Interdiffusion of K and Na in alkali feldspars: homogenization experiments

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Abstract

The rates of homogenization of coherent exsolution lamellae in cryptoperthites have been used to evaluate K–Na interdiffusion in alkali feldspars. An "average" interdiffusion coefficient ($\bar{D}$) is between 2 and 4×10^{-17} cm^2/sec for a synthetic cryptoperthite at 600°C in the composition range Or_{23}–Or_{53}, and between 6 and 12×10^{-16} cm^2/sec for a natural cryptoperthite at 650°C in the composition range Or_0–Or_{85}. These values are for diffusion normal to ($\bar{8}01$) at 1 atmosphere pressure. K–Na interdiffusion coefficients calculated from published K and Na self-diffusion coefficients and thermochemical solution data for alkali feldspars depend strongly on composition. The minimum $\bar{D}$'s calculated are similar to the "average" $\bar{D}$'s determined from the homogenization experiments. Finite-difference models of the homogenization experiments using the calculated, composition-dependent interdiffusion coefficients are in good agreement with our experimental results. Homogenization experiments appear to be successful in determining average interdiffusion coefficients which are consistent with diffusion data obtained using other techniques. The method is especially useful for determining $\bar{D}$'s in the range of 10^{-16} to 10^{-19} cm^2/sec.

Introduction

During the last decade or so there has been a surge of interest in the use and measurement of diffusion data for minerals (Freer, 1981). Nevertheless, important diffusion data are still not available for many common mineral groups such as plagioclase feldspars and amphiboles. This absence of data is due in part to the difficulty of measuring the very small diffusion coefficients that are typical of many minerals at crustal temperatures. In this paper we report the results of a "simple" diffusion experiment that can yield diffusion data for minerals that contain exsolution lamellae. Because the technique can be used to measure very small diffusion coefficients (*e.g.*, 1×10^{-19} cm^2/sec for runs of 1 to 4 weeks), we feel that it will be useful to geologists.

The basic procedure is to homogenize fine-scale exsolution lamellae by annealing at temperatures and pressures in a single-phase region. Geometrically the experiment is analogous to a simple diffu-

sion couple of finite dimensions. The important differences are (1) the diffusion distances required for homogenization can be on the scale of nanometers, and (2) a very good or even coherent interface exists between the crystals in the couple. The very small diffusion distances make it possible to measure very small diffusion coefficients with comparatively short run times. The good interface should minimize any blocking effect that the interface might have on diffusion.

Brady and McCallister (1980, 1983) reported diffusion data obtained from experiments in which a kimberlitic diopside containing pigeonite exsolution lamellae was homogenized during high temperature annealing. Their results were not in agreement with other diffusion data reported for clinopyroxenes. The question arose as to whether there might be something in the nature of the homogenization experiments that could lead to incorrect diffusion data. The alkali feldspars were selected to test the homogenization method because independent self-

diffusion data were already available. As we show below, diffusion data obtained using the homogenization method are in good agreement with diffusion data obtained in other ways for feldspars. Price (1981) has used homogenization experiments to obtain diffusion data for titanomagnetites. Although his method of interpretation differs somewhat from ours, his results are also consistent with diffusion data obtained by other methods.

Experimental procedures

Most of the homogenization experiments were performed on high sanidine-high albite coherent cryptoperthites prepared from a natural adularia following the procedures of Sipling and Yund (1976, p. 898). The crystals selected had a homogenized composition of $Ab_{57}Or_{43}$ as determined from the (201) d-spacing, with an anorthite content of less than 0.1 mole percent as determined by electron microprobe. The cryptoperthite was produced by annealing the disordered, ion-exchanged crystals at 525°C for 24.85 days in air. The average lamellar spacing (center to center of like (801) lamellae) for this material is 15.5 nm (Yund and Davidson, 1978).

