American Mineralogist, Volume 65, pages 174-182, 1980

Crystal-chemical factors affecting the mobility of ions in minerals

ERIC DOWTY

Department of Geological and Geophysical Sciences
Princeton University
Princeton, New Jersey 08540

Abstract

Simple considerations of crystal geometry and bonding theory can be used to illuminate many of the hitherto puzzling or unsystematized data on diffusion or diffusion-related properties of minerals. The main crystal-chemical factors postulated to influence diffusion rates in oxide and silicate minerals are: (1) *Anion porosity* of the structure (one minus volume of anions divided by volume of unit cell)—this strongly influences the relative mobility of a given ion in different minerals. (2) *Electrostatic site energy* of the ion (which for cations is proportional to charge squared, divided by cation–anion distance)—this influences relative mobility of different ions in the same structure, as does (3) *size of the ion,* but site energy appears to be more important. Relative mobilities of ions, judged from isotopic and petrologic observations as well as measured diffusivities, agree qualitatively with predictions from these principles. It is predicted that under anhydrous conditions oxygen should diffuse about as rapidly as a large divalent cation (*e.g.* Ba^{2+}), whereas under hydrous conditions if it diffuses as hydroxyl it should be about as mobile as a large univalent cation (*e.g.* K^+). These predictions are in agreement with observation and explain the "anomaly" of rapid oxygen exchange and diffusion. It is also predicted that the presence of water should have little effect on the solid-state diffusion of cations, again as observed.

Introduction

The rates of a number of geologic processes are controlled by diffusion of ions through oxide and silicate minerals. Measurements of diffusion rates are becoming increasingly available, and one objective of such measurements has always been to determine atomic mechanisms. However, there has been no systematic attempt to identify or review in a comprehensive way the crystal-chemical and structural aspects of minerals which influence diffusion rates. In this paper simple concepts of geometry and ionic bonding theory are used qualitatively to rationalize ion-mobility data, explain some "anomalies," and make predictions about relative diffusion rates of ions in oxides and silicate minerals and melts.

Geometry—the role of porosity

The amount of open space in a crystal structure should be an important factor in ion mobility. Sippel (1963) found that the *anion valence electron density* (number of anion valence electrons per mole per cm^3) is directly correlated with T_D/T_F, the temperature at which the diffusivity of sodium in several minerals reached a certain arbitrary value, divided by the fusion temperature of the mineral. The *anion porosity* gives a more forthright measure of the closeness of packing of the structure than the anion valence electron density, and is applicable when more than one type of anion is present. The anion porosity is defined as the volume of the unit cell minus the volume of the included anions (obtained from standard ionic radii), divided by the unit-cell volume; it is expressed in percent. Cations could also be included if desired, but except for the alkali and alkaline earth ions, the volume of most common cations is negligible. The *packing index* of Fairbairn (1943) is similar to porosity. Fairbairn showed that the packing index of crystals is correlated with a number of important physical properties, such as refractive index, but did not mention a connection with diffusion.

Plotting Sippel's data as anion porosity *vs.* measured diffusivity at a given temperature yields a correlation not significantly worse than that between his parameters, valence electron density and T_D/T_F. Melting point has therefore been omitted from consideration in this paper, but future work may require its reconsideration.

0003–004X/80/0102–0174$02.00

Table 1. Anion porosity of common minerals (percent)

ideal c.p.	26.0	quartz	44.6
kyanite	27.7	tremolite	45.1
staurolite	32.3	anhydrite	45.3
rutile	33.0	chlorite	45.7
pyrope	33.4	prehnite	46.2
sillimanite	35.7	forsterite	46.4
zircon	35.9	muscovite	46.6
spinel	37.2	chrysotile	47.7
andalusite	39.2	apatite	48.3
epidote	39.3	calcite	48.9
enstatite	39.8	albite	49.7
ilmenite	40.9	gehlenite	51.3
acmite	41.5	cordierite	51.8
kaolinite	42.5	orthoclase	53.8
diopside	42.8	nepheline	54.1
magnetite	43.6	rhyolite glass	54.3
talc	44.2	analcite	61.0

Ionic radius of oxygen assumed to be 1.36Å. Porosity of rhyolite glass was derived from the average rhyolite analysis of Carmichael *et al.* (1974, p. 9) and a density of 2.37 g/cc.

Anion porosities of some common minerals are given in Table 1. These values show some interesting and important crystal-chemical and structural correlations. First, in silicates there is a general positive correlation of porosity with increasing degree of linkage (polymerization) of the silicon–oxygen tetrahedra. This is because increasing silicon content reduces the average coordination number of cations in the mineral, and lower coordination number usually implies looser packing. An oxygen bridging two tetrahedra is in contact with only six other oxygens, compared to twelve others in a closest-packing arrangement. There are deviations from this correlation, notably olivine, which has relatively high porosity for orthosilicates, and quartz, which has relatively low porosity for framework silicates. Second, most of the oxides and orthosilicates which do not contain large cations (those normally taking oxygen coordination number higher than six) have oxygen in either the hexagonal or cubic closest-packing arrangement, but the actual density is highly variable and always less than that of ideally closest-packed spheres, assuming standard radii for oxygen. This is not surprising, as the anions repel each other, and their closeness of packing is determined by the way they are held together by the cations.

