NaSi-CaAl interdiffusion in plagioclase

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Abstract

Average NaSi-CaAl interdiffusion coefficients ($\tilde{D}$) have been determined for the plagioclase Huttenlocher interval ($\sim An_{70}$ to $\sim An_{90}$) using the method of lamellar homogenization at 1500 MPa, 1050 to 900 °C, ~ 1.0 wt% H_2O added, and fugacities fixed at the magnetite/hematite buffer. There is a discontinuity in the Arrhenius relation at ~ 975 °C that may correlate with the destruction of the compositionally modulated structure in the $\sim An_{70}$ lamellae. The $\tilde{D}$ values are given by

$$\tilde{D} = 4 \times 10^{-16} \ m^2/s \ e^{(-103 \ kJ/mol/RT)} \quad (\sim 1050\text{--}1000 \text{ °C})$$

$$\tilde{D} = 11 \times 10^{-6} \ m^2/s \ e^{(-371 \ kJ/mol/RT)} \quad (\sim 975\text{--}900 \text{ °C}).$$

The $\tilde{D}$ values at these conditions are about 3 orders of magnitude larger than previously reported $\tilde{D}$ values for the same sample determined by dry annealing experiments in air (Grove et al., 1984). Average $\tilde{D}$ values for the peristerite interval ($\sim An_0$ to $\sim An_{26}$) were also determined at the conditions listed above and are given by

$$\tilde{D} = 3 \times 10^{-8} \ m^2/s \ e^{(-303 \ kJ/mol/RT)} \quad (1050\text{--}900 \text{ °C}).$$

Below about 975 °C there is little difference in the average $\tilde{D}$ values for the Huttenlocher and peristerite intervals, indicating that the effect of bulk composition is minor compared with the effect of H_2O or its components dissolved in a plagioclase crystal. Diffusion data for the Huttenlocher interval have been used to estimate cooling rates for chemically zoned plagioclase crystals reported in the Stillwater, Skaergaard, and Kiglapait intrusions. The cooling rates estimated using the dry, 1-atm data compare more favorably with independent estimates of cooling rates, although the latter are poorly constrained.

Introduction

A knowledge of NaSi-CaAl interdiffusion rates is important for understanding the kinetics of solid-state processes in plagioclase because compositional zoning and many microstructural relations are controlled by the slow rate of this process (Grove et al., 1984; Yund, 1986). Microstructures controlled by this coupled interdiffusion include the formation of exsolution lamellae associated with the peristerite, Huttenlocher, and Bøggild miscibility gaps as well as the development of *e* plagioclases (Smith, 1974). Most of these microstructures cannot be experimentally investigated because they form at low temperatures where the rate of NaSi-CaAl interdiffusion is very slow. One approach is to determine the rate of NaSi-CaAl interdiffusion at higher temperatures and to extrapolate the data to lower temperatures (Grove et al., 1984; Yund, 1986). This method yields information about the kinetics of transformations and can be used to constrain the thermal history of chemically zoned plagioclase crystals, provided that the mechanism of diffusion is the same at lower and higher temperatures.

When the interdiffusion rate is slow, it is difficult to use a conventional diffusion couple to determine diffusion coefficients. Brady and Yund (1983) used the lamellar homogenization method (Price, 1981) to estimate K-Na interdiffusion in alkali feldspars and found that the results from homogenization experiments were in good agreement with those obtained by tracer and diffusion-couple experiments. The lamellar homogenization method has been used to determine other diffusion rates, including those for pyroxenes (Brady and McCallister, 1983) and plagioclase (Grove et al., 1984; Yund, 1986; Yund and Snow, 1989). Grove et al. (1984) determined NaSi-CaAl interdiffusion rates in a Ca-rich plagioclase (An_{70-90}) with Huttenlocher lamellae by annealing samples in air. Yund (1986) determined NaSi-CaAl interdiffusion rates in an Na-rich plagioclase (An_{0-26}) with peristerite lamellae with added H_2O at 1500 MPa, and Yund and Snow (1989) determined the effects of f_{H_2} and H_2O pressure on NaSi-CaAl interdiffusion for the same Na-rich plagioclase (An_{0-26}) sample. The difference between the interdiffusion coefficients for bytownite (dry, 1 atm) and peristerite (H_2O present, 1500 MPa) is almost 5 orders of magnitude, which could be attributed to the difference in bulk composition or the effect of H_2O at high pressure or both.
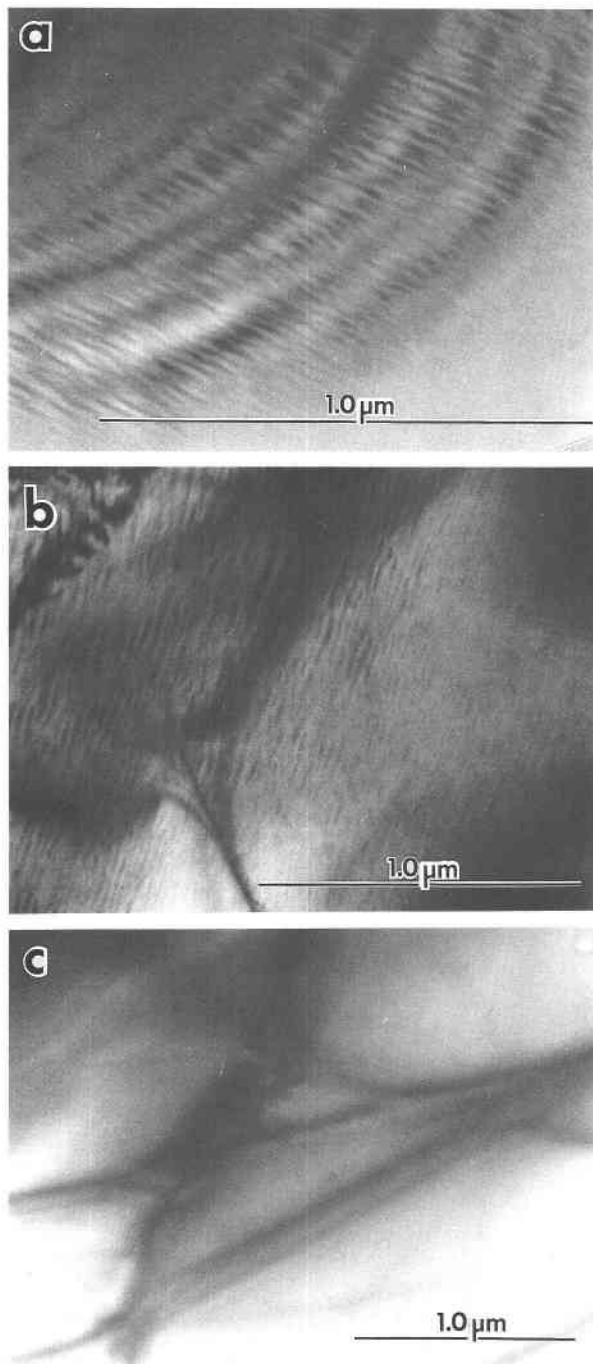
Fig. 1. TEM bright-field photomicrographs of Stillwater bytownite. (a) Starting material showing strong diffraction contrast of $(03\bar{1})$ Huttenlocher lamellae. (b) Partially homogenized sample showing weak lamellar contrast. (c) Completely homogenized sample with no indication of exsolution lamellae.

