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Fluid-absent diffusion kinetics of Al inferred from retrograde metamorphic coronas

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ABSTRACT

Estimates are obtained for diffusion coefficients of Al through polycrystalline hornblende layers during retrograde metamorphism using petrological studies of two types of coronas, with geologically based estimates of time scale. The observations indicate a combination of fluid-absent grain-boundary diffusion and intracrystalline diffusion in the presence of composition gradients whose magnitude for Al is constrained by mineral analyses. Corona growth is linked to diffusion by the results of steady-state modeling of the diffusion-controlled reaction. The estimated effective (bulk) diffusion coefficient D_{Al}^{eff} is $10^{(-24\pm2)}$ m^2/s, leading to a maximum estimate for the product of grain-boundary diffusion coefficient D_{Al}^{gb} and grain-boundary width, δ, of $10^{(-29\pm2)}$ m^3/s. In comparison with data in the literature, D_{Al}^{eff} is greater (by up to a few orders of magnitude) than intracrystalline Al diffusion coefficients (extrapolated from high-temperature experiments), as expected where grain-boundary diffusion is important. However, D_{Al}^{eff} is smaller than would be expected if grain boundaries had high contents of dissolved H_2O. The results are consistent with H_2O concentration being an important kinetic control on retrograde reaction.

INTRODUCTION

Mineralogical layering produced by metamorphism is characteristic of diffusion-controlled reaction (Fisher, 1978). Using the principles of steady-state diffusion of oxide components (e.g., $AlO_{3/2}$, MgO) with local equilibrium (Fisher, 1973), Joesten (1977) modeled the development of layers between two reactant minerals. An open-system extension of the method (Ashworth and Birdi, 1990) is applicable to layered coronas (e.g., Fig. 1), with the complication that the reaction changes during the growth of some coronas (Johnson and Carlson, 1990; Carlson and Johnson, 1991). Although interdiffusion of several major elements is involved, the modeling clearly implies different mobilities among the cation-forming elements. In the examples studied by Ashworth and Birdi (1990) and Ashworth et al. (1992), although the overall reaction progress is controlled by components with relatively large diffusive fluxes, the distribution of minerals among layers is strongly influenced by the relatively immobile elements Al and Si. Restricted diffusion of Al, in particular, produces an Al-rich layer (adjacent to the Al-rich reactant mineral, plagioclase), separated from an Al-poor layer (adjacent to reactant olivine or pyroxene) by a thin transition layer (Fig. 1) with intermediate Al content.

The modeling has no absolute time scale, and does not use concentration gradients (it implicitly relies on relative chemical-potential gradients). However, the transition layer suggests a gradient in Al concentration between the Al-rich and Al-poor layers. A rough estimate of diffusion coefficient D_{Al} (m^2/s), for comparison with other diffusion studies, can be obtained from Fick's first law,

$$J_i = -D_i \frac{dc_i}{dx} \quad (1)$$

if the gradient dc_{Al}/dx (mol/m^4) can be constrained along with the time scale for the flux J_{Al} (mol/m^{2}s) through the transition layer.

Equation 1 strictly applies to diffusion through a particular medium. If this is an aqueous fluid in grain boundaries, concentration gradients are small, but diffusion coefficients are so much greater than in solids that diffusion through the fluid should be dominant. Walther and Wood (1984) argued for this process during prograde metamorphism in which H_2O is produced by dehydration reactions. On the other hand, the corona-forming reactions of Ashworth and Birdi (1990) and Ashworth et al. (1992) are retrograde and consume H_2O. Their small scale (commonly ~100 μm, Fig. 1) compared with domains of diffusion-controlled reaction during prograde dehydration (commonly 1–10 mm: e.g., Foster, 1977) suggests that diffusion in the coronas was hindered by fluid absence (cf. Walther and Wood, 1984). If aqueous fluid infiltrated along fractures, the distribution of hydration products should be nonuniform (localized near the fractures: Rubie, 1986; Carlson and Johnson, 1991), whereas, in the rocks studied here, coronas grew at all contacts between the reactant minerals. It is very unlikely that a fluid phase penetrated all the grain boundaries within the corona (Fig. 1), yet the component H_2O was pervasively available for hydration reactions at internal contacts between layers. This is explained by diffusion of H_2O from fractures to

