MINERALOGICAL MAGAZINE, JUNE 1981, VOL. 44, PP. 195–200

Diffusion in the titanomagnetite solid solution series

G. D. PRICE*

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ

ABSTRACT. In order to be able to use the nature and scale of the exsolution microstructures developed in titanomagnetites as quantitative indicators of thermal history, it is necessary to have available accurate diffusion data for the system. Diffusion data for pure magnetite and Ti-poor titanomagnetites are available, but no data for diffusion in the centre of the solid-solution series exist. In order to obtain values for the activation energy (ΔE) and the pre-exponential factor (D_0) for the interdiffusion of Fe and Ti in ulvöspinel-rich titanomagnetites, the natural microstructures developed in titanomagnetites from the Taberg intrusion, Sweden, were homogenized over a range of temperatures from 490 to 730 °C. From the model describing homogenization, values of 49.8 kcal mole^{-1} and 2.38×10^{-3} cm^2 s^{-1} were calculated for ΔE and D_0 respectively. Although the results obtained from these homogenization experiments are slightly less accurate than those which could be obtained by more conventional methods, the homogenization technique has several advantages which outweigh this drawback, namely the ease with which the experiment can be performed and the fact that the diffusion data can be obtained at significantly lower temperatures than is usually possible with more conventional methods.

DIFFUSION is generally an extremely important process in all crystalline materials at temperatures above approximately one-third of their absolute melting-point. Understanding the laws of diffusion is indispensible, therefore, in describing such geologically important phenomena as exsolution, phase transformation kinetics, recrystallization, high-temperature flow, and, in general, all igneous and high-grade metamorphic events. In particular, if sufficient kinetic data were available for mineral systems, transformation-process theory (McConnell, 1975) could be used to give quantitative information on the time–temperature–pressure history of rocks from the scale and nature of the microstructures exhibited by their constituent minerals. This study is concerned with diffusion in titanomagnetites, with particular reference to the effect of diffusion on the development of exsolution microstructures. Accurate diffusion data for the system are required in order to be able to use these exsolution textures as indicators of thermal history. In this paper the results of some homogenization experiments, performed on natural, inhomogeneous titanomagnetites, are presented, and the resulting values calculated for the diffusion parameters are discussed.

Previous studies of diffusion in titanomagnetites. Several studies of diffusion in titanomagnetites have been published. The earlier studies of diffusion in titanomagnetites were based upon the rate of production of non-magnetic iron oxides from titanomagnetite during oxidation (Creer *et al.*, 1970; Petersen, 1970; Ozima and Ozima, 1972). However, it is unlikely that the results obtained from these experiments have any bearing on the diffusion processes involved in the unmixing of titanomagnetite solid solutions, or even on Fe–Ti interdiffusion, because oxidation–exsolution of ilmenite is unlikely to have, as a rate-determining step, the interdiffusion of iron and titanium, and because the oxidation–exsolution of ilmenite probably occurs by the breakdown of the non-stoichiometric spinel, titanomaghemite (Lindsley, 1976), in which diffusion is likely to be faster than in stoichiometric spinel (Dieckmann and Schmalzried, 1977).

The tracer diffusion of Fe^{59} in stoichiometric magnetite was studied by Dieckmann and Schmalzried (1977) over the temperature range of 900 to 1400 °C. From their data, Freer and Hauptman (1978) estimated the values of the diffusion parameters, D_0 and ΔE for tracer diffusion in magnetite as 0.056 cm^2 s^{-1} and 2.38 eV (54.5 kcal mole^{-1}), where D_0 and ΔE are respectively the pre-exponential factor and the activation energy of diffusion in the Arrhenius equation:

$$D = D_0 \exp(-\Delta E/RT). \qquad (1)$$

The values obtained by Dieckmann and Schmalzried are in good agreement with those obtained in

---

* Present address, Dept. of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Ave., Chicago, Illinois 60637.

previous studies of cation diffusion in spinels (Freer, 1980).