Previous studies indicate that the presence of H_2O, or one of its components, has a significant effect on several solid-state processes in feldspar. It increases the rate of O diffusion (Yund and Anderson, 1974; Elphick and Gra-

ham, 1988; Elphick et al., 1988; Farver and Yund, 1990), the rate of Al-Si disordering-ordering (Yund and Tullis, 1980; Goldsmith, 1987, 1988), the ease of dislocation creep (hydrolytic weakening) (Tullis and Yund, 1989), as well as the rate of NaSi-CaAl interdiffusion in peristerite (Yund, 1986). The effect is more pronounced at high confining pressure (Yund and Tullis, 1980; Yund and Snow, 1989). Yund and Snow (1989) assumed that the enhanced rate was due to an increase in the concentration of the defect or species associated with the H_2O in the crystal. It has been proposed that H_2O hydrolizes the Si-O-Si bonds, weakening the tetrahedra (Donnay et al., 1959; Griggs, 1967), or that H^+ forms OH^- groups by H hopping, producing a transient, locally negative activation volume (Goldsmith, 1987, 1988, 1991). Elphick and Graham (1988) have suggested that the increased O diffusion rates observed in quartz when H_2O is present could be attributed to fast proton transients that migrate rapidly through the framework silicate lattice. Graham and Elphick (1991) have interpreted the increased Al-Si interdiffusion rate with increasing pressure as due to an increase in the proton activity accompanying the rapid increase in the dissociation of H_2O. Farver and Yund (1990) have argued that the O transport species responsible for the enhanced O diffusion rate in feldspars under hydrothermal conditions is molecular H_2O. In this paper we will refer to the effect of H_2O on the interdiffusion rate without specifying the nature of the chemical species or the mechanism involved.

The goals of this study were to evaluate the effect of bulk composition on the average interdiffusion rate for the Huttenlocher and peristerite intervals and to determine the temperature dependence of the diffusion rate for both compositional intervals using buffered experiments with H_2O. The original data for the temperature dependence of diffusion in the peristerite interval (Yund, 1986) were unbuffered with respect to O and H, and subsequent studies (Yund and Snow, 1989) indicated that buffering was important when determining the interdiffusion rate. We have used our diffusion data for "wet" Huttenlocher samples as well as "dry" samples of Grove et al. (1984) to calculate the cooling rate of chemically zoned plagioclase crystals, and these values were compared with published cooling rates estimated by independent methods.

EXPERIMENTAL PROCEDURE

The bytownite used for this study is from the same sample used by Grove et al. (1984) and is from the Stillwater igneous complex, Montana. The sample contains equant, subhedral plagioclase crystals ($1.7 \times 1.7 \times 0.5$ mm) with tabular morphology. the crystals have a homogeneous core (An_{80-81}) and a thin rim (50–100 μm) that grades to An_{76} at the margin (Grove et al., 1984), and they contain submicroscopic coherent exsolution lamellae of the Huttenlocher type (see Fig. 1a). Heuer et al. (1972) and Nord et al. (1974) observed that the crystals have sharp b reflections ($h + k$ = odd, l = odd; Ribbe,

1983) with diffuse e reflections around them. The crystals contain zigzag-type b antiphase domain boundaries, and the e reflections are due to e ordering in the Ab-rich phase. Electron diffraction patterns of the two-phase intergrowths indicate that the compositions of the lamellae are ~An_{70-75} and An_{88-90} (Nord et al., 1974; Grove et al., 1983). Diffraction contrast experiments by Grove et al. (1984) showed that the lamellae are coherent and their morphology is consistent with having formed by spinodal decomposition. The measured spacings, from center to center of adjacent $(03\bar{1})$ lamellae in the An_{80-81} cores of the crystals, are between 135 and 225 Å, with a mean value of 175 Å (Grove et al., 1984).