It is suggested, then, that the relative mobility of a given ion in different minerals is strongly dependent on the porosity. The available quantitative measurements of diffusivities which could be used to test this proposition are scarcely satisfactory. Sippel's (1963) data were in some cases measured on dubious material, but the relative order of minerals may not be incorrect. The results of Muehlenbachs and Kushiro (1974) for oxygen diffusion in several minerals do not show good correspondence with porosities. However, these measurements were made at only one temperature for several minerals. Some other diffusivity data are discussed below, after energetic considerations have been introduced.

Studies of isotopic reequilibrium are pertinent to the relative diffusivity of minerals. For example, Garlick and Epstein (1966a) studied the reequilibrium of oxygen isotopes in the minerals of xenoliths incorporated in a quartz diorite pluton, and found that the order of increasing degree of reequilibration is garnet–quartz–ilmenite–mica. Ilmenite alone is out of order in terms of porosity in this sequence, but this may be due to its presumably smaller grain size.

Hollister (1969) classified those minerals as "refractory" which are comparatively resistant to eradication of elemental zoning patterns in change of metamorphic grade. Refractory minerals cited were garnet, staurolite, and ilmenite, all of which have low porosity. Sheet silicates and cordierite were classified as non-refractory. Other minerals which often preserve zoning (Hollister, 1970) and might be classified as refractory include andalusite, kyanite, and epidote.

Clayton *et al.* (1977) found that minerals in the supposed primitive condensate material in the Allende and similar meteorites show different contents of an "exotic" O^{16} isotopic component—spinel and pyroxene are enriched in this component while melilite is depleted and olivine is variable. Blander and Fuchs (1975) proposed that the O^{16} component was originally present in the same proportions in all minerals, but that the minerals later exchanged to varying degrees with more normal O^{16}-poor material, owing to differences in grain size and/or diffusivity. The required differences in diffusivity are predictable from the porosities (Table 1), and it may be further predicted that anorthite would also show a depletion in O^{16} if this hypothesis is correct. Nepheline, sodalite, and grossular also are depleted in the exotic component, but these minerals formed very late, probably during or after the postulated exchange.

Bonding—electrostatic (Madelung) site energies

In oxides and silicates, the principal contribution to the forces holding an atom in a particular site is

Table 2. Ranges of site energies in common minerals (−kcal/mole)

Na^+, K^+	270-320	mica, feldspar
OH^-	280-315	amphibole, mica
Ca^{2+}	950-1150	garnet, pyroxene, amphibole
Mg^{2+}, Fe^{2+}	1030-1210	olivine, pyroxene, amphibole, mica
O^{2-}	1200-1500	silicates, oxides
Al^{3+}_{IV}	2500	feldspar
Al^{3+}_{VI}	2600	garnet
Si^{4+}	4200-4700	silicates

Data from Raymond (1971) and Ohashi (1976; and personal communication)

the electrostatic or Madelung energy. The site energy is defined as the work required to bring the ion into the site from an infinite distance; it is often computed as an intermediate step or by-product of lattice- or crystal-energy calculations. Some typical values for common ions are given in Table 2.

In the process of diffusion, an energy barrier or activation energy is encountered, which is the principal determinant of rate. This activation energy is the difference between the total energy of the crystal when an atom is in its initial position, and that when the atom is in a high-energy interstitial position in the process of motion. The purely electrostatic contribution to this energy would be on the order of the site energy, if there were no readjustments of the structure, but such readjustments do occur, and the individual atoms polarize so that the net activation energy is usually less than a tenth of the site energy (*e.g.* Jost, 1952, p. 107; Dienes *et al.*, 1976). It is usually assumed that there is still a rough proportionality between site energy and activation energy, which requires that the electric potentials of interstitial positions are more uniform (*i.e.* closer to zero) than those of the regular sites. This has been verified empirically by Madelung calculations on a wide variety of mineral structures (Dowty, in preparation). Thus, in a given structure, ions with lower (less negative) site energies will tend to be more mobile. This is subject, of course, to the constraints of geometry—the porosity of the structure, compared to the size of the ion. We can expect that site energy will be dominant over geometric factors for small ions, such as silicon, or when the structure has very high porosity, as in zeolites. Very compact structures probably will not allow diffusion of large ions, no matter how low the site energy.

It is not necessary to carry out complete Madelung energy summations to obtain values for site energies of cations, because these values are strongly correlated with z^2/d, the formal charge squared, divided by the average cation–anion distance. This is shown in Figure 1. To demonstrate that this correlation applies to true energies, and is not an artifact of any assumptions about types of bonding or formal charges, Figure 2 shows a similar correlation for some simple oxides between z^2/d and the crystal energy (the energy gained on assemblage of the ions from infinite distance into a crystal) computed from the Born–Haber cycle. This crystal energy is derived entirely from thermochemical data.