Initial $hk0$ X-ray precession photos were taken for each crystal. The crystals were then annealed at 600±5°C in Pt containers open to the atmosphere. During the course of the annealing, each crystal was removed several times to monitor the homogenization with precession photos and then returned to the furnace. The maximum composition difference between the two sets of lamellae was estimated from the separation or combined length of the two (10·0·0) reflections. Although these estimates were used to construct the figures below, they are not required to obtain the reported diffusion data. The critical observation is the time required for the cryptoperthite to homogenize.

Homogenization data were also gathered for a natural cryptoperthite from Big Bend, Texas, with a bulk composition of $Ab_{60.8}Or_{39.2}An_{0.0}$. The lamellae in this cryptoperthite are largely coherent (see below), have a lamellar spacing of 110±20 nm as measured on transmission electron micrographs, and have compositions of about $Ab_{99.8}Or_{0.2}$ and $Ab_{15}Or_{85}$, based on a^* and corrected for coherency using the data of Tullis (1975). The Na-rich phase is albite-twinned. Measurement of 2θ for (060) and (204) (Wright, 1968) on a sample homogenized for 3 days at 800°C in air indicates nearly complete Al/Si disorder for this sample. Kinetic studies have shown that the degree of Al/Si disorder is not

significantly affected by the homogenization at 800°C (Sipling and Yund, 1974). The Big Bend cryptoperthite did not fully homogenize at 600°C. We conclude from this result that the lamellae are not perfectly coherent, due probably to the presence of dislocations at the lamellar interfaces. Complete homogenization was obtained at 650°C.

Results and interpretation

Approximate compositional differences between the lamellae as determined from the homogenization experiments are shown by the symbols on Figure 1a for the synthetic sample and on Figure 1b for the natural cryptoperthite. A constant or "average" K–Na interdiffusion coefficient ($\bar{D}$) can be calculated from these data, although it will be shown below that this coefficient is strongly dependent on composition. A solution to the diffusion equation for the finite, one-dimensional geometry of a lamellar intergrowth is available in the form of an infinite series for the case of a constant binary interdiffusion coefficient (Crank, 1975, p. 63). This solution is shown in Figure 1 in terms of the composition difference between centers of adjacent lamellae as a function of time and scaled appropriately for the two samples. Each solid line in Figure 1 gives the solution for a particular value (shown) of the constant $\bar{D}$. The dashed curves in Figure 1 are the results of a finite difference calculation using a variable $\bar{D}$ and will be described below.

Because the composition differences shown for intermediate times are only approximate, the criterion used to evaluate $\bar{D}$ was the attainment of complete homogenization. Consider the data for the Big Bend sample shown in Figure 1b. After about 1.4×10^4 seconds, the Big Bend sample still shows signs of inhomogeneity on $hk0$ precession photos. If the interdiffusion coefficient was constant at a value of 12×10^{-16} cm²/sec, the sample should have been homogenized within experimental uncertainty. Similarly, after about 2.2×10^4 seconds the Big Bend sample was found to be fully homogenized. If the interdiffusion coefficient was constant at a value of 6×10^{-16} cm²/sec, evidence for inhomogeneity should still be present. Thus, for the hypothetical constant $\bar{D}$ case, the data at 650°C constrain the K–Na interdiffusion coefficient within a factor of two. Similarly, the data in Figure 1a for the synthetic cryptoperthite constrain a "constant" K–Na interdiffusion coefficient to lie between 2 and 4×10^{-17} cm²/sec at 600°C. As a general rule, homogenization is essentially complete in the constant $\bar{D}$ case if the