Freer and Hauptman (1978) performed a series of interdiffusion experiments on couples of stoichiometric magnetite and titanomagnetite ($Fe_{2.8}Ti_{0.2}O_4$). Interdiffusion coefficients were determined for compositions between $Ulvö_0Mag_{100}$ and $Ulvö_{20}Mag_{80}$, for the temperature range 888 to 1034 °C. In general, they found that tracer diffusion of Ti in magnetite occurred more slowly than tracer diffusion of Fe in magnetite, but as the concentration of Ti increased, the interdiffusion coefficient increased towards that of Fe.

In theory, it is possible to calculate the Fe–Ti interdiffusion coefficient for a specific titanomagnetite composition from the known tracer diffusion coefficients of Fe and Ti in titanomagnetite. However, in the absence of an adequate atomistic model for diffusion in titanomagnetites, this calculation cannot be performed (Yurek and Schmalzried, 1974). Thus the Fe–Ti interdiffusion coefficient for titanomagnetites must be measured directly.

Diffusion experiment. The measurement of the interdiffusion coefficient ($\tilde{D}$) for Fe–Ti diffusion in titanomagnetites could be achieved in two main ways:

(i) The diffusion-couple method used by Freer and Hauptman (1978) could be adopted. The main disadvantage of this approach is that the experiment must be performed at temperatures above 800 °C. These temperatures are about 200–400 °C above the temperature range where exsolution in the system may occur.

(ii) A method based on homogenization experiments of pre-existing natural magnetite–ulvöspinel intergrowths may also be adopted to obtain D_0 and ΔE values for the interdiffusion of Fe and Ti, from the kinetics of the homogenization process. The main advantage of this method, and the reason why it was adopted in this study, is that complete homogenization can be achieved at relatively low temperatures ($\sim$500 °C), even on the laboratory time scale, because of the fine-scale of these natural intergrowths.

The homogenization of exsolution-derived microstructures, such as those found in titanomagnetites, is a diffusion-controlled process, since the exsolved and matrix phases are isostructural and the interface between them is coherent or semi-coherent (Price, 1980). As a result, the rate at which a microstructure (of a given size) can be homogenized, by annealing at temperatures above the solvus, is simply a function of the diffusion coefficient, and hence of temperature. In order to determine the diffusion parameters D_0 and ΔE, samples of rock from the Taberg instrusion, Sweden (Hjelmquist, 1950; Price, 1979), were heated for varying lengths of time, and at different temperatures. These rocks carried titanomagnetites of composition $Ulvö_{47}$ Mag_{53}, which had developed an exsolution-derived cloth-texture, with ulvöspinel lamellae on a scale of 1.8×10^{-5} cm wide (Price, 1979, 1980). From these experiments it was possible to determine the time required to homogenize the microstructure, over a range of temperatures. However, to obtain quantitative data on the diffusion coefficients from these experiments, a kinetic model for homogenization must be available. In this respect the work on the kinetics of precipitate dissolution, by Aaron *et al.* (1970) and by Aaron and Kotler (1971), has been closely followed.

Diffusion model. Much attention has been paid to the kinetics of exsolution processes, but less is known about homogenization processes. Aaron and Kotler (1971) have stressed the differences between these two phenomena. The major features of precipitation are, that after some incubation period a critical nucleus forms and the precipitate grows by depleting the matrix of solute, directly ahead of the advancing interface, fig. 1*a*, so that at any point in the matrix phase, the solute concentration decreases monotonically, with time. During homogenization, however, there is no incubation period. The precipitate has a finite, non-zero initial size, and decreases in size by transferring solute into the matrix behind a receding interface (fig. 1*b*). The manner in which solute concentration may vary with time is different from, and more complex than, that during growth, and depends upon the nature of the interface during homogenization. If the interface remains well defined, then it is found that in the matrix far from the precipitate the solute concentration increases with time; close to the precipitate, the solute concentration decreases with time; and at intermediate positions the solute concentration may increase, decrease, or remain unchanged. Furthermore, the regions corresponding to 'near', 'intermediate', and 'far' vary with time. These complications are the reasons why no closed, analytic solutions to the problem of diffusion-controlled dissolution have been found, and that in order to obtain a solution to the homogenization–diffusion equation, certain approximations must be made.