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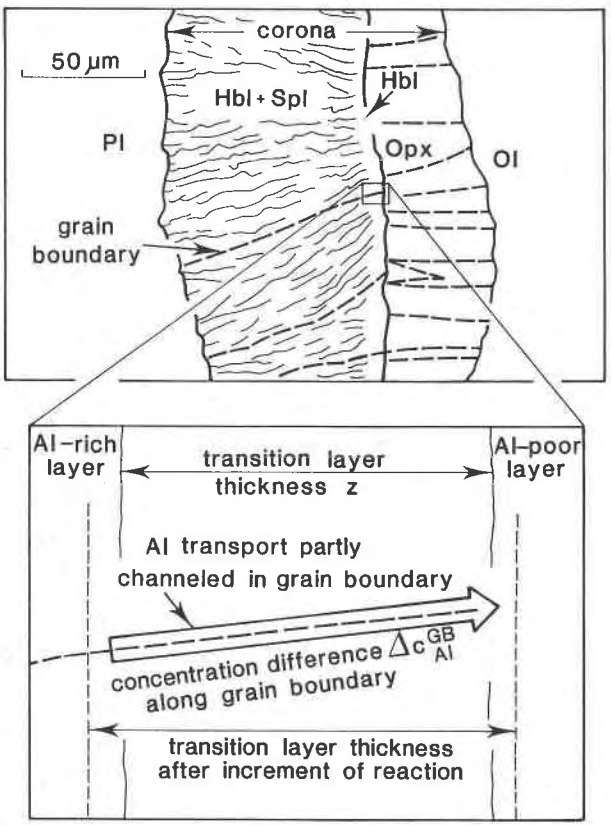

Fig. 1. Petrographic sketch of the layer structure of a corona (specimen 53P of Ashworth and Birdi, 1990) and diagram to illustrate growth accompanied by diffusion. The transition layer has an Al content intermediate between the Al-rich layer adjacent to the Al-rich reactant mineral (plagioclase) and Al-poor layer adjacent to olivine. During an increment of reaction, growth of the layer is coupled with diffusion through it, whereby Al diffuses toward the Al-poor layer. Part of this flux is pictured as channeled in the grain boundary rather than being volume diffusion through the bulk hornblende.

coronas and through them: H_2O was a fast-diffusing component in the open system.

Solid-state diffusion is consistent with the inferred immobility of Al relative to the large-flux elements, Mg and Fe in coronas around olivine (Ashworth and Birdi, 1990) and Ca around clinopyroxene (Ashworth et al., 1992), since Al is a slow-diffusing cation in experimental studies of intracrystalline diffusion (Sautter et al., 1988a). By comparison, Foster (1981) inferred relatively mobile behavior of Al in a prograde, possibly fluid-present reaction.

In addition to intracrystalline diffusion (also called volume or lattice diffusion), grain-boundary diffusion is possible in the solid state. The grain boundary can provide an easier route for diffusion than the crystal interior ($D_i^{gb} > D_i^{vol}$), particularly at low temperatures, because the grain-boundary region of the crystal is disordered (Fisher and Elliott, 1974; Rubie, 1986). It can be considered as a solid-solution medium and may contain relatively high concentrations of diffusion-catalyzing components, notably H_2O (Rubie, 1986). During corona-forming reactions studied by Ashworth et al. (1992), volume diffusion operated to produce both epidote inclusions clouding plagioclase and zoned amphibole in some Al-poor layers of coronas (Al-rich rims ~1 μm wide adjacent to grain boundaries, surrounding Al-poor cores of grains). Diffusion along grain boundaries is also indicated, which produces corona growth on a scale of ~100 μm without obvious intracrystalline concentration gradients for the mobile components. Many grain boundaries are available, since grain dimensions perpendicular to diffusion direction are typically 1–100 μm (Fig. 1).

Across the thin transition layers considered here, zoning is detected only in a direction perpendicular to the layer contacts, and diffusion should be approximately unidirectional, making Equation 1 applicable. Both grain-boundary and volume diffusion of Al are expected as parallel processes, the grain-boundary flux being associated with a grain-boundary concentration gradient (Fig. 1). The quantity to be estimated is a bulk diffusion coefficient, D^{eff}_{Al}, for combined grain-boundary and volume diffusion.