quantity $\tilde{D}t/L^2$ is greater than about 0.5, where $\tilde{D}$ is the interdiffusion coefficient, t is time, and L is one-half the lamellar spacing (see Brady and McCallister, 1983). For $\tilde{D}t/L^2 = 0.5$, the composition difference between adjacent lamellae will be less than 1% of the original composition difference.
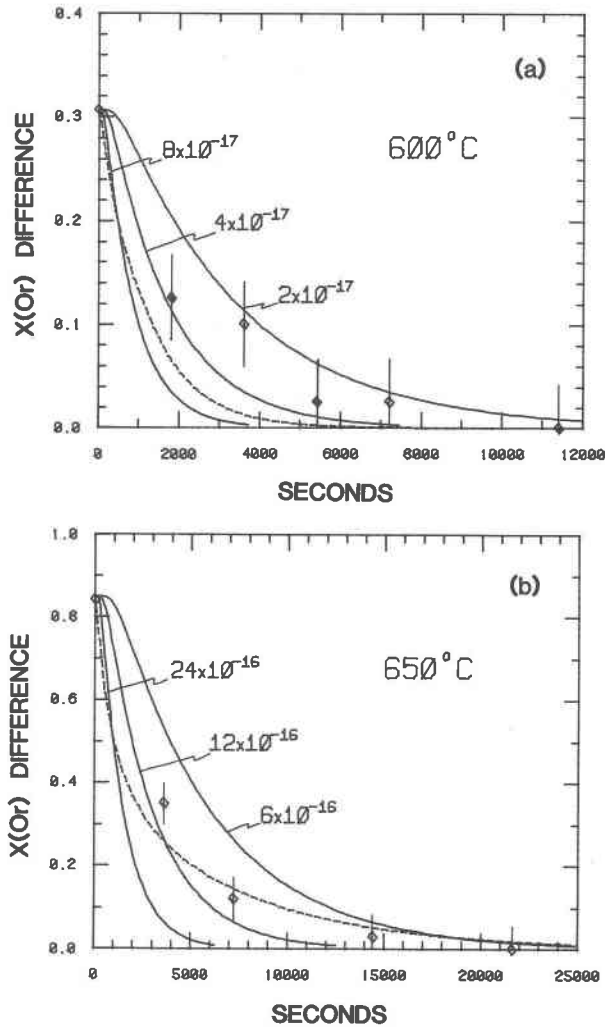

Fig. 1. Progress of the homogenization of cryptoperthite lamellae is shown in terms of the difference in composition of the centers of adjacent lamellae as a function of time for (a) a synthetic cryptoperthite (initial lamellar spacing = 15.5 nm) and (b) a natural cryptoperthite (initial lamellar spacing = 110 nm). The solid curves show the predicted homogenization path for the composition-independent diffusion coefficients as indicated. The dashed lines show predicted homogenization paths for variable diffusion coefficients as explained in the text. The symbols show observed homogenization data (difference in average lamellar composition) for two synthetic crystals at 600°C (open and closed symbols) and one crystal (Big Bend) at 650°C. Estimated compositional uncertainties reflect the precision with which we could measure the (10 · 0 · 0) separation.

As mentioned above, the K–Na interdiffusion coefficient cannot be constant for the conditions of our experiments. To see why this is so and to see how the above analysis can nevertheless be useful, it is necessary to draw upon other data available for the alkali feldspars. Yund (1982) has reviewed published alkali self-diffusion data for the alkali feldspars and recommends the data of Foland (1974) and Kasper (1975). Foland's data are for an orthoclase of Or_{94} composition and Kasper's data are for Amelia low albite. Diffusion coefficients based on the cylindrical models of Foland and Kasper are used in the following analysis (also see Christoffersen et al., 1981). Disregarding the possible effects of the state of Al/Si disorder on alkali diffusion, K–Na interdiffusion coefficients can be calculated from the alkali self-diffusion data of Foland and Kasper. The interdiffusion coefficient ($\tilde{D}(K-Na)$) is related to the self-diffusion coefficients ($D^*(Na)$ and $D^*(K)$) as follows:

$$\tilde{D}(K-Na) = \left[\frac{D^*(K)D^*(Na)}{X(Or)D^*(K) + X(Ab)D^*(Na)} \right] \left[\frac{d \ln a(Or)}{d \ln X(Or)} \right] \quad (1)$$

where $X(Or)$ is the mole fraction and $a(Or)$ is the molar activity of orthoclase in an Ab–Or binary solution (Manning, 1968, p.21; Brady, 1975).

