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Oxygen diffusion in leucite: Structural controls

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Abstract—Oxygen self-diffusion coefficients were measured in natural crystals of leucite by gas/solid isotope exchange. The diffusion rates can be expressed (from 1000 to 1300°C) by the Arrhenius relation

$$D = (1.3 \pm {}^{3}_{1}) \times 10^{-11} \exp[(-14 \pm 3)/RT].$$

The activation energy of diffusion in leucite, 14 kcal/mole, is the lowest yet reported for oxygen diffusion in an anhydrous silicate. Because of the low activation energy, oxygen mobility persists to lower temperatures in leucite than in other silicates. The isotopic disequilibrium between coexisting leucite and pyroxene observed in volcanic rocks results from post-solidus oxygen exchange in leucite.

Oxygen diffusion in leucite and a wide variety of other minerals follows the "compensation law" which states that the pre-exponential factor of the Arrhenius equation is proportional to the activation energy. Furthermore, these two diffusion parameters are both proportional to anion porosity of the minerals indicating that anhydrous self-diffusion of oxygen proceeds by a common interstitial mechanism. The correlations of anion porosity to the pre-exponential factor and activation energy can be converted to a numerical expression predicting oxygen diffusion in any mineral as a function of temperature and anion porosity.

Hydrous oxygen diffusion rates are known to be much faster than equivalent anhydrous rates. The explanation may be that the species carrying oxygen during hydrous diffusion is significantly smaller than the mobile species for anhydrous diffusion.

INTRODUCTION

OXYGEN DIFFUSION PROCESSES are of considerable geochemical interest. The intrinsic mobility of oxygen atoms in minerals determines how successfully the isotopic record can be preserved in geological samples. Some situations where diffusion of oxygen may thwart simple geological interpretations are isotopic paleothermometry of Mesozoic and older carbonate fossils, geothermometry of high-grade metamorphic rocks, and isotopic anomalies in meteorites. However, information on geological processes (cooling rates, metasomatism, etc.) may be gleaned from the $\delta^{18}O$ values of coexisting minerals that are out of isotopic equilibrium if one knew the actual rates of oxygen movement in the various components as function of temperature.

Experimental measurements of diffusion rates are difficult and usually not very precise. Furthermore, the results depend on extrinsic variables such as water pressure (YUND and ANDERSON, 1978; FARVER and YUND, 1991), presence of hydrogen (ELPHICK and GRAHAM, 1988), or defect density in the minerals. Despite simple experimental designs, more than one mechanism of oxygen movement may be operating, thus confusing interpretation of the results. Theoretical insights into the controls on oxygen mobility in silicates would greatly simplify the extraction of information from the geochemical data base.

Oxygen is the largest and usually the most abundant ion in rock-forming minerals; thus, mineral structure likely controls oxygen diffusivity. DOWTY (1980) suggested that, generally, anion porosity (one minus volume of anions divided by volume of unit cell), electrostatic site energy, and size of ions all affect the mobility of ions in minerals. His model is relatively successful but he could not directly relate published oxygen diffusion rates in minerals with their anion porosity. CONNOLLY and MUEHLENBACHS (1988) showed that anion porosity was proportional to the activation energy of oxygen diffusion.

In this paper we present measurements of oxygen diffusion rates in leucite. Leucite was chosen for study because leucite phenocrysts are often out of isotopic equilibrium with their volcanic host (TAYLOR *et al.,* 1984), suggesting rapid oxygen diffusion. Furthermore, leucite has a high anion porosity and would, according to the model of CONNOLLY and MUEHLENBACHS (1988), have a proportionately low activation energy of oxygen diffusion. We also examine published anhydrous diffusion rates in other silicate minerals and suggest a simple relationship that predicts oxygen diffusion coefficients based solely on anion porosity. This relationship will be compared to a similar one proposed by FORTIER and GILETTI (1989) for hydrous oxygen diffusion.

EXPERIMENTAL PROCEDURE

Starting materials

Natural leucite ($KAlSi_2O_6$) was obtained from amygdules from the Civita Castellana basalt, Italy. Leucite was extracted from the vesicles, and ultrasonically cleaned to remove any altered surface layers adhering to the grains. Leucite crystals were hand picked from the concentrate under a binocular microscope. The purified leucite was carefully checked by XRD for the common alteration minerals of analcime, orthoclase, and nepheline. The leucite was further examined by electron microprobe to test if any alteration had occurred that might not be detected by XRD. Sulfide minerals were identified and removed using heavy liquids. Pure leucite was ground and sieved, using laser etched sieves, to a uniform size fraction (10 to 20 μm); further uniformity was achieved by using selective settling. Photographs were taken of the starting materials and final products using scanning electron microscopy.