Relation between modeling and diffusion coefficients

The modeling is one dimensional; i.e., bulk diffusive fluxes are modeled as perpendicular to planar contacts between layers. This is reasonable where coronas are thin relative to reactant grain size. Modeling gives computed fluxes through the transition layer, J_i^{model}, per unit of reaction progress ξ, associated with molar amounts of minerals k produced, which can be converted (using molar volumes V^k) to the amount of layer growth G (symbols and units are listed in Table 1). It has been inferred by Ashworth and Birdi (1990) and Ashworth et al. (1992) that the transition layer grows at both contacts (and would contain an inert marker placed at the contact between reactant minerals before reaction: Joesten, 1977). The reference frame for diffusion is given by the instantaneous positions of the layer contacts (Nishiyama, 1983). In diffusion studies in general, fluxes depend on the choice of reference frame (Brady, 1975), and an apparent flux of a nondiffusing component may arise from bulk flow of the other components. However, in the coronas, fluxes are linked to layer-contact reactions. If the Al fluxes were spurious, the real reactions would be Al-conserving, and the intermediate Al content of the transition layer could only be an accident of fortuitous addition and subtraction of other components. It is much more likely that the transition layers, found in two quite different types of corona, are produced by Al transport toward the Al-poor layer.

The growth rate of the layer, dz/dt, and the flux, J_i, of Equation 1 are related to G and J_i^{model} by

$$\frac{dz}{dt} = \left(\frac{G}{A}\right)\frac{d\xi}{dt} \tag{2}$$

and

$$J_i = \left(\frac{J_i^{model}}{A}\right)\frac{d\xi}{dt}. \tag{3}$$

In the steady-state modeling, minerals are treated as homogeneous (unzoned) phases. Nevertheless, diffusion implies concentration gradients. A reasonable assumption is that each flux J_i is constant throughout a given layer, i.e., reaction is confined to layer contacts (Joesten, 1977; Ashworth and Birdi, 1990). If, in Equation 1, D_i is also approximately constant, then so is dc_i/dx. For diffusion in medium k through a layer of thickness z,

$$\left(\frac{dc_i}{dx}\right)^k \approx \frac{\Delta c_i^k}{z}.$$

For pure volume diffusion, Equation 1 becomes

$$J_i \approx \frac{-D_i^{vol}\,\Delta c_i^{vol}}{z}. \quad (4)$$

The concentration difference Δc_i^{gb} in the grain boundary may differ from Δc_i^{vol} (see below). Since the flux is measured per unit cross-sectional area (perpendicular to flux) of the bulk layer, it is related to concentration gradients by the bulk or effective diffusion coefficient, D_i^{eff} (Joesten and Fisher, 1988, p. 724). For pure grain-boundary diffusion,

$$J_i \approx \frac{-D_i^{eff}\,\Delta c_i^{gb}}{z}. \quad (5)$$

For combined grain-boundary and volume diffusion, with a weighted average or effective concentration difference Δc_i^{eff},

$$J_i \approx \frac{-D_i^{eff}\,\Delta c_i^{eff}}{z} \quad (6)$$

of which Equations 4 and 5 are limiting cases. Combining Equations 2, 3, and 6, and integrating gives the equation used below to estimate D_{Al}^{eff}:

$$z^2 \approx \frac{-2G\,\Delta c_i^{eff} D_i^{eff} t}{J_i^{model}}. \quad (7)$$

This is comparable with Equation 2 of Brady (1983).

For pure grain-boundary diffusion,

$$D_i^{eff} = \tau\beta D_i^{gb}$$

(symbols defined in Table 1). Tortuosity (τ) is discussed by Brady (1983). For straight grain boundaries approximately parallel to the bulk flux (a fair approximation in the coronas, Fig. 1), $\tau \approx 1$ and $\beta \approx N\delta$. Strictly, τ is slightly less than 1 for grain boundaries oblique to bulk flux, whereas $N\delta$ slightly underestimates β (by a factor of $\pi/2$ if grain-boundary orientation is random in the plane perpendicular to flux: Smith and Guttman, 1953). These two small uncertainties tend to cancel out. Unlike N, δ is not readily measured (estimates range from ~1 to ~100 nm: Rubie, 1986; Joesten, 1991; Farver and Yund, 1991), so the quantity usually estimated is the product $D_i^{gb}\delta$. This can be calculated from

$$D_i^{gb}\delta \approx \frac{D_i^{eff}}{N} \quad (8)$$

which gives a maximum estimate because volume diffusion is neglected.