By far the most reliable and exhaustive data on diffusivity in minerals are those obtained on feldspar (Sippel, 1963; Merigoux, 1968; Bailey, 1971; Lin and Yund, 1972; Foland, 1974; Yund and Anderson, 1974, 1978; Petrovic, 1974; Kasper, 1974; Anderson and Kasper, 1975; Giletti *et al.*, 1978) and olivine (Buening and Buseck, 1973; Misener, 1974). Diffusion of Fe^{2+} and Mg in olivine seems to occur at roughly the same rate as diffusion of alkalis in feldspar, when measurements are extrapolated to the same temperature. The lower site energies of alkalis and the higher porosities of feldspars evidently compensate for the much larger size of the ions. As expected, diffusion of sodium is faster than that of potassium in a given feldspar. There is no strong evidence that diffusion of either ion is faster in potassium feldspar than in albite (if anything the data suggest the opposite), but the difference in porosity between K-feldspar and albite is proportionally much less than the difference in ionic radii of K and Na. Verhoogen (1952) found that the diffusivities of Li^+, Na^+, and K^+ in quartz decreased in that order, and that the diffusivities of Mg^{2+}, Fe^{2+}, Ca^{2+}, and Al^{3+} were undetectably small. Here we see that ionic radius has an effect, but charge is apparently more important. Measurements on a number of simple oxides are available (*e.g.* Kofstad, 1972), but a dismaying variety of techniques and materials have been used, and it is difficult to judge the reliability of individual measurements.

Many types of geologic observations have shown that silicon diffuses relatively slowly compared to cations such as Mg and Fe^{2+} normally found in octahedral sites, and that alkalis are extremely mobile elements. A comparison of the rates of Al–Si ordering or disordering in feldspars (Sipling and Yund, 1974) and the rates of Mg–Fe^{2+} ordering in pyroxenes and amphiboles (Virgo and Hafner, 1969; Seifert and Virgo, 1975) bears this out. Again the observations show the dominance of site energy over ionic size.

Hart (1964) inferred the relative isotopic age stabilities of minerals in contact metamorphic rocks to be feldspar Rb–Sr > hornblende K–Ar > biotite Rb–Sr > biotite K–Ar > feldspar K–Ar at low temperature, and hornblende K–Ar > feldspar Rb–Sr > feldspar K–Ar > biotite Rb–Sr > biotite K–Ar at high temperatures. We expect the Rb–Sr system to equilibrate more slowly than K–Ar because Sr is divalent, whereas the K–Ar system is probably reset by diffusion of neutral and univalent atoms. It is also likely that micas have higher diffusivity than overall porosity would indicate, because the open space is concentrated between the silicate sheets.

The annealing of fission tracks must depend to at least some extent on diffusion. The temperatures for complete annealing after one hour of heating (Fleischer *et al.*, 1975, p. 80–83) are mostly in the range 500–800°C for silicates, and generally lower (100° to 300°) for non-silicate minerals such as apatite, monazite, and calcite. There is no apparent correlation with either melting temperature or porosity. It seems reasonable that annealing in silicates is dominated by mobility of silicon, but all ions in the structure must contribute to the behavior. Haack (1972) reported a correlation of both annealing temperature and activation energy of annealing with lattice energy (which is simply the sum of all site energies), although several minerals deviated rather markedly from the relationships.

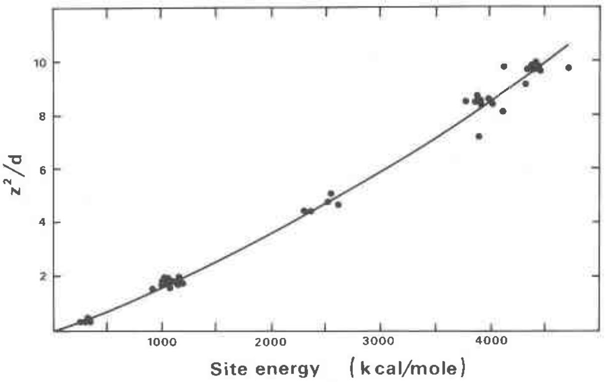

Fig. 1. Electrostatic site energy of cations in silicates and oxides *vs.* z^2/d, formal charge squared divided by average cation–anion distance. Data from Raymond (1971) and Ohashi (1976, and personal communication).

The significance of single covalent bond energies

Covalent energies of single bonds, especially Si–O, have often been considered to be important in diffusion in silicates, sometimes being related to measured activation energies. There is no real justification for this, as the true energies of atoms in ionic crystals are determined by a summation over a large number of atom pairs, and activation energies depend strongly on structural readjustments and atomic polarizations as well. The activation energies of 75–100 kcal/mole inferred for Si/Al interdiffusion in alkali feldspars (Sipling and Yund, 1974) are in fact close to the Si–O single covalent bond value of 88 kcal/mole, but this must be largely coincidence. Even if the bonding is regarded as wholly covalent, it is difficult to imagine long-range diffusion of Si occurring without breaking more than one bond. Likewise, long-range movement of oxygen in framework structures should generally break two Si–O bonds for a total covalent energy of 176 kcal, but measured activation energy for anhydrous diffusion is 90 kcal per mole in anorthite (Muehlenbachs and Kushiro, 1974) and 71 kcal/mole in silica glass (Sucov, 1963).