Gas for the exchange experiments was high purity, dry, CO_2 gas obtained commercially. The isotopic composition of the gas was monitored closely during the experiments and did not change.

Diffusion experiments

The method of MUEHLENBACHS and KUSHIRO (1974) was used to determine oxygen diffusion in leucite. Leucite ($\delta^{18}O = +8.94$) was suspended in a Pt basket within a gas-tight, vertical tube furnace. Air was purged from the system by flushing with CO_2 gas ($\delta^{18}O = +30.36$); this same gas was used subsequently for the high temperature isotopic exchange experiments. Diffusion constants calculated from exchange with either CO_2 or O_2 are identical within experimental error (MUEHLENBACHS and KUSHIRO, 1974; CANIL and MUEHLENBACHS, 1987). The temperature (1000 to 1400°C) in the furnace was monitored with a Pt-$Pt_{87}Rh_{13}$ thermocouple; the uncertainty in temperature was ±3°C. The advantage of the above method is that the isotopic composition of the gas does not change and therefore, only the changes in isotopic composition of the mineral need to be determined to calculate the diffusion coefficient.

Diffusion coefficients were calculated from the partial exchange experiments using the following diffusion equation (JOST, 1960):

$$\frac{\delta^{18}O_f - \delta^{18}O_e}{\delta^{18}O_i - \delta^{18}O_e} = \frac{6}{\pi^2} \sum_{\nu} \frac{1}{\nu^2} \exp\left[\frac{-\nu^2\pi^2}{r_0^2} Dt\right] \qquad (1)$$

where D is the diffusion coefficient (cm^2/s); t is time (sec); r_0 is the sample radius (cm); $\delta^{18}O_f$ is the isotopic composition of the exchanged sample; $\delta^{18}O_i$ is the isotopic composition of the starting material; and $\delta^{18}O_e$ is the isotopic composition of material at isotopic equilibrium with the flowing gas. The equilibrium fractionation between CO_2 gas and leucite was taken to be 2.3 per mil as in previous studies (HAYASHI and MUEHLENBACHS, 1986; CONNOLLY and MUEHLENBACHS, 1988). Equation (1) converges depending on the degree of exchange; a minimum of 50 terms was used for each calculation. Equation (1) assumes spherical symmetry of the mineral grains and no limiting surface reactions such as grain boundary or surface diffusion. Evidence that these conditions are met is that similar diffusion coefficients are obtained at the same temperature regardless of run time.

$\delta^{18}O$ analyses of the minerals were done using the BrF_5 method (CLAYTON and MAYEDA, 1963) and the isotopic ratios were determined by gas source mass spectrometry. Replicate analyses had a reproducibility of better than ±0.1 per mil. Results are reported in the usual δ-notation relative to the SMOW standard.

RESULTS

The results of the exchange experiments and the calculated oxygen diffusion coefficients for leucite are presented in Table 1. Exchange experiments ranged in temperature from 1000 to 1400°C at 100 degree intervals for durations of from 2 to 90 hours. At least three run durations were made at each temperature. The percentage of oxygen exchanged in the leucite samples ranged from 7 to almost 70%, and no systematic variation in calculated diffusion coefficient with exchange time was noted.

The calculated oxygen diffusion coefficients are plotted against $1/T$ (K) on an Arrhenius diagram in Fig. 1. Inspection of the figure shows that oxygen diffusion rates in leucite are relatively insensitive to temperature from 1000 to 1300°C, implying a very low activation energy. The diffusion data at 1400°C seem fast in comparison with the trend established by the lower temperature runs. However, SEM observations of leucite products from the 1400°C experiments show them to be substantially sintered to rounded, shapes that violate the conditions for the diffusion Eqn. (1) and thus invalidating the calculated log D values. In the subsequent discussion the 1400°C runs will be ignored.

The 1000 to 1300°C data fit a simple linear Arrhenius diffusion relation:

$$D = D_0 e^{-E_{act}/RT}$$

where D (cm^2/sec) is the diffusion coefficient, D_0 is the pre-exponential factor (Arrhenius frequency factor), E_{act} is the activation energy (in kcal) of diffusion, R is the gas constant, and T is absolute temperature. The data for leucite (1000–1300°C) yield the following equation:

$$D = (1.3 \pm {}^{3}_{1}) \times 10^{-11} \exp[(-14 \pm 3)/RT]. \qquad (2)$$

The activation energy of oxygen diffusion in leucite is 14 ± 3 kcal/mole, the lowest yet observed in any silicate.