For both growth and dissolution processes, the mathematical description of diffusion-controlled development of an isolated precipitate in an infinite matrix requires the solution of Fick's second law of diffusion (Aaron *et al.*, 1970):

$$\tilde{D}\nabla^2 C = \partial C/\partial t \qquad (2)$$

For the dissolution of a planar precipitate of initial half-width S_0, equation (2) has a solution of the form (Aaron *et al.*, 1970)

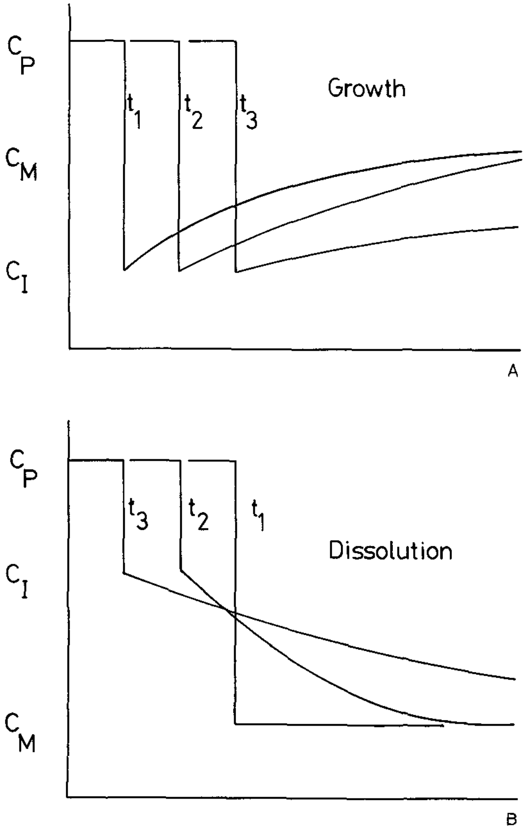

FIG. 1. (*a*) The evolution of lamellar width and compositional profiles during the isothermal, diffusion-controlled growth of a lamella into an infinite matrix. (*b*) The evolution of a resorbing precipitate during homogenization, in which the precipitate-matrix interface remains well defined (after Aaron *et al.*, 1970).

$$0 = S_0 - \lambda(Dt)^{0.5} \qquad (3)$$

where $\lambda = \beta/2$, and $\pi^{1/2}\beta\exp(\beta^2)\operatorname{erfc}(\beta) = k/2$ where

$$k = 2(C_I - C_M)/(C_P - C_I) \qquad (4)$$

here C_I is the bulk composition of the system (assumed to be the equilibrium interface composition during homogenization), C_M is the initial matrix composition, and C_P is the initial precipitate composition (assumed to remain constant during homogenization). Thus, for complete homogenization

$$S_0^2 = \lambda^2 D t_H$$

and hence from equation (1)

$$S_0^2 = \lambda^2 D_0 t_H \exp(-\Delta E/RT)$$

$$\text{and} \quad \Delta E/RT = \ln(t_H) - \ln(S_0^2/\lambda^2 D_0). \qquad (5)$$

Thus, from equation (5), it can be seen that a plot of $\ln(t_H)$ (where t_H is the time required for homogenization) against $1/T$ (in Kelvin) should give ΔE and D_0 from the slope and intercept. The significance and accuracy of the D_0 and ΔE values obtained from such an analysis depend, however, on the validity of the assumptions which were made in the formulation of equations (3) and (5).

The significant assumptions which have been made in the above analysis are (i) that the matrix is infinite, and that no impingement of the diffusion fields of resorbing precipitates occurs; (ii) that $\tilde{D}$ is independent of composition; and (iii) that k, and hence λ, is independent of time.

The validity of these assumptions, and their effect on the diffusion data determined from the homogenization experiments, can be assessed as follows;

(i) The impingement of the diffusion fields of resorbing precipitates will undoubtedly occur during the homogenization of a microstructure, which is on such a fine scale as that of the Taberg titanomagnetites. The effect of impingement would be to slow down the rate of homogenization, so that the time measured for homogenization will be longer than that which would be required if no impingement occurred. The lengthening of the time required for homogenization will not affect the calculated values of ΔE, but will affect the value of D_0, such that the calculated value of D_0 will be smaller than the correct value of D_0.