Mobility of oxygen

A general preconception seems to have arisen that oxygen should be relatively immobile compared to

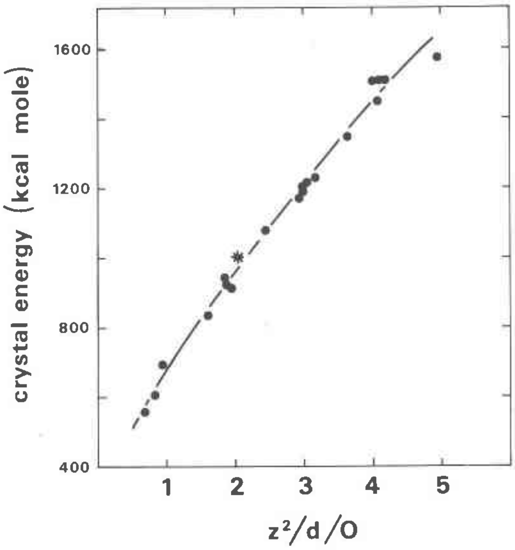

Fig. 2. Crystal energy per oxygen of simple oxides computed with the Born-Haber cycle, *vs.* z^2/d per oxygen. The oxides, in increasing order of crystal energy, are K_2O, Na_2O, Li_2O, CaO, FeO, MgO, MnO, H_2O, BeO, Ti_2O_3, Fe_2O_3, V_2O_3, Cr_2O_3, Al_2O_3, ZrO_2, B_2O_3, TiO_2, VO_2, MnO_2, and SiO_2. H_2O is shown with a star.

cations, perhaps because it occupies most of the space in oxide and silicate structures. It was therefore surprising to many when isotope studies indicated that oxygen readily exchanges in rocks and that it is more mobile than most cations (Wyart *et al.*, 1959; Fructus-Ricquebourg *et al.*, 1963; Taylor and Epstein, 1963, 1968; Garlick and Epstein, 1966b). Laboratory measurements of oxygen diffusion in feldspar under hydrous conditions (Merigoux, 1968; Yund and Anderson, 1974; Anderson and Kasper, 1975; Giletti *et al.*, 1978) demonstrated that rates of solid-state diffusion are in fact rather high, although it was also shown that oxygen exchange by solution and reprecipitation is a probable mechanism under conditions of chemical disequilibrium (O'Neill and Taylor, 1967). The reasons for the unexpectedly high diffusion rates of oxygen can be deduced from the geometric and energetic concepts developed above.

The site energy of oxygen is roughly the same as that of the octahedrally coordinated cations Mg and Fe^{2+}. However, the oxygen ion is much larger than these cations and therefore should be considerably less mobile, unless the structure is very porous. Measurements on "closest-packed" oxides generally bear out this prediction (Birchenall, 1968; Kofstad, 1972).

When water is present, however, the situation is known to be drastically different, with diffusion and reaction rates often being greatly accelerated. Wyart and Sabatier (1958) and Donnay *et al.* (1959) pointed out that certain effects due to the presence of water are probably due to a weakening of the bonds between oxygen and silicon, as the former is converted to hydroxyl. However, they gave few specifics in terms of bonding theory, and did not discuss diffusion of oxygen.

On entering a silicate structure, each water molecule probably reacts with an oxygen ion to form two hydroxyls (Wyart and Sabatier, 1958; Griggs, 1967; Burnham, 1975). One way to envision the result is in terms of one hydroxyl in a regular oxygen site and the other in an interstitial position. The mobility of oxygen in the form of these hydroxyls will depend on their binding energies. If we convert an oxygen ion in a regular site to a hydroxyl, the site energy is halved, since the formal charge is halved. We see from Table 2, however, that the actual site energies of normal hydroxyl ions are about a quarter those of oxygen ions. Local readjustments of the structure would probably reduce the site energy of a hydroxyl substituting for oxygen, so that it approaches the value for normal hydroxyl. The site energy of an interstitial hydroxyl is difficult to predict exactly, but there is no reason to expect it to be greater than that of a normal structural hydroxyl. Thus since the site energy of hydroxyl is about the same as that of alkali ions, and hydroxyl is about the same size as potassium, the barriers to diffusion of oxygen as hydroxyl are no greater than those for large alkali ions.

If the water does not dissociate or react to form hydroxyls, its binding energy, which could only be due to hydrogen bonds and/or atomic polarizations, must be very small and the prediction is similar. However, the measured activity of water in albite melts (Burnham and Davis, 1971) and the infrared spectra of hydrated quartz (Brunner *et al.*, 1961; Kats *et al.*, 1962) demonstrate that the dissociation does take place.