TABLE 1. Explanation of symbols and units

c_i^k	concentration of component i in medium k* (mol/m³)
$(dc_i/dx)^k$	spatial gradient of c_i^k (mol/m⁴)
Δc_i^k	difference in c_i^k across a layer (mol/m³)
Δc_i^{eff}	effective average Δc_i^k for combined grain-boundary and volume diffusion (mol/m³)
D_i^k	diffusion coefficient of component i in medium k (m²/s)
D_i^{eff}	effective (bulk) diffusion coefficient of component i (m²/s)
J_i	bulk (volume + grain boundary) diffusive flux of component i (mol/m²s)
n_i^k	$= c_i^k V^k$ for mineral k (moles of the component per mole of the mineral)
t	time (s)
V^k	molar volume of mineral k (m³/mol)
β	fraction of cross-sectional area occupied by grain boundaries
δ	width of a grain boundary (m)
τ	tortuosity factor for grain boundaries
	Properties of a layer of a corona
A	cross-sectional area parallel to layer contacts (m²)
N	number of grain boundaries per unit length of a traverse parallel to layer contacts (number/m)
z	thickness perpendicular to layer contacts (m)
	Quantities in steady-state local-equilibrium modeling of a layer
ξ	reaction progress (moles PI consumed)
G	growth during unit of reaction progress (m³/mol Pi consumed)
J_i^{model}	flux of component i during unit of reaction progress (moles of the component per mole of PI consumed)

* Medium k = gb (grain boundary) or vol (for volume diffusion).

GEOLOGICAL CONSIDERATIONS

The duration of reaction, t in Equation 7, must be constrained. Temperature is also important for comparison with other studies. In northeast Scotland (Ashworth and Birdi, 1990) the coronas formed under amphibolite-facies conditions (Kneller and Leslie, 1984: estimated temperature range 600 ± 100 °C), in gabbroic intrusions emplaced during regional metamorphism at approximately 500 Ma. The samples from Norway (Ashworth et al., 1992) are granulites of Precambrian origin, in which the corona reaction was associated with thrust transport of the Jotun Nappe (Ashworth et al., 1992), ending at approximately 395 Ma. The suggested conditions are epidote-amphibolite facies (550 ± 100 °C). Both field areas show evidence of more complete hydration near fractures, leading to thorough amphibolitization in fault zones or shear zones (Emmett, 1980; Kneller and Leslie, 1984) due to infiltrating fluid.

The time scale of regional cooling and deformation can hardly have been less than 1 m.y. Detailed radiometric work in the Scottish orogenic belt indicates a cooling history lasting tens of millions of years (Dempster, 1985). In northeast Scotland, pegmatites approximately 30 m.y. younger than the gabbro postdate its deformation (Kneller and Leslie, 1984). In Norway, stratigraphic synthesis (Hossack et al., 1985; Hossack and Cooper, 1986) gives a maximum duration of 40 m.y. for the thrusting. Though metamorphic reaction may have outlasted deformation,

Table 2. Summary of data and results

Area	NE Scotland	Jotun Nappe, Norway
Specimen no.	53P	359
Layer	Hbl	Hbl + Qtz
Layer thickness, z (m)	$(10 \pm 2) \times 10^{-6}$	$(10 \pm 4) \times 10^{-6}$
Grain boundary count, N (number/m)	$(3 \pm 1) \times 10^{4}$	$(9 \pm 3) \times 10^{4}$
Model growth/flux ratio, G/J_{Al}^{model} (m^3/mol Al)	$(9.6 \pm 3.0) \times 10^{-5}$	$(3.3 \pm 1.8) \times 10^{-4}$
Concentration difference, Δc_{Al}^{eff} (moles Al/m^3)	$-1.3 \times 10^{(3.5 \pm 0.5)}$	$-3.2 \times 10^{(2.5 \pm 0.5)}$
Time, t (s)	$3 \times 10^{(14 \pm 1)}$	$3 \times 10^{(14 \pm 1)}$
Effective bulk diffusion coefficient: D_{Al}^{eff} (m^2/s)	$10^{(-24.4 \pm 1.8)}$	$10^{(-24.3 \pm 2.1)}$
Assuming dominantly grain-boundary diffusion: $D_{Al}^{gb}\delta$ (m^3/s)	$10^{(-28.9 \pm 2.0)}$	$10^{(-29.3 \pm 2.3)}$