(ii) The diffusion coefficient, $\tilde{D}$, is not independent of composition, but can vary markedly across a solid solution series. The value of $\tilde{D}$ involved in the above kinetic analysis will, therefore, be some mean value of $\tilde{D}$, the Fe–Ti interdiffusion coefficient in titanomagnetite, over a range of titanomagnetite compositions. Similarly, the D_0 and ΔE values calculated from the homogenization kinetics will represent some average values of D_0 and ΔE over the same range of compositions.

(iii) The assumption that k is independent of t is unlikely to be strictly true, since C_M and C_P will vary, as the homogenization proceeds. However, for materials with bulk compositions near the centre of a solid-solution series, C_M and C_P vary at about the same rate, and to the same degree, consequently k remains approximately constant. Any error introduced into the calculated $\tilde{D}$ values as a result of this assumption will only effect D_0 and not ΔE.

(iv) A further shortcoming of this model is that it assumes that the precipitate-matrix interface remains well defined during the course of dissolution. This may not be true, however, particularly during the late stages of dissolution. The effect of this on the calculation of ΔE and D_0 is not expected to be significant, however, since calculation on models with more diffuse interfaces (Shewmon,

1969) produce virtually identical results to those performed with sharp interfaces.

Thus, by applying the model described above to the results of a homogenization experiment, little error is expected in the calculated value of ΔE, but more uncertainty rests in calculating D_0.

Experimental procedure. Homogenization experiments were performed on titanomagnetites from a sample of magnetite-feldspar peridotite from the Taberg intrusion (Hjelmquist, 1950). These titanomagnetites carried oxidation-exsolution lamellae of ilmenite, lamellae of pleonaste, and a cloth-texture intergrowth of ulvöspinel and magnetite (fig. 2*a*). The inhomogeneous oxide grains showed no signs of low-temperature oxidation, when studied by optical microscopy or by TEM. The average composition of the titanomagnetite is given in Table I, and is the mean of a number of analyses, obtained by electron microprobe, of ilmenite-free areas of the oxide.

TABLE I. *Mean analysis of titanomagnetites from the Taberg intrusion, Sweden (no. 54252 in the Harker Collection)*

SiO_2	0.32	V_2O_3	0.82
TiO_2	15.63	FeO	44.02
Al_2O_3	2.91	MnO	0.34
Fe_2O_3	34.84	MgO	1.43
Cr_2O_3	0.00	CaO	0.00
		Total	100.33
$MgAl_2O_4$	6.49	$FeCr_2O_4$	0.00
$MgCr_2O_4$	0.00	Fe_3O_4	47.62
$MgFe_2O_4$	1.60	Fe_2TiO_4	44.32
$FeAl_2O_4$	0.00		

Since the electron-microprobe spot size was larger than, or equal to, the size of the various spinel exsolution textures, the analyses are bulk analyses of all the spinel phases present. The mean analysis has been recast into idealized spinel end-members (Table I), assuming stoichiometry. It is also assumed that the bulk composition of the titanomagnetite intergrowth is given by the proportion of ulvöspinel and magnetite in the recast analysis. The mean analysis yields an ulvöspinel: magnetite ratio of 47:53, with a deviation of ±1 mole%.

Fragments of the Taberg specimen of approximate size $1 \times 0.25 \times 0.25$ cm were heated in small, sealed, evacuated, silica-glass tubes, at temperatures between 490 and 730 °C. The duration of the homogenization experiments ranged from 30 min to 100 days. By sealing the rock fragments in evacuated tubes (total pressure $< 1 \times 10^{-4}$ torr), the system was approximately self-buffering, since the number of moles of O_2 in the atmosphere was many orders of magnitude less than the number of moles of titanomagnetite. Neither the olivine, nor the titanomagnetite, showed signs of oxidation (or reduction) after these heating experiments.

After heating and quenching the titanomagnetites were studied by reflected-light microscopy, to determine the degree of homogenization which had been achieved. If the cloth-texture was not visable optically (fig. 2*b*) the specimen was prepared for study by TEM, where it was inspected for any residual inhomogeneity. The TEM observations revealed no changes in the nature of the ilmenite or pleonaste lamellae, nor the development of any titanomaghemite.