In general, self-diffusion coefficients will be a function of composition (Reynolds et al., 1957; Vignes and Birchenall, 1968). Foland and Kasper each give $D^*(Na)$ and $D^*(K)$ for one composition only. Therefore, we must estimate $D^*(Na)$ and $D^*(K)$ for intermediate compositions. A linear extrapolation on a log $\tilde{D}$ vs. composition diagram (Fig. 2) was used because a simple linear extrapolation leads to a negative $\tilde{D}$ for pure Or at 600°C. If the alkali feldspars formed an ideal solution, then the thermodynamic factor on the right side of equation (1) would be unity and the interdiffusion coefficients predicted from the self-diffusion data would have the values shown by the dashed line in Figure 2. For most feldspar compositions, the K–Na interdiffusion coefficient should be nearly equal to $D^*(K)$ and significantly smaller than $D^*(Na)$.

Because the alkali feldspars do not form an ideal solution, the thermodynamic factor in (1) must be evaluated to obtain a more accurate estimate of the interdiffusion coefficients. The thermodynamic properties of the sanidine–high albite series have been well characterized by the work of Thompson and Waldbaum (e.g., 1969). Their data should be
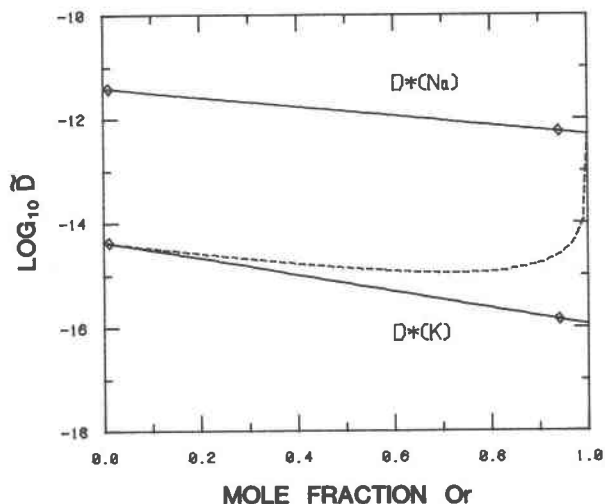
Fig. 2. K–Na interdiffusion coefficients (dashed line) (cm²/sec) calculated for the alkali feldspars at 600°C are shown on a logarithmic scale as a function of composition along with the K and Na self-diffusion coefficients (solid lines) used in the calculation. The self-diffusion coefficients were estimated from the four data points (shown) from Foland (1974) and Kasper (1975). For illustration the alkali feldspars were assumed to be a thermodynamically ideal solution.

decrease of the thermodynamic correction with rising temperature, and (3) the very significant variation of the K–Na interdiffusion coefficient with composition. Christoffersen (1981) has measured K–Na interdiffusion coefficients for alkali feldspars at 1000°C from diffusion couples annealed at high pressures. Using a Boltzmann–Matano type analysis (see Wagner, 1969), he found a compositional dependence of the interdiffusion coefficients that closely matches that predicted using the methods that led to Figure 3.