Note: Ranges quoted for z and N are observed ranges in typical coronas. Uncertainties in G/J_{Al}^{model}, Δc_{Al}^{eff}, and t are discussed in the text. The full ranges for all these quantities are used in calculating the ranges quoted for D_{Al}^{eff} and $D_{Al}^{gb}\delta$; from Equations 7 and 8.

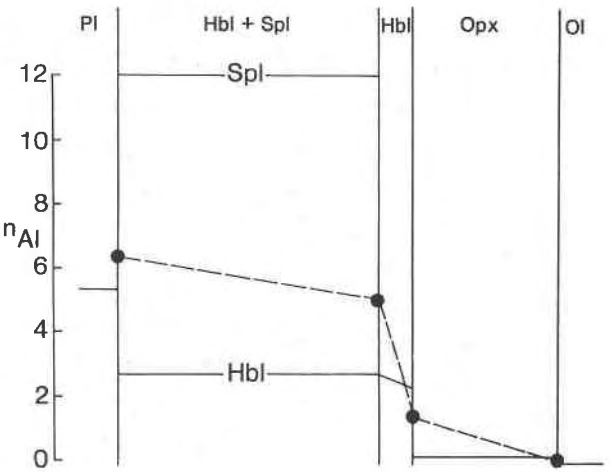

Fig. 2. Approximate Al contents, n_{Al} atoms per 24-O formula unit of mineral, indicated by typical data for the coronas from northeast Scotland. Relative thicknesses of layers are based on measurements in specimen 53P (Mongkoltip and Ashworth, 1983). The mineral-average model for grain-boundary composition is indicated by solid circles at layer boundaries, connected by dashed lines. The likely concentration difference, Δc_{Al}^{eff}, across the transition layer (Hbl) is considered to be bracketed between this model and the zoning estimated from electron probe data (solid line).

a time scale exceeding 100 m.y. is very unlikely, because the cooling history in Scotland was essentially over at 400 Ma (Dempster, 1985) and because unmetamorphosed lower and middle Devonian sediments unconformably overlie both uplifted metamorphic belts (Hossack, 1984; Mykura, 1991). To avoid any spurious impression of accuracy, a generous range of uncertainty (1–100 m.y.) is adopted for the time scale available for reaction in both areas. However, the corona-forming reactions require a supply of H_2O to produce hydrous minerals, so that the true duration of a reaction may be less than the time scale of metamorphic cooling, if H_2O is available for diffusion from fractures during only a small part of the retrograde history. In this case, the estimates to be derived for diffusion coefficients will be too low. The implications are discussed below.

Data and numerical results

In the coronas of Ashworth and Birdi (1990), the layer sequence is Pl|Hbl + Spl|Hbl|Opx|Ol (Fig. 1). The coronas considered from the study of Ashworth et al. (1992) have the sequence Pl|Ep + Qtz|Hbl + Qtz|Act ± Hbl + Qtz|Cpx. Although only two specimens are considered here, these are typical of their respective localities. The central layer in each sequence is the transition layer (Fig. 1). Table 2 shows values of z and N for this layer, measured microscopically, with the range of G/J_{Al}^{model} computed for the range of fluxes approximately reproducing the modal compositions of the layers.