In minerals which are open enough to allow high mobility of alkalis, such as feldspars and micas, the mobility of oxygen should also be high under hydrous conditions, while in more compact structures in which alkali movement is slow, such as olivine, pyroxene, quartz, and iron–titanium oxides, oxygen diffusion will be slow. The relative porosities should be a guide to this, although here it might be more appropriate to include the volumes of cations. Of course, the more compact structures generally do not contain alkalis in the first place. In feldspars, the only minerals for which thoroughly reliable oxygen diffusion data are available for hydrous conditions, the values for oxygen fall between those of K and Na in the temperature range 300–700°C (Giletti *et al.*, 1978). The activation energies for oxygen (about 20 kcal/mole) are lower than those for alkalis (40–70 kcal/mole), which may be due to the low binding energy of interstitial hydroxyls. Observations on oxygen isotope reequilibration of igneous and metamorphic minerals (cited above) are also thoroughly consistent with the predictions. Feldspars and micas reequilibrate readily with solutions, whereas quartz, olivine, pyroxene, and oxides often retain their igneous or other original isotopic composition. Sometimes the latter minerals show little evidence of alteration, although most of the oxygen in the micas and feldspars has been exchanged. In feldspars, it has been observed that igneous Ca–Na zoning can persist even when oxygen isotopes have been largely exchanged with meteoric waters (Taylor, 1974). The immobility of Ca and Na in such cases is attributable to the fact that local distribution of these ions is tied to that of Si and Al by requirements of charge balance (Goldsmith, 1952), and Si and Al are predicted to be relatively immobile.

O'Neill and Taylor (1967) showed that when alkali feldspars are in cationic disequilibrium with an aqueous solution, exchange of both cations and oxygen may take place by a process of dissolution and reprecipitation. Some instances of large-scale oxygen exchange of rocks, when original textures are highly altered or obliterated, may be due largely to this process. However, when original textures are preserved, it is more reasonable to assume that exchange has taken place by diffusion, in view of the fact that oxygen mobility is both predicted and observed to be high.

Although the effect of the presence of water on the diffusivity of oxygen is thus predicted to be large, and this difference has been verified for feldspar (Yund and Anderson, 1974, 1978) and quartz (Kofstad, 1972, p. 349), the effect on solid-state diffusion of cations should generally be small. The concentration of hydrogen not localized on specific structural water molecules or hydroxyls is generally low in crystals, and it is unlikely that more than one of the adjacent oxygen atoms surrounding a given cation would be replaced by hydroxyl at any given time. The effect of the conversion of one oxygen to a hydroxyl on the electrostatic site energy may readily be calculated; it is $\Delta E = ze^2/d$, where d is the cation–oxygen distance, z is the valence of the cation, and e is the charge of an electron. For silicon, ΔE would be about +200 kcal/mole, compared to total site energy of about 4400 kcal/mole, and for Mg or Fe^{2+} about +166 kcal/mole compared to site energies of about 1200 kcal/mole. These are only approximate values, as some structural adjustments and changes in atomic polarization would take place. Conversion of more distant oxygens would also change the site energy, but by smaller amounts. These reductions in cation site energy by about 1/20 to 1/7 are less than the reductions by 1/2 to 3/4 expected for oxygen ions, and it is not surprising that diffusivities of cations appear to be relatively insensitive to the presence or absence of water (Lin and Yund, 1972; Petrovic, 1974; Sipling and Yund, 1974; Yund and Anderson, 1974).

The presence of water or other hydrogen-bearing species may have indirect effects on the diffusion of cations, through various types of reactions. For example, the oxidation state is important in diffusion in ferrous minerals such as olivine because it determines the concentration of cation vacancies (Buening and Buseck, 1974). Also, in some of the silicate reactions which Donnay *et al.* (1959) explained as being catalyzed by hydrogen, long-range diffusion may not be required. In a polymorphic transformation, a rearrangement of the structure of a framework silicate could be effected without removing more than one oxygen at a time from the first coordination sphere of each silicon atom. This is probably the correct way to visualize the process of "prying open" of the silicate tetrahedra postulated by Donnay *et al.*, rather than actual escape of the silicon atom. Polymorphic transformations, and especially reactions involving large changes in composition, may also take place by solution–reprecipitation (Goldsmith and Laves, 1954; O'Neill and Taylor, 1967; Sipling and Yund, 1974). The Si–Al mobility observed by Wyart and Sabatier (1958) in the reaction of plagioclase with KCl solution was probably of this nature.

The general approach used above is also applicable to situations in which the bonding is not entirely ionic. In carbonates, carbon, with three strong covalent C–O bonds, must be bound more firmly than oxygen, with only one strong C–O bond and two weak Ca–O bonds. Thus Anderson (1969) found slightly higher diffusivity for oxygen than carbon in calcite, and Blattner and Cooper (1974) and Schoell *et al.* (1975) found greater relative variation in δC^{13} values than δO^{18} values in metamorphic rocks, suggesting that oxygen isotopes are more easily homogenized. Northrup and Clayton (1966) measured higher diffusivities for Ca–Mg than oxygen in dolomites. This is consistent with the larger size of oxygen and its somewhat larger site energy in ionic crystals (Table 2).

Igneous melts

In igneous melts with low silica and/or high water contents, which are largely unpolymerized, Si, Al, and O are probably fairly mobile as the SiO_4^{4-} and AlO_4^{5-} radicals. In high-silica, low-water melts, these ions are mostly tied into large polymers or frameworks, and their mobilities should be correspondingly smaller. Ions which are not part of the Si/Al–O framework may be subject to two opposing effects of decreasing silica content; decreasing the polymerization increases the overall fluidity, which tends to increase mobility, but it also decreases the porosity. The decrease in porosity with decreasing silica content is shown by porosity values of 61% and 54% for rhyolite and basalt at 1000°C, calculated from the density measurements of Murase and McBirney (1973). Thus it is not surprising that diffusivities of several mono- and divalent ions in rhyolite are about the same as or higher than those in basalt at 1000°C (Jambon and Carron, 1973, 1978; Hofmann and Magaritz, 1977; Magaritz and Hofmann, 1978; Smith, 1974).