The time (t_H) required to homogenize the cloth texture, at a specific temperature, was determined by studying samples of titanomagnetite, heated for differing lengths of time.

Results. A plot of $\ln(t)$ against $1/T$ is shown in fig. 3. The line corresponding to the locus of (t_H, T) points was taken to lie between those points which

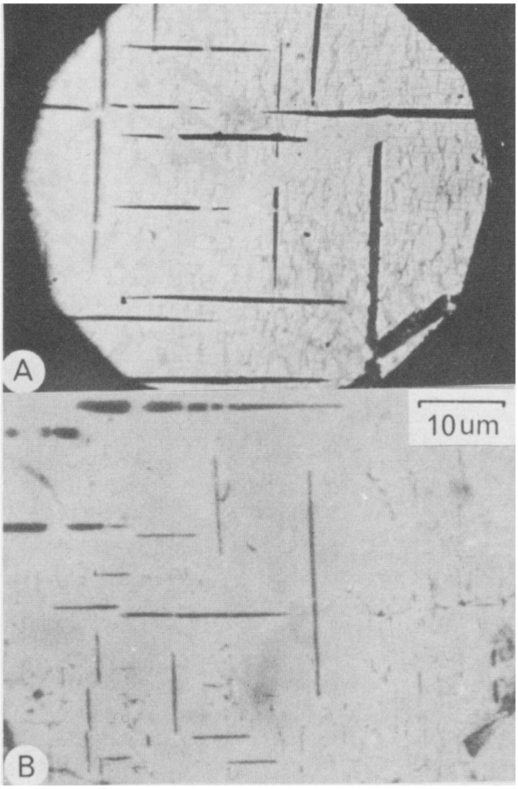

FIG. 2. (*a*) Optical micrograph of an untreated Taberg titanomagnetite. Black pleonaste lamellae are cross-cut by grey ilmenite lamellae, while the titanomagnetite is shown to have developed a fine-scale cloth-texture. (*b*) A similar titanomagnetite after annealing. The cloth-texture has been completely homogenized, leaving the pleonaste and ilmenite lamellae uneffected. TEM study of the titanomagnetite revealed neither any heterogeneity within the titanomagnetite nor any extensive oxidation effects.

indicate optical homogeneity and TEM homogeneity. The equation of this line gives

$$\Delta E = 49.8\,\mathrm{kcal\,mole^{-1}}$$
$$D_0 = 2.38 \times 10^{-3}\,\mathrm{cm^2\,s^{-1}}$$

using $S_0 = 0.9 \times 10^{-5}$ cm, obtained from several measurements of optical and electron-optical micrographs (normal to $\{100\}$), and $\lambda = 0.85$ calculated from compositions for the lamellar phase of $\mathrm{Ulvö_{86}Mag_{14}}$ and the host phase of $\mathrm{Ulvö_{13}Mag_{87}}$, obtained by analytical electron microscopy and X-ray diffraction.

Error analysis. The errors in the values calculated for D_0 and ΔE arise from three sources: (i) errors introduced by uncertainties in experimental measurements; (ii) errors involved in data analysis; and (iii) errors resulting from the inapplicability of the kinetic model used to describe homogenization.

