in the geologic conditions they experienced, or estimates of diffusivity for minerals for which no experimental determinations have been made.

Tests of the FGB model and grain boundary mobility

The applicability of the FGB model to a given size domain in a rock could be tested by conventional stable isotope thermometry of cogenetic suites having large variations in mode, and by in situ microanalysis of isotope zonation of minerals in a variety of textural surroundings from the same rock. Tests of the scales at which the FGB model succeeds and fails will also allow study of the extent of grain boundary mobility during a rock's retrograde history. Determination of which style of grain boundary mobility (extensive over thin section size domain, only between touching grains, or an intermediate case) best describes the fractionations and profiles observed in a rock could be used as evidence for the nature of the grain boundary environment in the setting experienced by that rock. Future modeling to accompany such studies should include an integration of diffusional penetration or double diffusive models with the FGB model.

Summary

The FGB model provides a framework in which the results of stable isotope interdiffusion can be interpreted. The inherent assumptions of this model, most importantly the description of grain boundaries as regions of relatively rapid diffusion, require careful consideration of the system the user describes and models. This model can be used to describe cases of grain boundary mobility ranging from one dimensional exchange between touching grains to three dimensional grain boundary equilibration over any

scale. The primary contribution of this model, however, is that it allows one, for the first time, to consider the effects of diffusion between non-touching grains, without needing to make assumptions about the diffusivity, profiles or isotopic change of any of the minerals involved.

When mass balance terms are included in a description of stable isotope diffusion, closure temperatures become a strong function of modal abundance and the differences in diffusion coefficients between all coexisting minerals. These factors can be as significant as the thermal history and the grain size, shape and diffusion coefficient of a slow diffusing mineral. The FGB model is a flexible method for incorporating all of these variables in solving a stable isotope diffusion problem.

Appendix

Scaling factors for two mineral interdiffusion

Lasaga (1983) derived two scaling factors, β/γ and γ', which uniquely describe the profiles produced in the diffusion couple between touching grains. Lasaga (1983) provides examples of the expected cation zonation within a very slow diffusing mineral (garnet) undergoing exchange with a relatively fast diffusing mineral (cordierite) for various values of these scaling factors. The additional mass balance terms used in our model to describe diffusional exchange between the surfaces of non-touching grains can be inserted into Lasaga's formulation for β, both allowing the conceptual comparison of the two models and providing a means of estimating the results of interdiffusion as described by our model before undertaking the detailed numerical calculations. The scaling factors calculated using the modified equations below cannot be directly compared to those of Lasaga because of changes made to conform with conventions used to describe stable isotope ratios and fractionations. The modified equations can, however, be used to calculate the approximate difference in the preservation of profiles between the physical conditions described by the model of Lasaga (diffusion between touching surfaces) and those described by the FGB model (diffusion between non-touching grains).

The model of Lasaga is formulated for cation diffusion between two semi-infinite sheets at their points of contact only, and will provide only approximations for the calculations involving three or more minerals. We recommend that any final calculations involving rocks in which non-touching grains may have undergone stable isotope exchange be made with the FGB model. References below to equations from Lasaga et al. (1977) are discriminated by an asterisk.

The additional terms considered in the FGB model must be included in the flux balance equation (Eq. 38*). Equation 34* states:

$$D_j(t) * \frac{\partial C_j^i}{\partial x} \cong 2 * \alpha_j * \sqrt{\frac{D_j^i * t}{\pi}}$$

(evaluated at x = 0)

If concentrations are approximated with δ values, and the concentration of the element whose isotopes are being considered is allowed to vary from mineral to mineral, the substitution can be made:

$$\delta_j = \delta_j * \frac{v_j}{V_j} \tag{A1}$$

where v_j is the stoichiometric coefficient of the element of interest in phase j, and V_j is the molar volume of phase j. If we assume $\partial(v_j/V_j)/\partial X = 0$, then Eq. (34*) simplifies to:

$$D_j(t) * \frac{\partial \delta_j}{\partial x} \cong 2 * \alpha_j * \frac{V_j}{v_j} * \sqrt{\frac{D_j^i * t}{\pi}}$$

The left hand side is equal to the flux per unit area of species i through the surface of phase j. The surface integration, and imposition of flux balance may now be included to arrive at the mass balance equation analogous to Eq. (38*):

$$\alpha_1 * \sqrt{\frac{D_1 * t}{\pi}} = \alpha_2 * \sqrt{\frac{D_2 * t}{\pi}} * \phi \qquad (A2)$$

where

$$\phi = \frac{Xg_2 * W_2^2 * V_2 * v_1}{Xg_1 * W_1^2 * V_1 * v_2}$$

and where α_1, α_2 are the α_j values for minerals 1 and 2 of a two mineral interdiffusion problem, Xg_j is the fraction of the total number of grains which are mineral i, and W_j is the width of the (square) face of mineral i through which diffusion occurs. ϕ is the term which contains the mass balance effects of exchange between non-touching grains. Xg_j can be easily related to the modal abundance, given W_j and grain thicknesses. ϕ is equal to 1 for diffusion between faces of touching grains with equal oxygen concentrations.