The addition of water also decreases the polymerization and the porosity. The decrease in porosity is shown by the measurements of Burnham and Davis (1971) on albite–water melts, in which the partial molar volume of water was found to be 11.2 cm^3/mole at room temperature, and those of Shaw (1974) on rhyolite–water, from which a value of 10.4 cm^3/mole can be derived (his data are almost perfectly linear, despite his suggestion to the contrary). These molar volumes yield "partial" porosities for water of 44 percent and 39 percent respectively, compared with values of 50 percent for pure albite glass (also calculated from the data of Burnham and Davis) and 54 percent for rhyolite (Table 1; this rhyolite contains 0.78 percent water).

Similarity in structure between high-silica melts and framework silicate crystals suggests that the diffusion properties should be similar (Shaw, 1974). The diffusivity data for cations in rhyolite at 800°C (Hofmann, 1980) are qualitatively consistent with the principles applied above to crystals. Univalent ions are mostly more mobile than divalent ions, and within each group the mobility decreases with ionic radius. The diffusivity values for water in rhyolite measured by Shaw (1974) are very similar to the value for K in rhyolite found by Jambon and Carron (1973), again as predicted above assuming water diffuses as OH. The values of about 10^{-7} to 10^{-9} at 800°C are much higher than the values of about 10^{-12} at the same temperature for both ions in feldspars (Foland, 1974; Giletti *et al.*, 1978). This is attributable to (1) somewhat higher porosity of rhyolite *vs.* feldspar at room temperature and the presumed greater thermal expansivity of rhyolite; (2) lower site energies in the partially randomized melt structure; and (3) some degree of fluid rather than crystalline behavior in the rhyolite. Thus, although the same factors are important in high-silica melts as in crystals and relative mobilities of ions tend to be similar, absolute diffusion rates are usually higher.

In basalts, the diffusivity values for non-framework cations are much less sensitive to crystal-chemical factors, although Hofmann (1980) found a good correlation of diffusivity at 1000°C with z^2r, charge-squared times ionic radius of cations. In low-silica melts, fluid behavior seems to dominate over crystalline behavior.

Conclusion

The crystal-chemical factors discussed in this paper by no means constitute a complete theoretical model of diffusion. The diffusion mechanisms of atoms in different structures are diverse, and may change with composition, stoichiometry, temperature, and pressure. The porosity can only be a rough guide to the freedom of movement of ions in crystal structures and site energies are only a part of the description of the energetics of diffusion. Nevertheless, the factors of porosity, site energy and ionic radius are obviously influential in the majority of cases, and can be very useful in the qualitative understanding of relative mobilities of ions.

Acknowledgments

I thank K. S. Deffeyes for helpful discussions. This work was supported in part by NSF grant EAR 76-22543.

References

Anderson, T. F. (1969) Self-diffusion of carbon and oxygen in calcite by oxygen isotope exchange with carbon dioxide. *J. Geophys. Res., 74,* 3918–3932.

——— and R. B. Kasper (1975) Oxygen self-diffusion in albite under hydrothermal conditions. *EOS, 56,* 459.

Bailey, A. (1971) Comparison of low-temperature with high temperature diffusion of sodium in albite. *Geochim. Cosmochim. Acta, 35,* 1073–1081.

Birchenall, C. E. (1968) Diffusion in oxides: assessment of existing data and experimental problems. In J. B. Wachtman and A. D. Franklin, Eds., *Mass Transport in Oxides,* p. 119–127. National Bureau of Standards Spec. Pub. 296.

Blander, M. and L. H. Fuchs (1975) Calcium–aluminum-rich inclusions in the Allende meteorite: evidence for a liquid origin. *Geochim. Cosmochim. Acta, 39,* 1605–1619.

Blattner, P. B. and A. F. Cooper (1974) Carbon and oxygen isotopic composition of carbonatite dikes and metamorphic country rock of the Haast schist terrain, New Zealand. *Contrib. Mineral. Petrol., 44,* 17–27.

Brunner, G. O., H. Wondratschek and F. Laves (1961) Ultrarotuntersuchungen über den Einbau von H in natürlichen Quarz. *Z. Elektrochem., 65,* 735–750.

Buening, D. K. and P. R. Buseck (1973) Fe–Mg lattice diffusion in olivine. *J. Geophys. Res., 78,* 6852–6862.

Burnham, C. W. (1975) Water and magmas: a mixing model. *Geochim. Cosmochim. Acta, 39,* 1077–1084.

——— and N. F. Davis (1971) The role of H_2O in silicate melts I. *P–V–T* relations in the system $NaAlSi_3O_8$–H_2O to 10 kilobars and 1000°C. *Am. J. Sci., 270,* 54–79.

Carmichael, I. S. E., F. J. Turner and J. Verhoogen (1974) *Igneous Petrology.* McGraw-Hill, New York.