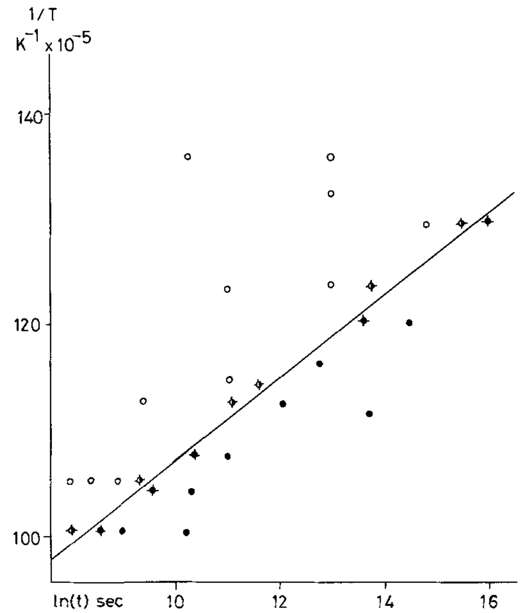

FIG. 3. Specimens of titanomagnetite from the Taberg intrusion were heated for varying lengths of time, and over a range of temperatures, in order to homogenize the microstructures developed in them. A plot of ln t (the time in seconds) for which they were heated, against the reciprocal of the temperature (in K) at which they were heated, is shown. Runs which did not achieve homogenization are indicated as open circles. Half-filled circles correspond to runs which achieved homogenization on the optical scale, but not on the electron optical scale, while full circles correspond to runs which achieved homogenization on the electron optical scale. The slope of the line, which separates the electron optically homogeneous runs from the rest, is equal to $-\Delta E/R$, where ΔE is the activation energy of interdiffusion, since for homogenization of a microstructure of a given size, the time for homogenization (t) is $t \propto \exp\{-\Delta E/RT\}$.

TABLE II. *Values used in the calculation of D_0, and their probable errors*

	X_i	σ_{X_i}
ΔE (kcal mole^{-1})	49.8	1.5
C_I (mole fraction)	0.53	0.01
C_M (mole fraction)	0.87	0.02
C_p (mole fraction)	0.14	0.02
k	1.76	0.19
$\ln \lambda$	−0.16	0.45
$\ln(t'_H)$	−16.84	0.55
$\ln(S_0)$	−11.6	0.15
$\ln(D_0)$	−6.04	1.1

The likely sources of error for the latter case have been discussed above, the quantification of these errors, however, poses a more difficult problem than the quantification of the errors involved with experimental measurements, which can be summarized thus:

(i) the uncertainty in the determination of $T(\pm 2\,^\circ\mathrm{C})$ and $t(\pm 100\,\mathrm{secs})$ is negligible compared with the scatter of points in fig. 3. The error in ΔE introduced by this scatter of data points is about $\pm 1.5\,\mathrm{kcal\,mole^{-1}}$ (corresponding to a percentage error of $\pm 3\%$) as calculated by a least-squares analysis.

(ii) The error in D_0 was calculated from the uncertainties in t_H, S_0, and λ from the defining equation

$$\ln(D_0) = 2\ln(S_0) - 2\ln(\lambda) - \ln(t'_H)$$

where t'_H is the time required for homogenization at $1/T = 0\,\mathrm{K}^{-1}$.

From the various measurements made, estimates of these uncertainties are (see Table II)

$$\sigma_{\ln(t'_H)} = 0.55$$
$$\sigma_{\ln(S_0)} = 0.15$$
$$\sigma_{\ln(\lambda)} = 0.45$$

The resulting uncertainty in $\ln(D_0)$, by error propagation is $\sigma_{\ln(D_0)} = 1.1$.

(iii) As described above, all errors introduced into the estimation of the diffusion coefficient, using the model of Aaron *et al.*, are thought only to affect D_0 and not ΔE. These errors are, however, difficult to quantify, but an attempt will be made, as follows:

The effect of the impingement of dissolving particles will tend to lower the calculated value of D_0. For spherical precipitates, where the geometry of the precipitate makes the effect of impingement more serious, calculations (Aaron and Kotler, 1971) indicate that impingement can affect the time required for homogenization by a factor of about three. The resorption of planar precipitates, with a less complex geometry, is likely, however, to be less seriously affected by impingement.

To a certain extent the effect of impingement on the calculated value of D_0 is likely to be counteracted by the effect of oxygen partial pressure disequilibrium. As pointed out by Freer and Hauptman (1978), an assemblage like $\text{Ulvö}_{10}\text{Mag}_{90}$ and $\text{Ulvö}_{90}\text{Mag}_{10}$ cannot be in equilibrium with the same f_{O_2}, at temperatures above the solvus. Thus the oxides will tend to be slightly non-stoichiometric during homogenization, although not to such an extent as to cause the development of titanomaghemite, etc. The effect of this slight non-stoichiometry would be to allow diffusion to occur slightly faster than it would under equilibrium conditions. However, the difference in rate would be relatively small compared with the effects of larger deviations from stoichiometry discussed by Dieckmann and Schmalzried (1977). The slight increase in diffusion rate would, therefore, partially compensate for the underestimate of D_0 caused by impingement.