DISCUSSION

Application to volcanic rocks

Oxygen diffusion rates in leucite are compared to those in nepheline, melilite, and diopside on an Arrhenius plot in Fig. 2. Oxygen diffuses slower in leucite than in melilite or nepheline, although all have low activation energies. Oxygen diffusion rates in diopside, although comparable to those in leucite at high temperatures, decrease rapidly with temperature due to a high activation energy. This implies that in rocks, oxygen exchangeability in leucite

Table 1. Experimental conditions and results for oxygen diffusion in leucite crystals

Temperature (°C)	Time (h)	$\delta^{18}O_f$	Exchange* %	log D (cm^2/s)
1000	2	10.55	7.9	−13.29
1000	4	10.98	9.8	−13.41
1000	8	11.86	14.0	−13.39
1000	32	12.82	15.5	−13.35
				−13.36 ± 0.05
1100	8	11.57	12.6	−13.48
1100	16	14.97	29.9	−12.99
1100	32	15.90	34.5	−13.15
1100	90	18.29	44.8	−13.33
				−13.24 ± 0.21
1200	2	11.61	12.5	−12.89
1200	16	15.93	34.4	−12.85
1200	32	16.17	35.8	−13.11
1200	68	20.14	55.5	−12.99
				−12.94 ± 0.12
1300	4	12.77	18.3	−12.84
1300	8	12.81	18.5	−13.13
1300	16	15.81	33.8	−12.86
				−12.94 ± 0.16
1400	2	13.18	20.9	−12.42
1400	8	15.59	31.8	−12.62
1400	16	20.49	56.9	−12.33
1400	32	22.62	67.4	−12.43
				−12.45 ± 0.12

* Starting leucite = 8.94 per mil; Exchange CO_2 gas, 30.36‰ (SMOW).

(or nepheline and melilite) may persist to low temperatures, whereas diffusion rates in diopside become vanishingly small at similar temperatures. The diffusion data can explain the oxygen isotope disequilibrium observed between leucite and pyroxene in the lavas from New South Wales, Australia (TAYLOR *et al.,* 1984). Small phenocrysts of leucite can exchange with air or water at temperatures as low as 500°C in a matter of decades while the $\delta^{18}O$ of pyroxene crystals would remain unaffected. However, diffusion rates in leucite are slow enough that larger size crystals would take thousands of years to exchange oxygen with an external fluid at sub-solidus temperatures.

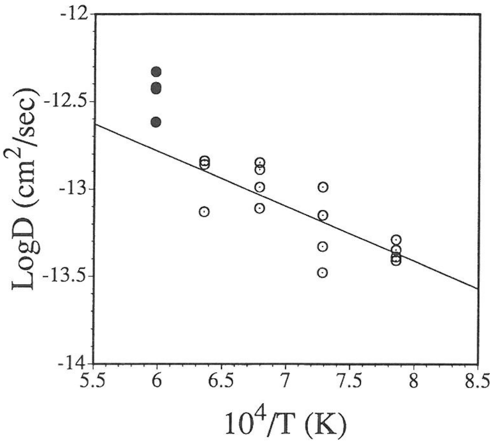

FIG. 1. Oxygen diffusion rates in leucite crystals as function of temperature—1400°C data not included in the regression line (see text).

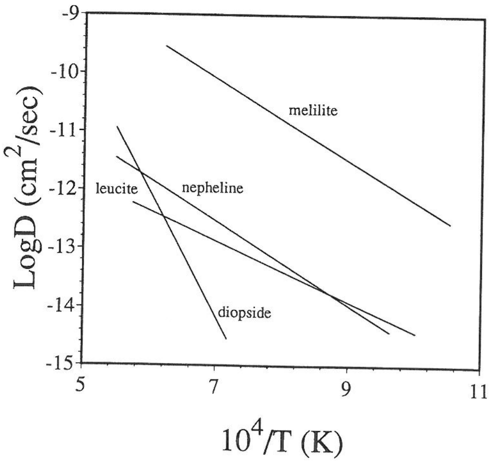

FIG. 2. Comparison of oxygen diffusion rates in leucite, melilite (HAYASHI and MUEHLENBACHS, 1986), nepheline, and diopside (CONNOLLY and MUEHLENBACHS, 1988).

Structural controls on diffusion

Oxygen mobility varies enormously in minerals. Not only do the diffusion coefficients of minerals vary by many orders of magnitude at any one temperature, but their temperature sensitivity, as reflected in the E_{act}, can vary by nearly a factor of ten. Table 2 lists anhydrous oxygen diffusion data, compiled from the literature, obtained from gas/mineral exchange experiments analogous to those of this study. Cursory inspection of Table 2 reveals that the minerals with low activation energies for oxygen diffusion, including leucite (14 kcal/mol), nepheline (25 kcal/mol) and melilite (31 kcal/mol) are all characterized by loosely packed, open structures. In contrast, the minerals with high activation energies; diopside (96 kcal/mol), forsterite (70–99 kcal/mol), spinel (100 kcal/mol), and sapphire (148 kcal/mol) are all characterized by densely packed lattices. It is possible that in minerals with low activation energies, the open structures allow the passage of mobile species capable of exchanging with the lattice oxygen, such as in SiO_2 glass (SCHAEFFER and MUEHLENBACHS, 1978). The greater oxygen mobility in melilite compared to leucite may be a result of the sheet-like structures in the former, which allow continuous passage of the diffusing species in contrast to the non-intersecting channels in the latter (DEER *et al.*, 1966).