Clayton, R. N., N. Onuma, L. Grossman and T. K. Makeda (1977) Distribution of the pre-solar component in Allende and other carbonaceous chondrites. *Earth Planet. Sci. Lett., 34,* 209–224.

Dienes, G. J., D. O. Welch, C. R. Fischer, R. D. Hatcher, O. Lazareth and M. Samberg (1976) Shell-model calculation of some point-defect properties in α-Al_2O_3. *Phys. Rev. 11B,* 3060–3070.

Donnay, G., J. Wyart and G. Sabatier (1959) Structural mechanism of thermal and compositional transformations in silicates. *Z. Kristallogr., 112,* 161–186.

Fairbairn, H. W. (1943) Packing in ionic minerals. *Geol. Soc. Am. Bull., 54,* 1305–1374.

Fleischer, R. L., P. B. Price and R. M. Walker (1975) *Nuclear Tracks in Solids.* University of California Press, Berkeley.

Foland, K. A. (1974) Alkali diffusion in orthoclase. In A. W. Hofmann, B. J. Giletti, H. S. Yoder and R. A. Yund, Eds., *Geochemical Transport and Kinetics,* p. 77–98. Carnegie Inst. Wash. Publ. 634.

Fructus-Ricquebourg, J., G. Sabatier and H. Curien (1963) Sur le mechanisme structural des changements de phases dans les tectosilicates: échange isotopique d'oxygene et recristallisation des verres. *Bull. Soc. fr. Mineral. Cristallogr., 86,* 90–91.

Garlick, G. D. and S. Epstein (1966a) Oxygen isotope ratios in coexisting minerals of regionally metamorphosed rocks. *Geochim. Cosmochim. Acta, 31,* 181–214.

——— and ——— (1966b) The isotopic composition of oxygen and carbon in hydrothermal minerals at Butte, Montana. *Econ. Geol., 61,* 1325–1335.

Giletti, B. J., M. P. Semet and R. A. Yund (1978) Studies in diffusion—III. Oxygen in feldspars, an ion microprobe determination. *Geochim. Cosmochim. Acta, 42,* 45–47.

Goldsmith, J. R. (1952) Diffusion in plagioclase feldspars. *J. Geol., 60,* 288–291.

——— and F. Laves (1954) The microcline–sanidine stability relations. *Geochim. Cosmochim. Acta, 5,* 1–19.

Griggs, D. (1967) Hydrolytic weakening of quartz and other silicates. *Geophys. J., 14,* 19–31.

Haack, V. (1972) Systematics in the fission track annealing of minerals. *Contrib. Mineral. Petrol., 35,* 303–312.

Hart, S. R. (1964) The petrology and isotopic mineral age relations in a contact zone in the Front Range, Colorado. *J. Geol., 72,* 493–525.

Hofmann, A. W. (1980) Diffusion in natural silicate melts: a critical review. In R. B. Hargraves, Ed., *Physics of Magmatic Processes.* Princeton University Press (in press).

——— and M. Magaritz (1977) Diffusion of Ca, Sr, Ba and Co in a basalt melt: implications for the geochemistry of the mantle. *J. Geophys. Res., 82,* 5432–5444.

Hollister, L. S. (1969) Contact metamorphism in the Kwoiek area of British Columbia: an end member in the metamorphic process. *Geol. Soc. Am. Bull., 80,* 2465–2494.

——— (1970) Origin, mechanism and consequences of compositional sector-zoning in staurolite. *Am. Mineral., 55,* 742–766.

Jambon, A. and J.-P. Carron (1973) Etude experimentale de la diffusion des elements alcalins K, Rb, Cs dans une obsidienne granitique. C. R. *Acad. Sci. Paris, 276D,* 3069–3072.

——— and ——— (1978) Etude experimentale de la diffusion cationique dans une verre basaltique—alcalins et alcalinoterreux. *Bull. Soc. fr. Mineral. Cristallogr., 101,* 22–26.

Jost, W. (1952) *Diffusion in Solids, Liquids, Gases.* Academic Press, New York.

Kasper, R. B. (1974) Cation diffusion in a low albite (abstr.). *Geol. Soc. Am. Abstracts with Programs, 6,* 815.

Kats, A., Y. Haven and J. M. Stevels (1962) Hydroxyl groups in α-quartz. *Phys. Chem. Glasses, 3,* 69–75.

Kofstad, P. (1972) *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides.* Wiley-Interscience, New York.

Lawrence, J. R. and M. Kastner (1975) $^{18}O/^{16}O$ of feldspars in carbonate rocks. *Geochem. Cosmochim. Acta, 39,* 97–102.

Lin, T.-H., and R. A. Yund (1972) Potassium and sodium self-diffusion in alkali feldspar. *Contrib. Mineral. Petrol., 34,* 177–184.

Magaritz, M. and A. W. Hofmann (1978) Diffusion of Sr, Ba and Na in obsidian. *Geochim. Cosmochim. Acta, 42,* 736–742.

Merigoux, H. (1968) Etude de la mobilite de l'oxygene dans les feldspaths alcalins. *Bull. Soc. fr. Mineral. Cristallogr., 91,* 51–64.