The peristerite used for this study is from the same sample used by Yund (1986) and Yund and Snow (1989). This peristerite is a large ($5 \times 5 \times 1$ cm), single crystal from Hybla, Ontario (Brown University collection no. 2583), clear to pink in color, and displaying blue iridescence on the (010) cleavage. An electron-probe analysis gave a bulk composition of $Ab_{91.9}An_{6.7}Or_{1.4}$ with no detectable Fe, Mg, Ba, Ti, or Mn (less than about 0.05 wt%). There is only one orientation of exsolution lamellae, and it is approximately parallel to $(0\bar{4}1)$ when indexed using $c = 14$ Å. A typical bright-field micrograph is shown in Figure 2a. The average lamellar spacing is 554 ± 77 Å from center to center of adjacent (unlike) lamellae (Yund, 1986). A composition of An_{26} for the An-rich lamellae is estimated from the bulk composition, the relative widths of the albite and anorthite-rich lamellae (2.9:1), and the assumption that the albite lamellae are Ab_{100}. Twins on the albite law are also present, but generally they are larger than the exsolution lamellae, much fewer in number, and not as evenly spaced.

When exsolution lamellae are heated above their solvus, they homogenize by diffusion normal to the lamellae. The diffusion coefficient is given by $(\tilde{D} \times t_h)/L^2 = 0.5$, where $\tilde{D}$ is the average interdiffusion coefficient, t_h is the time needed to homogenize the lamellae, and L is the homogenization distance, i.e., the distance between centers of unlike lamellae (Brady and McCallister, 1983; Crank, 1975). The reason we choose $(\tilde{D} \times t_h)/L^2 = 0.5$ is that when $(\tilde{D} \times t_h)/L^2$ has reached a value of 0.5 the compositional difference between lamellae is 0.01 and homogenization is essentially complete (see Brady and Yund, 1983; Grove et al., 1984 for details). Because interdiffusion coefficients vary with bulk composition (Brady and Yund, 1983), the $\tilde{D}$ values determined by this method are average interdiffusion coefficients for the compositional interval represented by the lamellae.

The homogenization experiments for both bytownite and peristerite were conducted in sealed noble-metal tubes that were annealed at 900–1050 °C and at 1500 MPa confining pressure in a piston-cylinder apparatus using soft-fired pyrophyllite as the confining medium. The sample assembly is similar to that described by Kronenberg and Tullis (1984). For these experiments a sample core about 3 mm in diameter and 3.5 mm in length was prepared; the bytownite core contained ~5–10 grains,
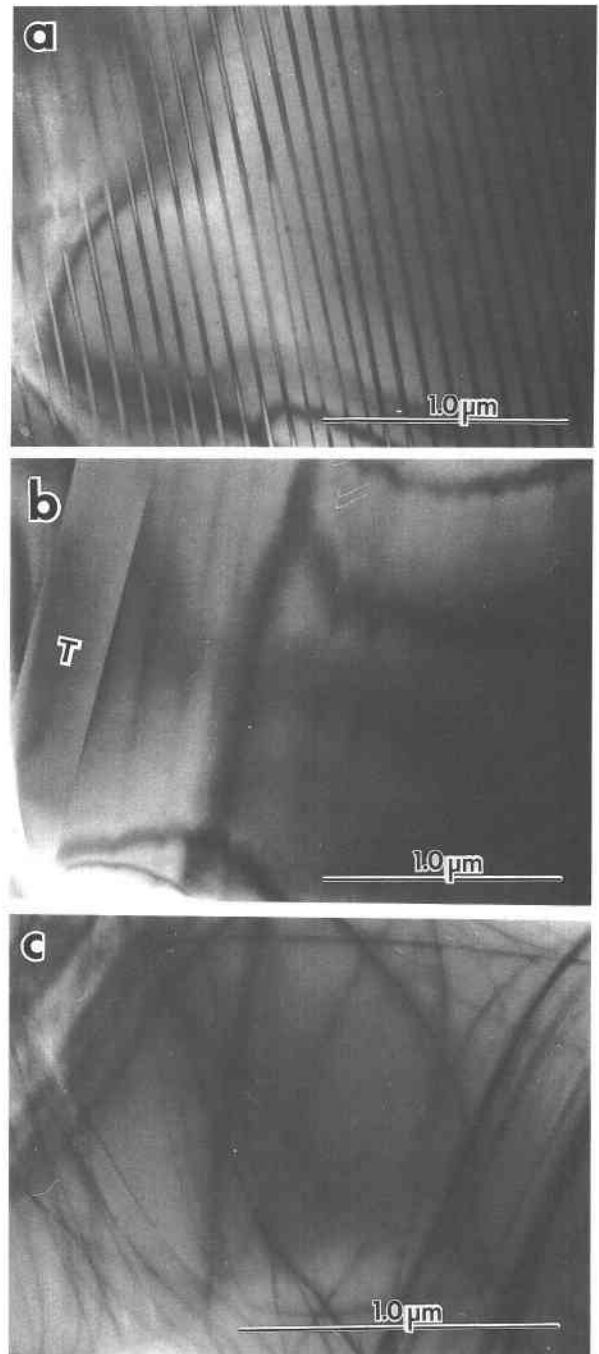

Fig. 2. TEM bright-field photomicrographs of the peristerite; all are (001) foils. (a) Starting material; wider lamellae are the Ab-rich phase. (b) Partially homogenized sample; the sharp bands are albite twins (T). (c) Completely homogenized sample with no indication of exsolution lamellae.

and the peristerite core was drilled perpendicular to the (001) cleavage. The sample core was sealed in a Pt tube together with about 25 mg of powdered plagioclase, to prevent rupture of the Pt tube by the sharp ends of the core, and about 0.6–2.5 wt% H_2O. The Pt tube was sealed

inside an Au tube (0.2-mm wall) with about 80–150 mg of magnetite/hematite buffer (4:1 by weight) and 10–30 mg H_2O. In all the reported experiments, H_2O was still present in the Au tube at the end of the experiments as evidenced by weight-loss measurements, and fluid was usually observed when the Au tube was cut open. At the end of an experiment the presence of both magnetite and hematite was confirmed by X-ray diffraction.