WINCHELL (1969) suggested that diffusion in silicates obeys the "compensation law" which states that, in the Arrhenius expression, the preexponential term is proportional to the activation energy. COLE and OHMOTO (1986) gave a detailed compilation of diffusion parameters in a wide variety of mineral types and reaction conditions and showed that separate compensation laws held for oxygen diffusion in silicates, sulfates, and carbonates. Figure 3 demonstrates that for anhydrous oxygen diffusion the "compensation law" is indeed observed. The high degree of correlation ($R = 0.80$) between $\ln D_0$ and E_{act} shown in Fig. 3 is surprising because the "compensation law" should hold only if similar mechanisms of oxygen diffusion are operative in these diverse minerals. The strong correlation is even more remarkable if one considers that the data come from different laboratories, using drastically different analytical methods on both natural and synthetic samples. The inference to be drawn is that oxygen diffuses in these minerals by predominantly one type of mechanism involving the same carrier species. Note that GERARD and

Table 2. Diffusion parameters for anhydrous oxygen diffusion in silicate minerals

Mineral	Anion porosity (%)	$\ln D_0$	E_{act} kcal/mole	Ref.
Leucite (lu)	58.0	−25.10	14	(1)
Nepheline (ne)	54.1	−18.95	25.0	(2)
Melilite (50) (mel)	51.4	−11.66	33.5	(3)
Melilite (75) (mel)	51.8	−11.84	31.9	(3)
Anorthite (an)	49.7	−11.51	56.3	(4)
Forsterite (fo)	42.0	−3.56	99.3	(5)
Forsterite (fo)	42.0	−12.98	70	(6)
Diopside (di)	42.4	+1.84	96.7	(2)
Quartz (q)	46.5	−15.02	53	(4)
SiO_2 glass (SiO_2)	53.5	−23.85	19.7	(7)
Mg-Spinel (sp)	36.2	−0.12	105	(8)
Mg-Spinel (sp)	36.2	−4.55	99.1	(9)
MgO (MgO)	43.5	−8.57	88.3	(10)
αFe_2O_3 (Fe_2O_3)	37.1	+6.45	99.7	(10)
Sapphire (saph)	25.5	+5.60	146.8	(11)
Perovskite (pr)	43.3	+1.61	74.8	(12)

(1) This work.
(2) CONNOLLY and MUEHLENBACHS (1988).
(3) HAYASHI and MUEHLENBACH (1986).
(4) ELPHICK *et al.* (1988).
(5) ANDO *et al.* (1981).
(6) JAOUL *et al.* (1983).
(7) SCHAEFFER and MUEHLENBACHS (1978).
(8) ANDO and OISHI (1974).
(9) REDDY and COOPER (1981).
(10) REDDY and COOPER (1983).
(11) REDDY and COOPER (1982).
(12) Revised from GAUTASON and MUEHLENBACHS (1991).