Misener, D. J. (1974) Cationic diffusion in olivine to 1400°C and 35 kbar. In A. W. Hofmann, B. J. Giletti, H. S. Yoder, and R. A. Yund, Eds., *Geochemical Transport and Kinetics,* p. 117–130. Carnegie Inst. Wash. Publ. 634.

Muehlenbachs, K. and I. Kushiro (1974) Oxygen isotope exchange and equilibrium of silicates with CO_2 or O_2. *Carnegie Inst. Wash. Year Book, 73,* 232–236.

Murase, T. and A. R. McBirney (1973) Properties of some common igneous rocks and their melts at high temperatures. *Geol. Soc. Am. Bull., 84,* 3563–3592.

Northrup, D. A. and R. N. Clayton (1966) Oxygen isotope fractionation in systems containing dolomite. *J. Geol., 74,* 174–196.

Ohashi, Y. (1976) Lattice energy of some silicate minerals and the effect of oxygen bridging in relation to crystallization sequence. *Carnegie Inst. Wash. Year Book, 75,* 644–648.

O'Neill, J. R. and H. P. Taylor (1967) The oxygen isotope and cation exchange chemistry of feldspars. *Am. Mineral., 52,* 1414–1437.

Petrovic, R. (1974) Diffusion of alkali ions in alkali feldspars. In W. S. McKenzie and J. Zussman, Eds., *The Feldspars,* p. 174–182. Manchester University Press.

Raymond, M. (1971) Madelung constants for several silicates. *Carnegie Inst. Wash. Year Book, 70,* 225–227.

Schoell, M., G. Morteani and P. K. Hormann (1975) $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios of carbonates from gneisses, serpentinites and marbles of the Zillertaler Alpen, Western Tauern area (Austria). *Neues Jahrb. Mineral. Monatsh.,* 444–459.

Seifert, F. A. and D. Virgo (1975) Kinetics of the Fe^{2+}–Mg, order-disorder reaction in anthophyllites; quantitative cooling rates. *Science, 188,* 1107–1109.

Shaw, H. R. (1974) Diffusion of H_2O in granitic liquids. Part I. Experimental data. In A. W. Hofmann, B. J. Giletti, H. S. Yoder and R. A. Yund, Eds., *Geochemical Transport and Kinetics,* p. 139–154. Carnegie Inst, Wash. Publ. 634.

Sipling, P. J. and R. A. Yund (1974) Kinetics of Al/Si disordering in alkali feldspars. In A. W. Hofmann, B. J. Giletti, H. S. Yoder and R. A. Yund, Eds., *Geochemical Transport and Kinetics,* p. 185–194. Carnegie Inst. Wash. Publ. 634.

Sippel, R. F. (1963) Sodium self-diffusion in natural minerals. *Geochim. Cosmochim. Acta, 27,* 107–120.

Smith, H. D. (1974) *An Experimental Study of the Diffusion of Na, K, and Rb in Magmatic Silicate Liquids.* Ph.D. Dissertation, University of Oregon.

Sucov, E. W. (1963) Diffusion of oxygen in vitreous silica. *J. Am. Ceram. Soc., 40,* 14–20.

Taylor, H. P., Jr. (1974) Oxygen and hydrogen evidence for large-scale circulation and interaction between ground waters and igneous intrusions, with particular reference to the San Juan volcanic field Colorado. In A. W. Hofmann, B. J. Giletti, H. S. Yoder and R. A. Yund, Eds., *Geochemical Transport and Kinetics,* p. 299–324. Carnegie Inst. Wash. Publ. 634.

——— and S. Epstein (1963) O^{18}/O^{16} ratios in rocks and coexisting minerals of igneous and metamorphic rocks. *J. Petrol., 4,* 51–74.

——— and ——— (1968) Hydrogen isotope evidence for influx of meteoric ground water into shallow igneous intrusions. *Geol. Soc. Am. Spec. Pap., 121,* 294–302.

Verhoogen, J. (1952) Ionic diffusivity and electrical conductivity in quartz. *Am. Mineral., 37,* 637–655.

Virgo, D. and S. S. Hafner (1969) Fe^{2+},Mg order–disorder in heated orthopyroxenes. *Mineral. Soc. Am. Spec. Pap., 2,* 67–81.

Wyart, J. and G. Sabatier (1958) Mobilité des ions silicium et aluminium dans les cristaux de feldspath. *Bull Soc. fr. Mineral. Cristallogr., 81,* 223–226.

———, ———, H. Curien, G. Ducheylard and M. Severin (1959) Echanges isotopiques des atomes d'oxygene dans les silicates. *Bull. Soc. fr. Mineral. Cristallogr., 82,* 387–389.

Yund, R. A. and T. F. Anderson (1974) Oxygen isotope exchange between potassium feldspar and KCl solution. In A. W. Hofmann, B. J. Giletti, H. S. Yoder and R. A. Yund, Eds., *Geochemical Transport and Kinetics,* p. 99–106. Carnegie Inst. Wash. Publ. 634.

——— and ——— (1978) The effect of fluid pressure on oxygen isotope exchange between feldspar and water. *Geochim. Cosmochim. Acta, 42,* 235–239.

Manuscript received, March 16, 1979;
accepted for publication, July 3, 1979.