In order to minimize melting, only between 0.6 and 2.5 wt% H_2O was added to the samples (Goldsmith and Jenkins, 1985). We did not observe melt in the samples, but minor melting may have occurred in the plagioclase powder, which was not carefully examined. It is expected that some of the H_2O would dissolve in the sample crystals of peristerite or bytownite or become incorporated along the grain boundaries of the bytownite sample. The homogenization rate was independent of the amount of H_2O added, indicating that the crystals were saturated with H_2O or the H_2O-related species that is responsible for the enhanced diffusion rate. No evidence was observed for a systematic variation of the degree of homogenization with position in a grain, indicating that the penetration of H_2O or its components was much faster than homogenization due to NaSi-CaAl interdiffusion.

Samples were first pressurized cold to about 300 MPa; the temperature was then raised to ~300 °C, and the samples were pressurized to 1500 MPa; finally the temperature was raised to the desired level. The samples were rapidly quenched (<2 min). The temperature was measured using a Pt-Pt$_{90}$Rh$_{10}$ thermocouple that was centered vertically on the sample, and a stepped graphite furnace was used to minimize thermal gradients near the sample. The temperature uncertainty is believed to be less than ±10 °C (Kronenberg and Tullis, 1984). Pressure was monitored on an external gauge and maintained within 50 MPa of 1500 MPa (not corrected for friction). Johannes (1978) reported that friction in a piston-cylinder apparatus with a pyrophyllite sample assembly can result in a gauge pressure about 400 MPa higher than the actual sample pressure at 600 °C. However, friction effects are reduced when pressurization is done at high temperature (Johannes, 1978). In the experiments reported here, pressurization was done at high temperature; thus the apparent pressure uncertainty due to friction is probably significantly less than 400 MPa and the pressure uncertainty is the same for all experiments. According to Yund and Snow's (1989) data, $\tilde{D}$ is relatively insensitive to a difference of several hundred MPa at pressures greater than 1000 MPa.

Following the experiments, the samples were prepared for TEM by ion milling. The thinned foils were examined using a Phillips model EM420 to determine the extent of homogenization. Exsolution lamellae become increasingly faint as they homogenize (Figs. 1b, 2b); the lamellae were considered to be homogenized when no evidence of the lamellae was observed in TEM (compare Figs. 1b and 1c as well as Figs. 2b and 2c). When the apparent homogenization is complete, the remaining compositional difference between lamellae is believed to be less than ~1% An (Grove et al., 1984). The proper orientation to observe the lamellae was confirmed by diffraction patterns of the randomly oriented grains in the bytownite sample. Occasionally a small area within a grain was observed in which the lamellae were still faint, although within most areas of that grain no trace of lamellae remained. These were presumed to be areas that had a slightly larger than average initial spacing, and they were ignored for the purpose of determining the average homogenization time.

EXPERIMENTAL RESULTS

The experimental results for the Huttenlocher interval are listed in Table 1 and presented on an Arrhenius plot of log $\tilde{D}$ vs. $1/T$ (K) in Figure 3. The value of homogenization time for calculating $\tilde{D}$ for a given temperature must lie between the shortest time required for homogenization and the next shortest time for which lamellae could still be observed. The maximum temperature for these experiments was limited by the homogenization time. If the annealing temperature is higher than 1050 °C, the homogenization time will be too short compared with the heating time. The minimum temperature of 900 °C was determined by the practical time limit for doing experiments in a piston-cylinder apparatus.

In spite of the limited temperature interval that could be experimentally explored, there is clearly a break or discontinuity in the data at about 975 °C, and consequently two lines have been drawn through the data on Figure 3. Using a program of linear regression to fit the logarithm values of midpoints between the $\tilde{D}$ values of the bracketing experiments, these two data sets give the following Arrhenius relations:

$$\tilde{D} = 4 \times 10^{-16} \ \text{m}^2/\text{s} \ e^{(-103 \ \text{kJ/mol}/RT)}$$

$$(\sim 1050\text{–}1000 \ °\text{C}) \qquad (1)$$

$$\tilde{D} = 11 \times 10^{-6} \ \text{m}^2/\text{s} \ e^{(-317 \ \text{kJ/mol}/RT)}$$

$$(\sim 975\text{–}900 \ °\text{C}). \qquad (2)$$

where $\tilde{D}$ is the average interdiffusion coefficient for An$_{70-90}$.

The experimental results for the peristerite interval are listed in Table 2 and plotted as log $\tilde{D}$ vs. $1/T$ (K) in Figure 4. Using the same linear regression method, these yield the following Arrhenius relation:

$$\tilde{D} = 3 \times 10^{-8} \ \text{m}^2/\text{s} \ e^{(-303 \ \text{kJ/mol}/RT)} \qquad (1050\text{–}900 \ °\text{C}) \ (3)$$

where $\tilde{D}$ is the average interdiffusion coefficient for An$_{0-26}$.