Although no exact solution to the diffusion equation is available for cases in which the diffusion coefficient varies in an arbitrary way with composition, numerical approximations are readily obtained. Results of a finite-difference computer simulation of the homogenization process using the estimated K–Na interdiffusion coefficients of Figure 3 are shown in Figure 1 as dashed lines. Agreement of our experimental observations with the numerical predictions based on Foland's and Kasper's data is very good. For both the Big Bend and the synthetic cryptoperthites, the observed time re-
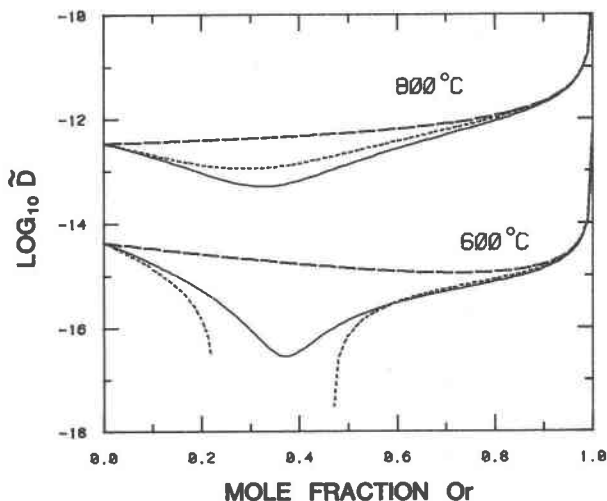
used to determine the thermodynamic factor for strain-free feldspars. However, the Gibbs energy expression for the feldspars of our experiments must be corrected for coherency strain (e.g., Cahn, 1967). Therefore, we have obtained Margules parameters from the coherent solvus of Sipling and Yund (1976), using the procedures of Thompson and Waldbaum (1969, p. 836) to evaluate the thermodynamic factor in (1). The corrected interdiffusion coefficients are shown as the solid lines in Figure 3 for temperatures of 600° and 800°C. Also shown for comparison in Figure 3 are the predicted interdiffusion coefficients for the hypothetical case of an ideal solution (long dashes) and for strain-free feldspars (short dashes). The strain of coherency is gradually eliminated during homogenization. For this reason, neither the Margules expression obtained from the Sipling–Yund coherent solvus nor the Thompson–Waldbaum expression is correct throughout the homogenization. Evaluating the strain at stages during the homogenization to compute other Gibbs energy functions is not warranted until more tracer diffusion data are available for intermediate compositions.

The important features of Figure 3 are (1) the size of the thermodynamic correction (about two orders of magnitude near the solvus), (2) the gradual

Fig. 3. K–Na interdiffusion coefficients (cm²/sec) calculated for alkali feldspar are shown on a logarithmic scale as a function of composition at 600° and 800°C. The lines of long dashes show interdiffusion coefficients for the hypothetical case of thermodynamic ideality. The solid lines show interdiffusion coefficients corrected for the thermodynamic non-ideality of coherent cryptoperthites. The lines of short dashes show interdiffusion coefficients corrected for the thermodynamic non-ideality of strain-free alkali feldspars (Thompson and Waldbaum, 1969). Note that the interdiffusion coefficients for strain-free feldspars at 600°C are not shown for compositions within the chemical spinodal where they are negative.

quired to complete homogenization is within 30% of the predicted time. There is an apparent discrepancy between our results and the model predictions for times early in the homogenization process, but this may well be due to the approximate nature of our composition estimates and/or the estimates used for self-diffusion coefficients at intermediate compositions. Considering the uncertainties of Foland's and Kasper's results and the complete lack of self-diffusion data for intermediate compositions, we feel that our data are entirely consistent with the data of Foland and Kasper.

The shape of the dashed line in Figure 1 is significantly different from the shape of any of the solid lines. However, in each case the dashed line is close to a comparatively high $\bar{D}$ solid line for short times and close to a lower $\bar{D}$ solid line for long times. This may be understood by observing that at long times all of the compositions in the homogenizing cryptoperthite are near the final (bulk) composition for which the interdiffusion coefficient has a very low value. Indeed, we have found that the constant $\bar{D}$ brackets to our homogenization data shown in Figure 1 are very close to the value of the minimum predicted K–Na interdiffusion coefficient. We have tested several other cases with concave-upward functions for the interdiffusion coefficient such as those shown in Figure 3. In each case the time required for homogenization predicted by the finite-difference model is about the same as the time required for the case of a constant $\bar{D}$ equal to the smallest possible $\bar{D}$. Because it is not possible to determine $\bar{D}$ as a function of composition from our experiments, we recommend the simple constant $\bar{D}$ interpretation that approximates the minimum $\bar{D}$ in the composition range considered.

In conclusion we would like to emphasize two results. (1) Homogenization experiments are a relatively easy way to obtain chemical diffusion information for minerals with exsolution textures. An average interdiffusion coefficient close to the minimum $\bar{D}$ for the composition range involved may be obtained by evaluating the expression $\bar{D}t/L^2 = 0.5$ on the basis of homogenization data. (2) Interdiffusion coefficients can be expected to vary considerably with composition at physical conditions for which a mineral deviates significantly from a thermodynamically ideal solution.

Acknowledgments

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