The effect on the value of D_0 of the variation of k with time is impossible to assess without detailed phase data. However, as discussed above, the assumption that k is invariant with respect to time is not considered to be grossly in error.

Discussion. The behaviour of Fe–Ti interdiffusion in titanomagnetites has been studied by homogenizing the exsolution-derived microstructures developed in these oxides. This technique for studying diffusion was chosen because it was relatively simple to perform, and because it could be performed at lower temperatures than the more traditional techniques. However, these advantages would be out-weighed if the results of the experiment were significantly less reliable than the results produced by other techniques. The relative reliability of these techniques can be assessed by comparing the errors involved in the homogenization experiment with the errors associated with other techniques.

The uncertainty associated with ΔE calculated from the homogenization experiment was $\pm 3\%$. This compares with an uncertainty of $\pm 1.8\%$ in the activation energy calculated by Freer and Hauptman (1978). Similarly, the error in the value of $\ln(D_0)$ calculated above was ± 1.1, while the best result of Freer and Hauptman (1978) gave an uncertainty of ± 0.36. Thus, although the homogenization experiment is less accurate than the experiments of Freer and Hauptman (1978), the difference in accuracy is not significant.

The original aim of this diffusion study was to obtain diffusion data which could be used in modelling exsolution in the titanomagnetite solid-solution series. It has been shown that the experiments performed in this study have succeeded in producing relatively accurate results, and it is suggested that these data could be used to model diffusion in titanomagmetite during exsolution. However, it must be stressed that exsolution in geological environments may occur under conditions which are different from those under which the diffusion experiments were performed. Perhaps the most geologically important of these features are hydrostatic pressure and oxygen fugacity. The former may affect the diffusion coefficient, but in a way which is currently unquantifiable; and the latter will certainly affect diffusion in a way described by Dieckmann and Schmalzried (1977). Thus, if the results of experiments, such as the one described above, are to be applied to geological problems, it is necessary to ensure that the processes, which were experimentally studied, are truly representative of natural processes.

Acknowledgements. I would like to thank Drs J. D. C. McConnell and A. Putnis for many helpful discussions and Mr B. Cullum for help with specimen preparation. I would also like to thank Drs R. Powell and R. Freer for critically reviewing and greatly improving the manuscript of this paper. I acknowledge the receipt of a NERC grant during the course of this research.

REFERENCES

Aaron, H. B., and Kotler, G. R. (1971). *Met. Trans.* **2,** 393–408.

—— Fainstein, D., and Kotler, G. R. (1970). *J. App. Phys.* **41,** 4404–10.

Creer, K. M., Ibbetson, J., and Drew, W. (1970). *Geophys. JR Astron. Soc.* **19,** 93–101.

Dieckmann, R., and Schmalzried, H. (1977). *Ber. Bunsenges. Phys. Chem.* **81,** 344–7.

Freer, R. (1980). *J. Mater. Sci.* **15,** 803–24.

—— and Hauptmann, Z. (1978). *Phys. Earth Planet. Inter.* **16,** 223–31.

Hjelmquist, S. (1950). *Sven. Geol. Unders. Arsbok.* **43,** 1–55.

Lindsley, D. H. (1976). In Rumble III, D. (Ed.). *Oxide minerals Min. Soc. Am.*

McConnell, J. D. C. (1975). *Ann. Rev. Earth Planet. Sci.* **3,** 125–55.

Ozima, M., and Ozima, M. (1972). *Phys. Earth Planet. Inter.* **5,** 87–9.

Petersen, N. (1970). Ibid. **2,** 175–8.

Price, G. D. (1979). *Geol. Mag.* **116,** 313–8.

—— (1980). *Phys. Earth Planet. Inter.* **23,** 2–12.

Shewmon, P. G. (1969). *Transformations in metals.* McGraw-Hill, New York.

Yurek, G. J., and Schmalzried, H. (1974). *Ber. Bunsenges. Phys. Chem.* **78,** 1379–86.

[*Manuscript received 7 July 1980;*
revised 17 November 1980]