It is difficult to know how to estimate the errors for the preexponential factor (D_0) and activation energy given in Equations 1–3. If only the error due to the width of the brackets at each temperature is considered, the errors in log $\tilde{D}$ values calculated from Equations 2 and 3 are about ±0.3 and the standard deviation in the activation energies is <35 kJ/mol. Given the small temperature interval for Equation 1, the errors are large but unknown.
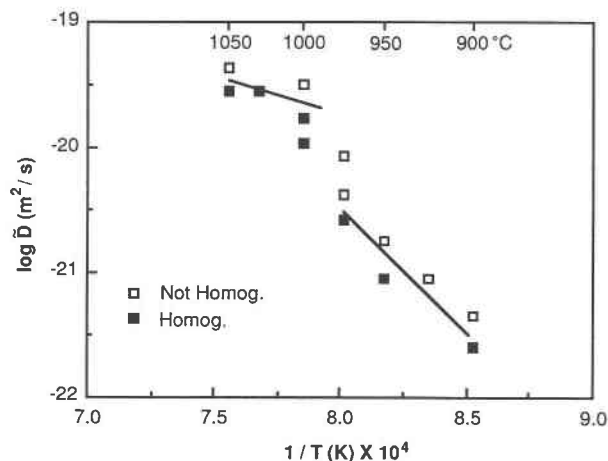
Fig. 3. Arrhenius plot showing the results of annealing experiments on Stillwater bytownite at 1500 MPa, H_2O added, and the MH buffer. There is a break at approximately 975 °C. D_0 and Q values are given in the text.

Fig. 4. Arrhenius plot showing the results of annealing experiments on peristerite at 1500 MPa, H_2O added, and the MH buffer. The Arrhenius relation is given in the text.

DISCUSSION

Within the uncertainty of the bracketing points, the Arrhenius plots (Figs. 3 and 4) define straight lines. These relations may not be strictly linear, however, because the $\tilde{D}$ values are an average for a compositional interval (An_{70-90} or An_{0-26}), and even interdiffusion coefficients for a fixed composition need not be strictly linear on an Arrhenius plot unless the solid solution is ideal (Yund, 1986). Therefore some caution is necessary when extrapolating these relations to lower or higher temperatures.

The break in the interdiffusion data for the Huttenlocher interval

The discontinuity in the diffusion data for the Huttenlocher interval (Fig. 3) must be associated with a change in the structure or microstructure of the plagioclase, a change in the atomic diffusion mechanism, or both. A change from intrinsically to extrinsically controlled diffusion is not expected to produce a discontinuity nor the observed increase in the activation energy with decreas-
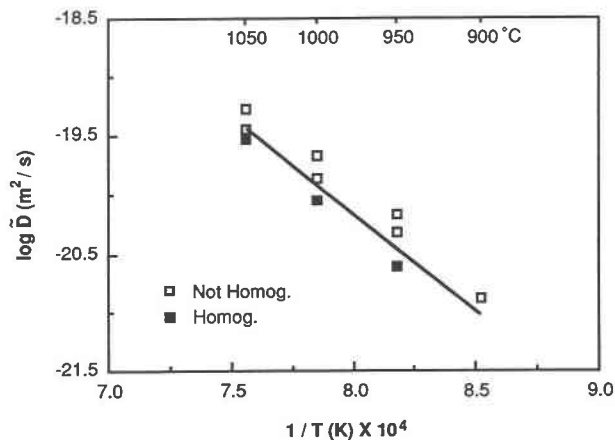
ing temperature. Another possibility is that a change in speciation of H_2O causes a change in concentration of the ions that catalyze the diffusion process (e.g., Graham and Elphick, 1991; Goldsmith, 1991). However, the concentration of species of H_2O is a continuous function of temperature and pressure, and there is no report of a large change in speciation of H_2O in such a narrow temperature interval (~750–1000 °C) (Eugster, 1977, 1986). Second, if a change of speciation of H_2O was responsible for this break, we would expect to see a similar effect in the peristerite data. Therefore a change in the structure or microstructure of the plagioclase is a more likely explanation.

In order to consider whether a structural-microstructural change may correlate with the break in the Huttenlocher diffusion data, we need to review the probable structural relations in the ~An_{70} Huttenlocher lamellae. The ~An_{90} lamellae are essentially homogeneous in composition, whereas the ~An_{70} lamellae are expected initially to have a compositionally modulated superstructure consisting of an intermediate plagioclase phase (Ab rich) and an $I\bar{1}$ phase (An rich) (Grove, 1977a). For example, this superstructure has been observed in plagioclases with bulk compositions between An_{68} and An_{78} by

TABLE 1. Experimental data for Huttenlocher homogenization

T (°C)	t (h)	TEM observation
1050	1.0	very faint lamellae
1050	1.5	no lamellae
1030	1.5	no lamellae
1000	1.3	lamellae visible
1000	2.5	no lamellae
1000	4.0	no lamellae
975	5.0	faint lamellae
975	10.0	faint lamellae
975	16.0	no lamellae
950	24.1	faint lamellae
950	48.0	no lamellae
925	48.0	very faint lamellae
900	96.0	very faint lamellae
900	168.0	no lamellae

Note: All experiments at 1500 MPa, H_2O added, MH buffer.