The equations relating equilibrium constant to initial and current concentrations (Eqs. 10*, 35* and 37*) have been modified to conform to conventional stable isotope notation. In order to retain the convenient $\Delta(i\text{-}j)$ notation, and to allow Δ to be linearized with time (required for Eq. 35*), we have assumed a cooling rate such that $1/T$ (degrees K) increases linearly with time, in which case $\Delta(t)$ can be well approximated as:

$$\Delta(t) = \Delta° * (1 - B * t) \qquad (A3)$$

where t is in millions of years from the start of cooling, $\Delta°$ is the isotopic fractionation at the start of cooling; and B is:

$$B = -2 * f * s * \sqrt{\frac{\Delta°}{f}} \qquad (A4)$$

where f is the constant describing the temperature dependence of Δ, and s is a constant describing the cooling path:

$$s = \frac{\dfrac{1}{T} - \dfrac{1}{T°}}{t} \qquad (A5)$$

where $T°$ is the temperature (degrees K) at the start of cooling.

The lineralization of δ_j^a with time is described by the equivalent of Eq. 36*:

$$\delta_1 = \delta_1° - \alpha_1^* t$$
$$\delta_2 = \delta_2° + \alpha_2^* t \qquad (A6)$$

If these are substituted into the equation describing the equilibrium fractionation:

$$\delta_2 - \delta_1 = \Delta(t) = \Delta° * (1 - B * t) \qquad (A7)$$

We may combine the resulting equation with Eq. A2 and solve for α_1 and α_2:

$$\alpha_1 = \frac{\phi * \sqrt{\dfrac{D_2°}{D_1°}} * (-\Delta° * B)}{1 + \phi * \sqrt{\dfrac{D_2°}{D_1°}}} \qquad (A8\text{-}1)$$

$$\alpha_2 = \frac{-\Delta° * B}{1 + \phi * \sqrt{\dfrac{D_2°}{D_1°}}} \qquad (A8\text{-}2)$$

The equation for α_1 is the equivalent to Eq. 31 from Lasaga (1983) defining β. For constant δ' and γ, the curves of Lasaga (1983) show that changes in β of approximately a factor of 10 dramatically changes the diffusion profiles preserved within minerals. In Fig. A1 we have plotted α_1 and α_2 as a function of Log(ϕ). When ϕ is equal to 1 the model of Lasaga applies, while the FGB model applies for
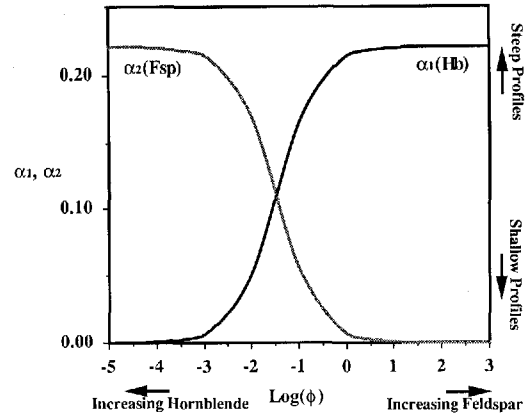

Fig. A1. Plot of α values for minerals 1 (hornblende) and 2 (feldspar) as a function of ϕ (see text for discussion). ϕ equal to 1 corresponds to diffusion only between touching faces of feldspar and hornblende. Values not equal to 1 correspond to a fast grain boundary model for diffusion between unequal modes. Increasing values of α correspond to steeper profiles. As the modal abundance of hornblende increases, its diffusion profile becomes more shallow and a diffusion profile develops in feldspar. Exact curves and their crossover points will differ for different mineral pairs

any value of ϕ. The diffusion coefficients for this example are those of hornblende (mineral 1) and feldspar (mineral 2), and s is a value corresponding to a cooling rate of approximately 10°/my at high temperature. If grain sizes and oxygen concentrations are approximately equal, then high ϕ values correspond to modal dominance of feldspar, and low ϕ values correspond to modal dominance of hornblende. Similar plots for minerals with other diffusion coefficient ratios could be made using (Eqs. A8-1, 8-2) as a preliminary test of the influence of the mode effect on diffusion profiles.

Appendix

Table of variables

T	temperature
T°	temperature at the start of cooling
T_c	closure temperature
t	time
x	distance
Q	diffusional activation energy
R	gas constant
A	diffusional geometric parameter
A_j	surface area of mineral grain j
W_j	width of mineral grain j
Xg_j	fraction of total grains being mineral j
V_j	molar volume of mineral j
v_j	stoichiometric coefficient of element of interest in mineral j
D_0	diffusional pre-exponential factor
D_j^i	chemical diffusion coefficient of species i in phase j
D_j	tracer diffusion coefficient of isotope of interest in phase j
a	grain size
C_j^i	concentration of species i in phase j
$\delta_{boundary}^r$	isotopic composition of reference mineral on the grain boundary
$\delta_{boundary}^j$	isotopic composition of mineral j on the grain boundary
$\delta_j°$	isotopic composition of mineral j at the start of cooling

δ_j	isotopic composition of mineral j
J_j	flux per unit area of isotope of interest from mineral j, at constant elemental concentration
B	linearization constant for change in isotopic fractionation with time
f	constant for temperature dependence of the fractionation between two minerals
s	constant describing cooling curve
ϕ	mass balance term for diffusional exchange between non-touching grains
α_j	linearization constant for change in isotopic composition of mineral j, on its grain boundary with time
Δ	fractionation of δ_j values between two minerals
Δ°	Δ value at the start of cooling

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