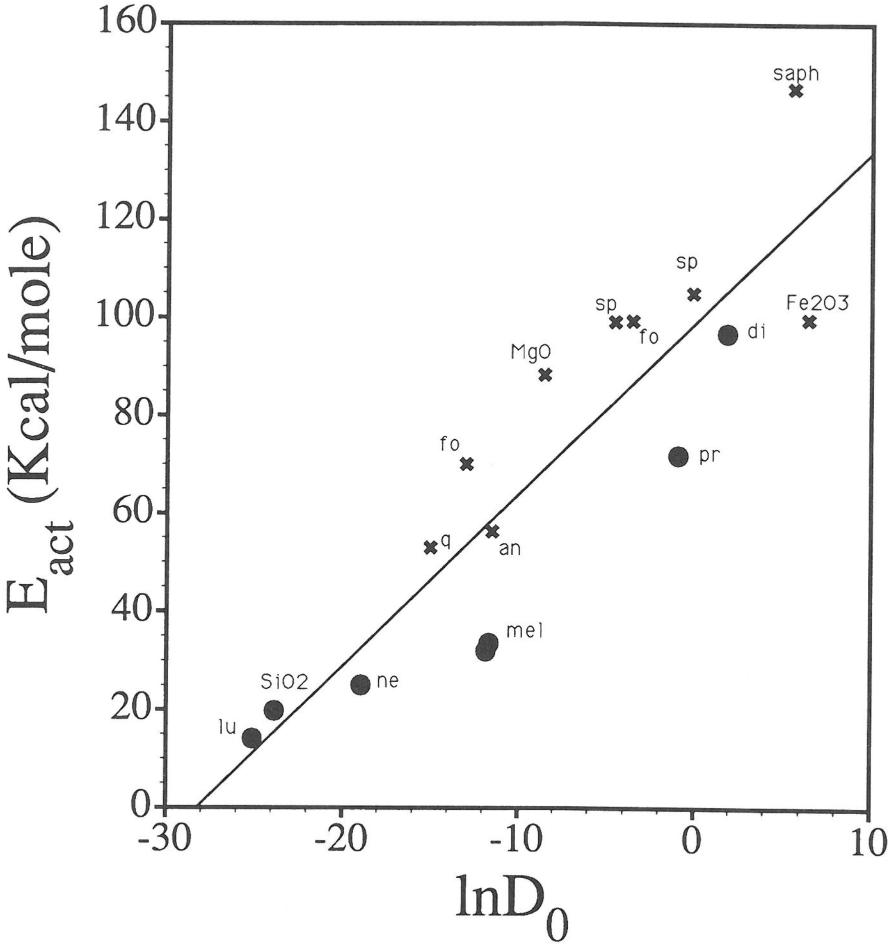

FIG. 3. The "compensation law." E_{act} vs. ln D_0 for anhydrous oxygen diffusion. Abbreviations and references given in Table 2 ($R = 0.80$).

JAOUL (1989) and RYERSON *et al.* (1989) concluded that oxygen diffused by an interstitial mechanism in San Carlos olivine. GERARD and JAOUL (1989) further suggest that the requisite interstitial defects can be produced by incorporation of gaseous oxygen into the olivine.

Anion porosities for each mineral are also given in Table 2. In a study of ionic diffusion in minerals, DOWTY (1980) suggested that anion porosity, electrostatic site energy, and the size of the diffusing ion are all factors in determining the diffusion rate. CONNOLLY and MUEHLENBACHS (1988) suggested that anion porosity correlates directly with the activation energy of oxygen diffusion. Figure 4 is a plot of those parameters taken from Table 2. A high degree of correlation ($R = 0.93$) is found between anion porosity and measured activation energies of oxygen diffusion in a wide variety of silicates and oxides ranging from leucite to sapphire. Closer examination of Fig. 4 reveals that the slope of the overall trend of anion porosity against E_{act} may be biased by the oxides: sapphire, spinel, and αFe_2O_3. Thus, the line drawn in Fig. 4 is based on regressing only the oxygen diffusion data measured by us ($R = 0.95$).

If, as is implied by the above arguments, anion porosity is proportional to E_{act}, then anion porosity should also be proportional to ln D_0 if the "compensation law" holds true. Figure 5 is a plot of ln D_0 vs. anion porosity. Again, a good correlation ($R = 0.73$) between anion porosity and ln D_0 for oxygen diffusion is observed in very diverse minerals. As in Fig. 4, the line on Fig. 5 is based on fitting our data alone ($R = 0.92$). From the above arguments, anhydrous oxygen diffusion rates in minerals appear to be controlled dominantly by the void space in the crystal.