The hornblende shows slight zoning, Δc_{Al}^{Hbl}, across the layer, which is measurable in favorable cases, such as unusually broad developments of the layer (Mongkoltip and Ashworth, 1983, their Fig. 5a). This is shown in Figure 2 (solid line across the hornblende layer) in terms of Al atoms per formula unit (n_{Al}^{Hbl}). It also gives a lower limit for the concentration difference along the grain boundary, the upper limit being one order of magnitude larger according to the following reasoning. Major-element contents in grain boundaries may smooth out some of the disparities between adjacent minerals and successive layers. The Al gradient across the transition layer should not greatly exceed that across the Al-rich layer, through which Al diffusion from the Al-rich reactant mineral is also required by the reactions (Ashworth and Birdi, 1990; Ashworth et al., 1992). A rough model fitting these requirements (dashed lines in Fig. 2) is based on the observation that in bimineralic layers (e.g., Hbl + Spl in Fig. 1) most grain boundaries are shared by both minerals. Thus their average Al content, $(n_{Al}^{Hbl} + n_{Al}^{Spl})/2$, gives an initial approximation to the grain-boundary Al content in this layer. The average between this and a typical Al content in the hornblende layer, n_{Al}^{Hbl}, gives the suggested grain-boundary Al content at the layer contact, $(3n_{Al}^{Hbl} + n_{Al}^{Spl})/4$; analogous averages are suggested at other contacts (solid circles in Fig. 2). In this picture, the difference in Al content across the transition layer accounts for much of the total difference across the corona and is regarded as placing an upper limit on Δc_{Al}^{gb} and hence also on Δc_{Al}^{eff}. Table 2 shows the possible range for Δc_{Al}^{eff} and the range of resulting D_{Al}^{eff} values from Equation 7.

Diffusion coefficients of other elements are poorly constrained because clear spatial trends in the mineral compositions are not seen. For Si, computed fluxes are also small, indeed zero in the Norwegian example because the assemblages are saturated with respect to SiO_2 (quartz present). For Ca, Mg, and Fe, since mineral compositions indicate that grain-boundary gradients are unlikely to be larger than for Al, the larger fluxes of Mg, Fe (Ashworth