TABLE 2. Experimental data for peristerite homogenization

T (°C)	t (h)	TEM observation
1050	8.0	faint lamellae
1050	12.0	faint lamellae
1050	14.0	no lamellae
1000	20.0	lamellae visible*
1000	31.0	faint lamellae
1000	48.0	no lamellae*
950	61.0	faint lamellae
950	90.0	lamellae visible
950	169.1	no lamellae
900	336.0	faint lamellae

Note: All experiments at 1500 MPa, H_2O added, MH buffer.
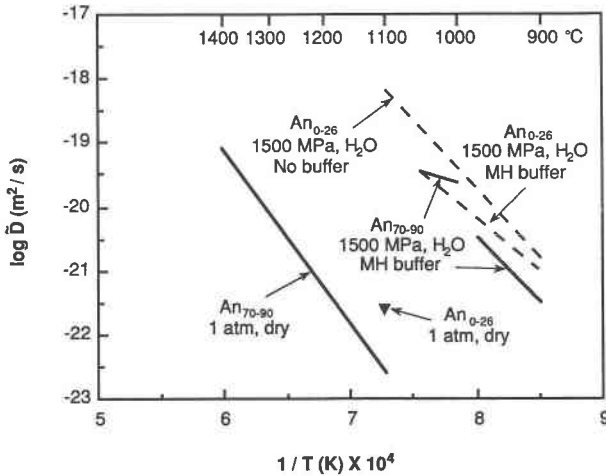* Data from Yund and Snow (1989).

Fig. 5. Comparison of average NaSi-CaAl interdiffusion data for the Huttenlocher and peristerite intervals at different experimental conditions. The solid line (1-atm, dry condition for An_{70-90}) is from Grove et al. (1984). The dashed line (1500 MPa, H_2O added) and the triangle (1-atm, dry conditions for An_{0-26}) are from Yund (1986). The other data are from Figures 3 and 4.

Grove (1977b) and in an An_{76} sample by McConnell (1974). There are weak e-type reflections that are due to this superstructure (Ribbe, 1983) in our initial Stillwater sample. The compositions of these modulations are not known, but the Ab-rich phase may be between An_{50} and An_{65} and the wavelength of the compositional modulation is probably near 50 Å (Grove, 1977a; Smith, 1983).

The temperature of the break in the diffusion data may correlate with the rapid loss of the modulated structure. McConnell (1974) annealed a plagioclase specimen of An_{76} bulk composition and found that the modulated structure disappeared above 960 °C. This suggests that the superstructure may have been quickly lost in our sample above ~975 °C. We cannot confirm this suggestion, however, because for our samples the e-type reflections are too faint to be observed even after a short anneal at the temperatures of our diffusion experiments. If this correlation is correct, it implies that the rate of destruction of the superstructure depends on some factor other than the rate of NaSi-CaAl interdiffusion. Possibly tetrahedral ordering within the compositional modulations lowers the Gibbs energy of the modulated structure and preserves it for a longer time below 975 °C. At a higher temperature the tetrahedral disordering is more rapid, the modulated structure is quickly destroyed, and the Huttenlocher lamellae homogenize more rapidly.

This break in the homogenization-diffusion rate raises a question of how to extrapolate the diffusion data to higher and lower temperatures. It seems likely that the modulated structure similar to those in this Stillwater sample is present in many natural plagioclases of about this bulk composition (McConnell, 1974; Grove, 1977b), and thus the lower temperature data shown on Figure 3 are probably more appropriate for applications below

about 975 °C. For higher temperature applications we favor the upper line on Figure 3, but we will also use an extrapolation of the lower temperature data when we discuss the preservation of compositional zoning in plagioclase crystals in a later section.

Comparison of different NaSi-CaAl interdiffusion data

A comparison of the average interdiffusion coefficients determined in this study for NaSi-CaAl in the Huttenlocher interval at 1500 MPa and H_2O added with the dry, 1 atm data of Grove et al. (1984) is presented in Figure 5. The diffusion coefficients in the wet, high-pressure experiments are about 3 orders of magnitude greater than those in the dry, 1 atm experiments. A large increase of $\tilde{D}$ when H_2O is present at high pressure was previously reported by Yund (1986) and Yund and Snow (1989) for the peristerite interval.

In contrast to the wet, high-pressure data, there is no discontinuity in the dry, 1-atm diffusion data of Grove et al. (1984). Their experiments were between 1100 and 1400 °C, and although homogenization of the modulated structure would be slower in their dry experiments, the high temperatures are likely to have resulted in rapid homogenization of the modulated structure. Thus their experiments would be similar to our experiments above 975 °C with no superstructure present during most of the annealing time.

Our new buffered diffusion data for the peristerite interval, which are shown by the lower dashed line on Figure 5, lie between the higher and lower temperature data sets for the Huttenlocher interval. These new peristerite data have $\tilde{D}$ values similar to the unbuffered peristerite data at 900 °C (Yund, 1986), shown by the upper dashed line on Figure 5, but they diverge at higher temperature because of the difference in activation energies (303 kJ/mol compared with 406 kJ/mol). This difference in activation energy must be viewed with some caution, given the narrow temperature interval of the data and the fact that they are based on average $\tilde{D}$ values. Nevertheless, the data do show the importance of buffering.

As noted in the introduction, H_2O or one of its components has a marked effect on the kinetics of solid-state processes in feldspars and other minerals, although the atomic diffusion mechanism and cause of the enhanced diffusion rate when H_2O or one of its components is present in the crystal have not been fully resolved (e.g., Graham and Elphick, 1991; Goldsmith, 1991). Although the data presented here do not add new constraints to solve this question, they do demonstrate that the effect is very similar for the peristerite and Huttenlocher intervals and presumably for the entire plagioclase series.