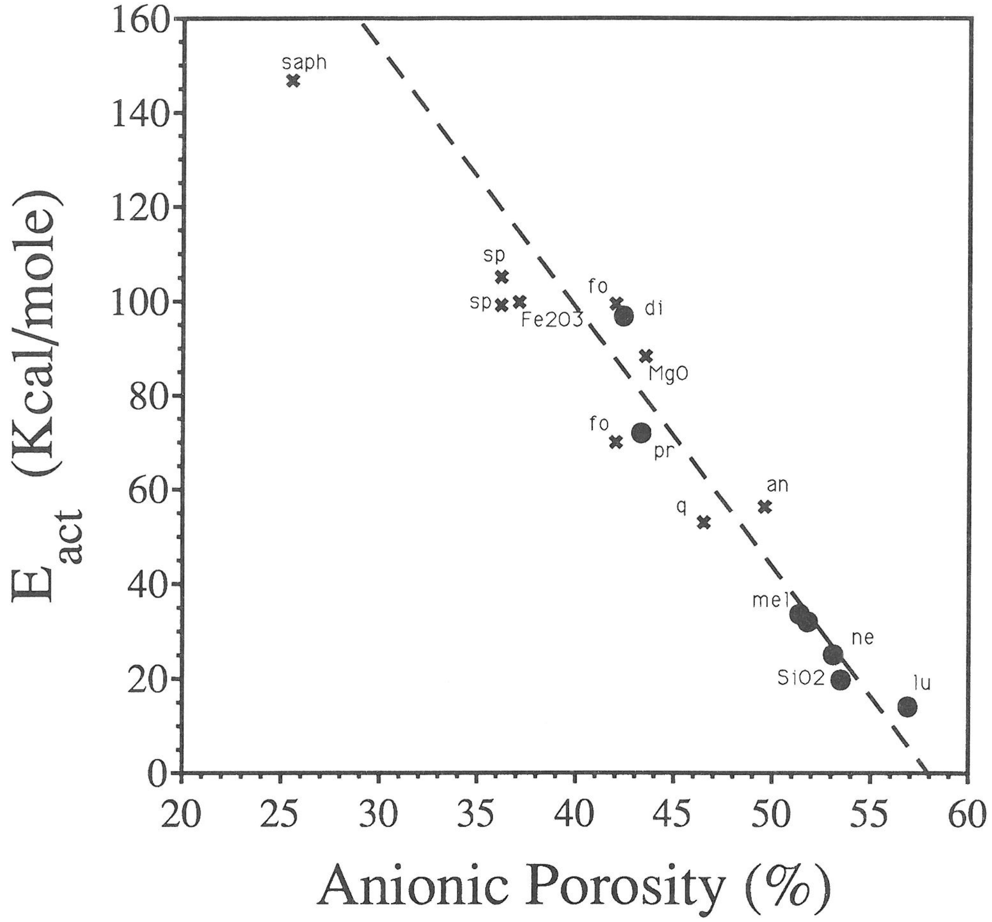

FIG. 4. E_{act} for anhydrous oxygen diffusion vs. anion porosity of crystal lattices. Abbreviations and references given in Table 2 ($R = 0.95$, our data only).

The relations between anion porosity and E_{act} (Fig. 4) or ln D_0 (Fig. 5) can be substituted directly into an Arrhenius equation to yield a numerical relation predicting the anhydrous oxygen mobility in any mineral at any temperature from its anion porosity (P, given as percent) alone:

$$D = \exp\left\{81.2 - 1.87 \times P - \left(\frac{318 - 5.49 \times P}{RT}\right)10^3\right\}. \quad (3)$$

The validity of Eqn. (3) is difficult to assess independently because Eqn. (3) is derived from most of the published measurements of anhydrous, gas/solid diffusion studies. However, MUEHLENBACHS and CHACKO (1991) showed that the rate of oxygen exchange between aragonite and sanidine above 50 kbars slows down substantially in proportion to the compressibility of sanidine, indirectly substantiating the logic behind Eqn. (3).

Comparison with hydrous diffusion

Equation (3) is similar to the relation proposed by FORTIER and GILETTI (1989) that predicts hydrous oxygen diffusion rates from ionic porosity. Both relations are based on the Arrhenius equation but the coefficients are significantly different. The apparent discrepancy in the coefficients is to be expected because, as many authors have commented (DOWTY, 1980; ELPHICK *et al.*, 1988; FARVER and YUND, 1991), hydrous and anhydrous oxygen diffusion experiments yield fundamentally different results, implying a crucial role for "water" during oxygen transport in silicates.

FARVER's (1989) hydrothermal oxygen diffusion rates in diopside (ln $D_0 = -13.4$; $E_{act} = 54$ kcal) fit