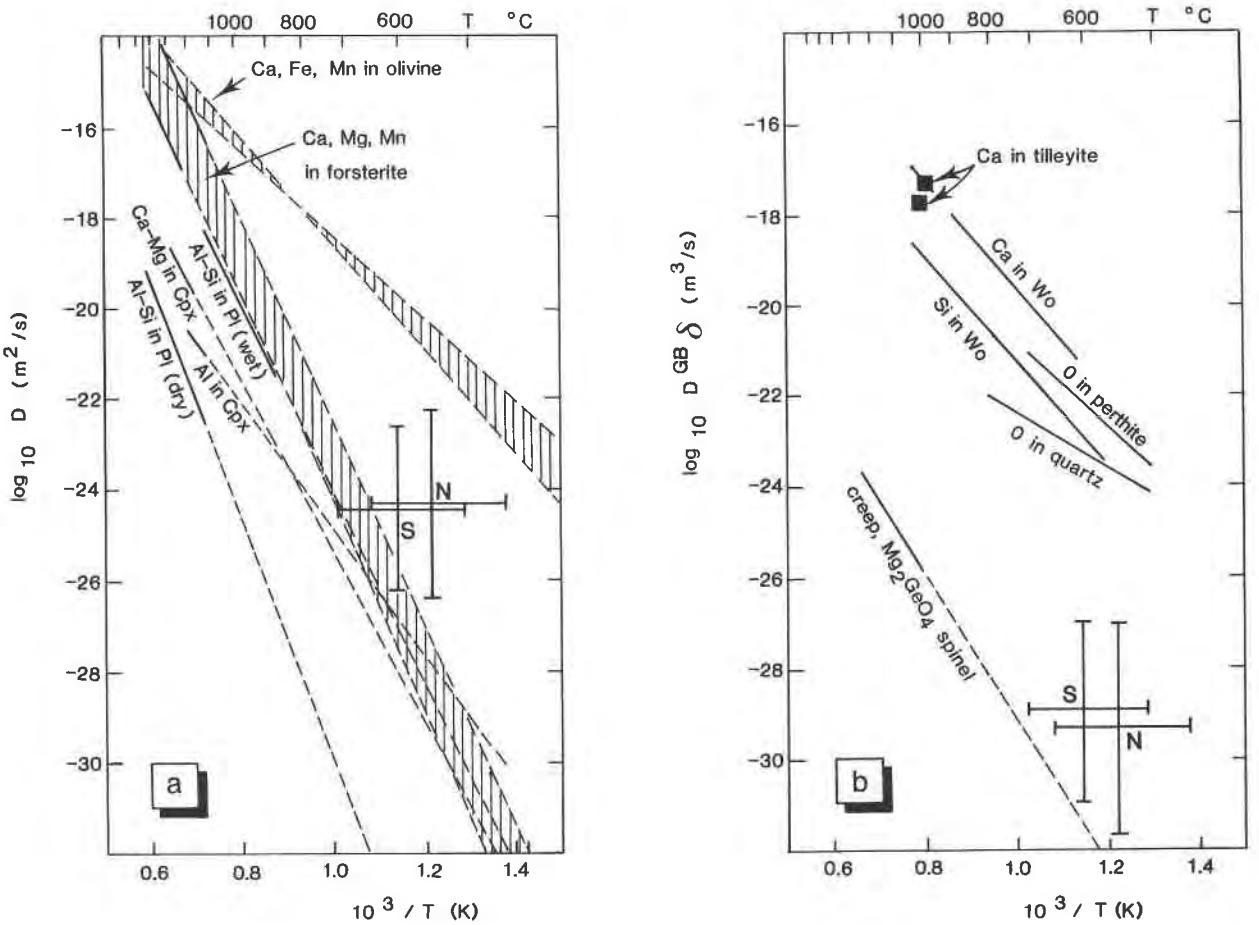

Fig. 3. Estimated kinetic parameters for the areas studied (N = Norway, S = Scotland), compared with data from the literature in Arrhenius diagrams. Dashed lines are extrapolations, from experimental temperature ranges indicated by solid lines. (**a**) Effective diffusion coefficients from the present study compared with intracrystalline diffusion coefficients from experimental studies. Data for Al-Si diffusion in plagioclase (An_{0-26}) under wet conditions (H_2O deliberately introduced) are from Yund (1986). Similar data for a wider range of plagioclase compositions are presented by Liu and Yund (1992). Other experimental studies are nominally H_2O-free (dry): Al-Si in plagioclase, Grove et al. (1984); Al in clinopyroxene, Sautter et al. (1988a, 1988b; Sautter, personal communication); Ca-Mg in clinopyroxene, Brady and McCallister (1983); Ca, Mg, and Mn in forsterite, Morioka (1981); Ca, Fe, and Mn in olivine (Fo_{90}) parallel to **c**, Jurewicz and Watson (1988). (**b**) Product of grain-boundary diffusion coefficient D^{gb} and grain-boundary width δ. Estimates from the present study are maxima (neglecting volume diffusion). Experimental data on creep deformation of dry Mg_2GeO_4 from Vaughan and Coe (1981) as treated by Rubie (1986). Hydrothermal experimental data for O, in perthite from Nagy and Giletti (1986) and in quartz from Farver and Yund (1991); inferred natural values for wollastonite and tilleyite from Joesten and Fisher (1988).

and Birdi, 1990), and Ca (Ashworth et al., 1992) indicate D_i^{eff} at least several times larger than D_{Al}^{eff}.

Diffusion kinetics in comparison with other studies

The two different reactions in different geological settings give consistent estimates for D_{Al}^{eff}, $10^{(-24\pm2)}$ m²/s (Table 2). Operation of grain-boundary diffusion implies $D_{Al}^{eff} > D_{Al}^{vol}$. Pure volume diffusion would imply $D_{Al}^{eff} = D_{Al}^{vol}$, and the upper part of the range, $10^{(-23.8\pm1.6)}$, should be preferred because Δc_{Al}^{vol} must be near the low end of the estimated range of Δc_{Al}^{eff} in Table 2. Comparison with experimental volume-diffusion data requires Arrhenius-law extrapolation from higher temperature experiments (Fig. 3a). Most data for Al refer to Al-Si interdiffusion in plagioclase, which may not be strictly comparable with hornblende, in which some Al is octahedral. There are some data for Al diffusion in clinopyroxene. The comparison is consistent with grain-boundary diffusion, because the D_{Al}^{eff} estimates are slightly higher than the extrapolated values, even for wet experiments in which H_2O catalyzes volume diffusion in feldspar (probably through H entering the crystal lattice: Liu and Yund, 1992). Because H_2O also catalyzes grain-boundary diffusion (Rubie, 1986), D_{Al}^{eff} for a corona is presumably time averaged over varying values at fluctuating H_2O contents. Relative

to Al, the greater mobilities of Ca, Mg, and Fe in coronas are comparable with their commonly higher intracrystalline diffusion coefficients (Fig. 3a).