It should be noted that although the orientations of the Huttenlocher (03$\bar{1}$) and peristerite (0$\bar{4}$1) lamellae are different, the angle between these planes is small. Using cell parameters of bytownite ($a = 8.178$, $b = 12.870$, $c = 14.187$, $\alpha = 93.50°$, $\beta = 115.90°$, $\gamma = 90.63°$; Borg and Smith, 1968), we calculate an angle of ~5° between these planes. Therefore the diffusion directions are very similar

for the Huttenlocher and peristerite samples and it is possible to compare directly these diffusion data.

As shown on Figure 5, there is very little difference in the average NaSi-CaAl interdiffusion rate for the Huttenlocher and peristerite intervals between 900 and ~975 °C when H_2O is present at high pressure. The activation energy for the peristerite data (303 kJ/mol) is less than that for the Huttenlocher data (371 kJ/mol) below the break at ~975 °C. The diffusion rate in peristerite at 1 atm (dry) has not been determined because the lamellar spacing of this peristerite is large and homogenization times on the order of years would be required. A single 1-atm experiment shown on Figure 5 (Yund, 1986) places an upper limit on $\tilde{D}$ for dry peristerite, and this limit is consistent with the 1-atm data of Grove et al. (1984) for the Huttenlocher interval. In our discussion of geological applications in the next section we will assume that there is no strong compositional dependence on the interdiffusion rate for plagioclases from their melting temperatures to about 900 °C.

GEOLOGICAL APPLICATION

Plagioclase crystals from volcanic and plutonic environments often contain complex oscillatory zoning features with a variety of wavelengths and amplitudes (Smith, 1974) that can provide information about the thermal history of the host rock. Taylor et al. (1975) have discussed methods for estimating cooling rates from the temperature dependence of the diffusion rate and the observed scale of zoning in a crystal. Grove et al. (1984) estimated cooling rates for the Stillwater and Skaergaard intrusions using their dry, 1-atm diffusion data for the Huttenlocher interval. Following the approach of Grove et al. (1984), we will use the new wet diffusion data for the same bytownite to estimate cooling rates in order to see whether the dry or wet diffusion data are more consistent with independent estimates of cooling rates of igneous bodies with zoned plagioclase crystals.

The initial assumption is that plagioclase acquires oscillatory zones during growth from a melt and that the oscillations have been isolated from further reaction with the melt. Compositional homogenization begins at the temperature of crystallization or isolation (T_0), and the assumed linear cooling rate (V) is given by (Walker et al., 1977)

$$V = \frac{D_0 T_0^2 R}{X^2 0.5 Q} \exp\left(-\frac{Q}{R T_0}\right) \qquad (4)$$

where X is the half-wavelength of the oscillatory zones, D_0 and Q are the Arrhenius parameters for the diffusion data, R is the universal gas constant, and T_0 is in kelvins.

Figure 6 was constructed using the above relation and the Huttenlocher diffusion data for the wet, 1500-MPa experiments plotted on Figure 3. For an assumed initial temperature (T_0) lower than ~975 °C, only the lower set of Huttenlocher data was used to calculate the cooling rate. For $T_0 > ~975$ °C, both the high-temperature data
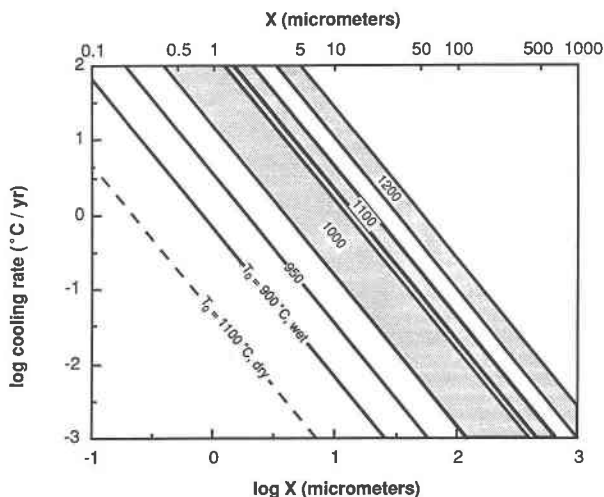

Fig. 6. Estimates of minimum cooling rate required to homogenize oscillatory zoning in plagioclase using the NaSi-CaAl interdiffusion data for An_{70-90} shown in Figure 3. The stippled areas give a range of cooling rates for >1000 °C based on different diffusion rates as explained in the text. The dashed line is calculated from the 1-atm, dry interdiffusion data (Grove et al., 1984) for comparison.

and the extrapolation of the lower temperature data on Figure 3 were used. Thus two lines connected by stippling are shown on Figure 6 for $T_0 = 1000$, 1100, and 1200 °C. The range of estimated cooling rates for a given initial temperature (T_0) and half-wavelength (X) can be directly read from Figure 6. For example, given an initial temperature (T_0) of 1100 °C, oscillatory zones with $X = 1.0$ μm would be homogenized if the cooling rate was slower than ~470–230 °C/yr. For $X = 10$ μm, homogenization would require a cooling rate slower than ~4.7–2.3 °C/yr. These rates are much faster than those estimated by Grove et al. (1984) using their 1-atm, dry diffusion data. The dashed line on Figure 6 labeled "$T_0 = 1100$ °C, dry" is calculated from their data and predicts a cooling rate that is nearly 4 orders of magnitude slower than that for the wet data.