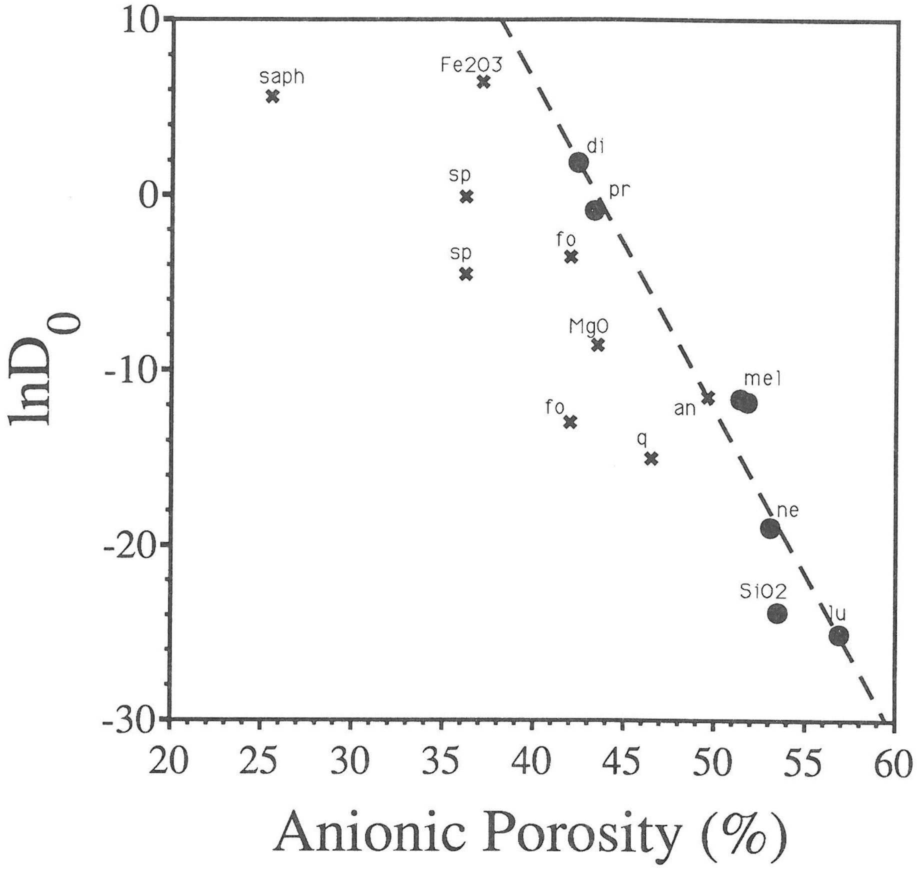

FIG. 5. ln D_0 for anhydrous oxygen diffusion vs. anion porosity of crystal lattices. Abbreviations and references in Table 2 ($R = 0.92$, our data only).

the "compensation law" (Fig. 3) but do not fall along the trends relating anhydrous diffusion parameters to porosity (Figs. 4 and 5). As is observed in many other minerals, oxygen diffusion in diopside is much faster under hydrothermal conditions than under 1 atmosphere anhydrous conditions. If both anhydrous and hydrous diffusion rates are controlled by porosity or vacant space within the diopside and the crystal does not expand with water pressure, then it must be concluded that the mobile "wet species" in oxygen diffusion is smaller than the oxygen carrier in dry systems. The apparent changes in porosity to reconcile wet diffusion rates to dry ones in diopside is substantial. Results from the wet and dry experiments are compatible if the space available for hydrous diffusion in diopside were 50% instead of the true 42.4%. We suggest that the correct interpretation is that the diffusing species in the wet experiments is correspondingly smaller (~1/6) than for anhydrous oxygen diffusion.

CONCLUSIONS

Oxygen self-diffusion coefficients for leucite from 1000 to 1300°C fit an Arrhenius relation of the form

$$D = (1.3 \pm {}^{3}_{1}) \times 10^{-11} \exp[(-14 \pm 3)/RT].$$

The activation energy for anhydrous oxygen self-diffusion in leucite is the lowest ever reported for an anhydrous silicate mineral. Significant oxygen mobility persists to sub-solidus temperatures in leucite crystals explaining the observed isotopic disequilibrium between leucite and pyroxene that has been observed in some volcanic rocks.

The activation energy of diffusion in a wide variety of silicates and oxides is proportional to the pre-exponential factor, implying one dominant mechanism of diffusion. Both the E_{act} and ln D_0 are proportional to anion porosity of the lattices, suggesting that diffusion occurs through the movement of some species through the interstices of the crystal. The leucite data, and previously published data, can be generalized to give numerical values of oxygen diffusion coefficients in minerals as functions of temperature and anion porosity (P in %):

$$D = \exp\left\{81.2 - 1.87 \times P - \left(\frac{318 - 5.49 \times P}{RT}\right)10^3\right\}.$$

The above relation applies only to anhydrous diffusion. Hydrothermal diffusion rates are described by a different equation (Fortier and Giletti, 1989) but one of the same form. These differing rate laws for "wet versus dry" diffusion can be reconciled if the diffusing species in the hydrothermal experiments were much smaller than the diffusing species in the anhydrous experiments.

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REFERENCES

Ando K. and Oishi Y. (1974) Self-diffusion coefficients of oxygen ion in single crystals of $MgO \cdot nAl_2O_3$ spinels. *J. Chem. Phys.* **61,** 625–629.

Ando K., Kurokawa H. and Oishi Y. (1981) Self-diffusion coefficient of oxygen in single-crystal forsterite. *Com. Amer. Ceram. Soc.* **64,** C30.

Canil D. and Muehlenbachs K. (1987) Self-diffusion of oxygen in an Fe-rich basal melt. *Geol. Soc. Amer. Abstr. Prog.* **19,** 610.

Clayton R. N. and Mayeda T. K. (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta* **27,** 42–52.