The closeness of extrapolated D_{Al}^{vol} to D_{Al}^{eff} estimates in Figure 3a is consistent with pure volume diffusion on a slightly smaller scale than grain-boundary diffusion (as the petrography requires). A measure of volume-diffusion range is $\sqrt{D_i^{vol}t}$ (e.g., Freer, 1981). Comparably, across the transition layer, $z \sim \sqrt{D_{Al}^{eff}t}$, because the factor $(-2G\Delta c_{Al}^{eff}/J_{Al}^{model})$ of Equation 7 is close to unity in both examples. The scale of rim to core Al zoning in some Jotun corona amphiboles (~ 1 μm) is within an order of magnitude of z (~ 10 μm), suggesting D_{Al}^{vol} within two orders of magnitude of D_{Al}^{eff}. It has been mentioned that the D_{Al}^{eff} estimates are minima because the time scale may have been overestimated if duration of reaction was controlled by H_2O availability for hydration reactions. However, if a time scale many orders of magnitude shorter were invoked, it would imply D_{Al}^{eff} values higher by the same factor, i.e., no longer comparable with experimentally based estimates of D_{Al}^{vol}. Thus the results favor long time scales, unless the extrapolated D_{Al}^{vol} values are too low because a different intracrystalline mechanism comes into effect as temperatures fall below the experimental range, or because hornblende is not comparable with the experimental minerals.

Vance and O'Nions (1990) studied a prograde natural reaction that can be compared with this work. At approximately 550 °C, D^{eff} (species unspecified) is estimated to be $0.4–6.1 \times 10^{-17}$ m^2/s in rock matrix around growing garnets. Though much higher than the present results, this is regarded as too low to be attributable to diffusion in a fluid (Vance and O'Nions, 1990). Probably, in the prograde reaction, grain-boundary diffusion was assisted by higher H_2O contents than in the coronas.

The D_{Al}^{eff} values lead to maximum estimates for $D_{Al}^{gb}\delta$ of $10^{(-29\pm2)}$ m^3/s (Table 2) from Equation 8 (volume diffusion neglected). These are consistent with low H_2O content, being just above the minimum entertained by Rubie (1986) for H_2O-bearing solid grain boundaries. Experimental data for dry grain-boundary diffusion extrapolate below the present results (Fig. 3b). Much higher values have been obtained for grain-boundary diffusion in quartz and perthite (Fig. 3b), probably in fluid-absent grain boundaries nearly saturated with dissolved H_2O (Rubie, 1986). These wet experiments measure O isotope diffusion, which is not exactly comparable with cation diffusion, though it is also catalyzed by H_2O (Elphick et al., 1988; Farver and Yund, 1990). The wet experimental results are similar to estimates for natural cation diffusion (Fig. 3b) by Joesten and Fisher (1988). In their very thorough study of contact-metamorphic reaction between chert nodules and surrounding limestone, the diffusion coefficients were estimated indirectly by a method using chemical potential gradients and assuming c_i^{gb} values similar to c_i^{vol} in the minerals (Joesten and Fisher, 1988, p. 728). The reactions are prograde decarbonation reactions, e.g., calcite + quartz → wollastonite + CO_2, probably in the absence of aqueous fluid (Olsen et al., 1990), but presumably with CO_2 dissolved in grain boundaries and possibly with a CO_2 fluid phase present (Baumgartner et al., 1991; Joesten, 1991, p. 571). Evidently, CO_2 enhanced the diffusion rates in comparison with the coronas.

Conclusions

Despite admittedly large uncertainties, a consistent set of results emerges from the semiquantitative treatment of diffusion in the coronas. The two different reactions give similar estimates for D_{Al}^{eff} that are compatible with the petrographic evidence for fluid-absent grain-boundary diffusion interacting with volume diffusion. Extrapolation of available experimental data suggests that long time scales (>1 Ma) are required to account for the volume diffusion. Implied grain-boundary diffusion rates are much lower than in the prograde, CO_2-producing reactions studied by Joesten and Fisher (1988). Estimates of $D_{Al}^{gb}\delta$ are also lower than expected for highly hydrated grain boundaries (Rubie, 1986). Although H_2O diffused into the rocks to produce hydrous minerals, low contents of dissolved H_2O in the solid grain boundaries are indicated. The small scale of retrograde coronas can be attributed to the retarding effect of low H_2O concentrations on grain-boundary diffusion rates.

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