The question is whether the cooling rate calculated from the wet, high-pressure interdiffusion data or from the dry, 1-atm data or neither is appropriate for an igneous plagioclase from gabbroic rocks. Yund and Snow (1989) found that in addition to the temperature dependence of $\tilde{D}$, the f_{H_2} and H_2O pressure or f_{H_2O} also affect the interdiffusion rate for the peristerite interval. Because our data show that there is little dependence of $\tilde{D}$ on bulk composition of plagioclase, it is reasonable to assume that a similar dependence exists for other plagioclase compositions. Therefore, for a given cooling rate, the preservation of chemical zoning in a plagioclase crystal is probably more strongly dependent on the H_2O content or f_{H_2O} than on the crystal's bulk composition.

Yund and Snow (1989, Fig. 5) determined the dependence of $\tilde{D}$ for the peristerite interval as a function of

confining pressure at f_{H_2} defined by the wüstite/magnetite (WM) and magnetite/hematite (MH) buffers. Their results show that at a fixed confining pressure there is a small increase in $\tilde{D}$ with increasing f_{H_2} from the MH to the WM buffers, namely, about half an order of magnitude for these buffers at 1000 °C and between 500 and 1500 MPa confining pressure. This observation seems to be consistent with the proton activity model suggested by Graham and Elphick (1991) and Goldsmith (1991). In addition, the increase in $\tilde{D}$ with increasing confining pressure may be due to an increased H_2O content of the plagioclase with increased f_{H_2O} or due to an increased proton activity (e.g., Graham and Elphick, 1991; Goldsmith, 1991). A similar effect has been observed for the O self-diffusion rate in feldspar (Farver and Yund, 1990).

Many igneous rocks are buffered near quartz-fayalite-magnetite (QFM) (Haggerty, 1976a, 1976b), and Yund and Snow's (1989) data indicate that at 1000 °C and a similar f_{H_2} there is an increase of approximately one and a half orders of magnitude in $\tilde{D}$ from 0.1 to 1500 MPa. The 0.1-MPa data are for samples annealed in H gas (probably containing a trace of H_2O), whereas 0.5–2.5 wt% H_2O was added to the experiments between 500 and 1500 MPa. $\tilde{D}$ increases very slowly at higher confining pressure. Thus it seems likely that these diffusion rates, together with those shown in Figure 3, should be applicable to the cooling of igneous complexes that contain some H_2O and that were buffered near QFM.

Plagioclase crystals from the Stillwater complex are compositionally zoned but only on a scale greater than a few micrometers (McCallum et al., 1980). If the cooling rate estimated by Hess (1972) of ~0.001 °C/yr for layers 2 km from the base is correct, and taking $T_0 = 1200$ °C, compositional oscillations ≤ 20–30 μm would be homogenized if the diffusion rate determined from dry, 1-atm experiments was applicable (Grove et al., 1984), or oscillations ≤ 1000–1550 μm would be homogenized if the diffusion rate determined from the wet, 1500-MPa Huttenlocher experiments was applicable (Fig. 6).

In the case of the Skaergaard intrusion, 10-μm-scale oscillations in plagioclase crystals are observed in the lower and hidden zones of the intrusion (Maaloe, 1976). Norton and Taylor (1979) suggested that the cooling rate experienced by the plagioclase of the hidden zone, lower zone, and much of the border group was about 0.01 °C/yr. The temperature (T_0) for the first appearance of plagioclase in the Skaergaard parent melt has been estimated between 1150 (Norton and Taylor, 1979) and 1230 °C (Biggar, 1974). Using 1200 °C as an average, oscillations ≤ 11 μm would be homogenized using diffusion data of Grove et al. (1984), whereas oscillations ≤ 315–490 μm would be homogenized using the data in Figure 6.

Huntington (1979) concludes that the Kiglapait intrusion crystallized in a low-H_2O environment. In addition, compositional zoning of plagioclase crystals on a scale of 5 to 10 μm has been found in troctolite samples from stratigraphic levels at least as high as 5 km above the base of the Kiglapait intrusion (Morse, 1969). The in-ferred crystallization temperature is 1250 °C (Morse, 1979). The cooling rate of the Kiglapait intrusion estimated from the dry, 1-atm diffusion data (Grove et al., 1984) is between ~0.2 and ~0.05 °C/yr, or about 100 °C/yr using the wet data. The dry data are closer to Morse's (1984) estimated cooling rate for the interior of the intrusion, which he gives as 0.001 °C/yr between 1200 and 1000 °C.

The above discussion demonstrates the difficulty of estimating cooling rates for zoned plagioclase crystals because of uncertainties in the crystallization temperature and the uncertainty in comparing with the cooling rates estimated by other methods. The available data suggest, however, that for the first few hundred degrees of cooling after plagioclase crystallization in these three large gabbroic bodies the scale of compositional zoning is more consistent with the dry, 1-atm data of Grove et al. (1984) than with the hydrothermal diffusion data (Fig. 3). Correction of the hydrothermal data for a lower pressure, using the data of Yund and Snow (1989) and assuming a crystallization temperature of 1200 °C, would lower the minimum cooling rate that would preserve 10-μm compositional zoning from about 15 °C/yr at 1500 MPa to about 2 °C/yr at 300 MPa.

It is surprising if these gabbroic magmas were as dry as the diffusion data suggest. Micropores, which were probably sites of fluid, are much less common in gabbroic plagioclases than in those from most granitic rocks (Montgomery and Brace, 1975). The concentration of structurally bound H_2O molecules is very low in at least some plagioclase crystals, although the OH$^-$ concentration is high and more variable (Hofmeister and Rossman, 1986). Before definite conclusions can be drawn about the dryness of these magmas, a comprehensive study of a selected intrusive body is needed. This should include a careful estimate of the cooling rate from heat-flow models, determination of the scale of compositional zoning and the variability of this zoning, and characterization of the plagioclase by IR spectroscopy and perhaps other means.

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