Cole D. R. and Ohmoto H. (1986) Kinetics of isotope exchange at elevated temperatures and pressures. In *Stable Isotopes in High Temperature Geologic Processes* (eds. J. W. Valley, H. P. Taylor, Jr. and J. R. O'Neil), *Reviews in Mineralogy 16,* pp. 41–87. Mineralogical Society of America.

Connolly C. and Muehlenbachs K. (1988) Contrasting oxygen diffusion in nepheline, diopside and other silicates and their relevance to isotopic systematics in meteorites. *Geochim. Cosmochim. Acta* **52,** 1585–1591.

Deer W. A., Howie R. A. and Zussman J. (1966) *An Introduction to the Rock-Forming Minerals.* J. Wiley & Sons, New York.

Dowty E. (1980) Crystal-chemical factors affecting the mobility of ions in minerals. *Amer. Mineral.* **65,** 174–182.

Elphick S. C. and Graham C. M. (1988) The effect of hydrogen on oxygen diffusion in quartz: evidence for fast proton transients. *Nature* **335,** 243–245.

Elphick S. C., Graham C. M. and Dennis P. F. (1988) An ion microprobe study of anhydrous oxygen diffusion in anorthite: A comparison with hydrothermal data and some geological implications. *Contrib. Mineral. Petrol.* **100,** 490–495.

Farver J. R. (1989) Oxygen self-diffusion in diopside with application to cooling rate determinations. *Earth Planet. Sci. Lett.* **92,** 386–396.

Farver J. R. and Yund R. A. (1991) Oxygen diffusion in quartz: Dependence on temperature and water fugacity. *Chem. Geol.* **90,** 55–70.

Fortier S. M. and Giletti B. J. (1989) An empirical model for predicting diffusion coefficients in silicate minerals. *Science* **245,** 1481–1484.

Gautason B. and Muehlenbachs K. (1991) Rapid oxygen diffusion in $CaTiO_3$ perovskite. *Geol. Assoc. Canada Prog. Abstr.* **16,** A43.

Gerard O. and Jaoul O. (1989) Oxygen diffusion in San Carlos olivine. *J. Geophys. Res.* **94,** 4119–4128.

Hayashi T. and Muehlenbachs K. (1986) Rapid oxygen diffusion in melilite and its relevance to meteorites. *Geochim. Cosmochim. Acta* **50,** 585–591.

Jaoul O., Houlier B. and Abel F. (1983) Study of ^{18}O diffusion in magnesium orthosilicate by nuclear microanalysis. *J. Geophys. Res.* **88,** 613–624.

Jost W. (1960) *Diffusion in Solids, Liquids, and Glasses.* Academic Press, New York.

Muehlenbachs K. and Chacko T. (1991) The effect of very high pressure (35–85 Kbar) on oxygen isotope exchange rates between potassium feldspar and calcium carbonate. *Geol. Assoc. Canada Progr. Abstr.* **16,** A86.

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

Reddy K. P. R. and Cooper A. R. (1981) Oxygen diffusion in magnesium aluminate spinel. *J. Amer. Ceram. Soc.* **64,** 368–371.

Reddy K. P. R. and Cooper A. R. (1982) Oxygen diffusion in sapphire. *J. Amer. Ceram. Soc.* **65,** 634–638.

Reddy K. P. R. and Cooper A. R. (1983) Oxygen diffusion in MgO and α-Fe_2O_3. *J. Amer. Ceram. Soc.* **66,** 664–666.

Ryerson F. J., Durham W. B., Cherniak D. J. and Lanford W. A. (1989) Oxygen diffusion in olivine: Effect of oxygen fugacity and implications for creep. *J. Geophys. Res.* **94,** 4105–4118.

Schaeffer H. A. and Muehlenbachs K. (1978) Correlations between oxygen transport phenomena in non-crystalline silica. *J. Mat. Sci.* **13,** 1146–114.

Taylor H. P., Jr., Turi B. and Cundari A. (1984) $^{18}O/^{16}O$ and chemical relationships in K-rich volcanic rocks from Australia, East Africa, Antarctica, and San Venanzo-Cupaello, Italy. *Earth Planet. Sci. Lett.* **69,** 263–276.

Voltaggio M. (1985) Estimation of diffusion constants by observations of isokinetic effects test for radiogenic argon and strontium. *Geochim. Cosmochim. Acta* **49,** 2117–2122.

Winchell P. (1969) The compensation law for diffusion in silicates. *High Temp. Sci.* **1,** 200–215.

Yund R. A. and Anderson T. F. (1978) Oxygen isotope exchange between feldspar and fluid as a function of fluid pressure. *Geochim. Cosmochim. Acta* **42,** 235–239.