Oxygen diffusion studies. I. A preliminary ion microprobe investigation of oxygen diffusion in some rock-forming minerals

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ABSTRACT. The self diffusion of oxygen has been studied in prepared natural crystals of albite, grossular garnet, quartz, and rutile by isotope exchange with hydrothermal water enriched in ^{18}O, and subsequent analysis by ion microprobe. Measured oxygen diffusion coefficients (D) in quartz ($\|c$) may be described by $D = 1.08 \times 10^{-11}$ $\exp(-31.5 \text{ kcal}/RT)$ $\text{cm}^2 \text{ s}^{-1}$ at 600-750 °C and 1 kbar water pressure. For grossular, $D = 2.5 \times 10^{-16}$ $\text{cm}^2 \text{ s}^{-1}$ at 1050 °C and 8 kbar, and $D = 4.8 \times 10^{-17}$ $\text{cm}^2 \text{ s}^{-1}$ at 850 °C and 2 kbar. All rutile crystals exhibited variable amounts of corrosion, and an approximate diffusion coefficient of $D(\|c) = 3.16 \times 10^{-15}$ $\text{cm}^2 \text{ s}^{-1}$ was obtained at 1050 °C and 1 kbar. Oxygen diffusion coefficients in albite, perpendicular to (001) faces, have been determined as a function of pressure at 600 °C. Between 0.5 and 8.0 kbar pressure no systematic variation in the results was observed and most of the data may be described by $D = 4.1 (\pm 0.5) \times 10^{-15}$ $\text{cm}^2 \text{ s}^{-1}$. Slow oxygen diffusion rates in quartz and garnet suggest that these minerals should have high 'closure temperatures' for oxygen exchange, and may provide reliable oxygen isotope exchange geothermometers.

THE transport properties of oxygen in the rock-forming minerals have received considerable attention in recent years because of the importance of stable isotope equilibration rates in interpreting isotope data for metamorphic and igneous rocks, and fluid-mineral interactions. Giletti et al. (1978) summarize a number of processes which require a knowledge of the kinetics of oxygen isotope exchange as a function of temperature; these include oxygen isotope geothermometry, the interaction of seawater with basalt on or below mid-ocean ridges, the equilibration of xenoliths with their host rocks, and the plastic deformation of minerals due to volume diffusion.

Experimental studies of oxygen diffusion in

silicate minerals under hydrothermal conditions have been largely confined to feldspars (Merigoux, 1968; Yund and Anderson, 1974; Kasper, 1975; Anderson and Kasper, 1975; Giletti et al., 1978; Yund and Anderson, 1978), phlogopite (Giletti and Anderson, 1975), forsterite (Giletti et al., 1979), and quartz (Choudhury et al., 1965). Data are also available for the exchange of oxygen between water vapour and magnetite at 1 bar total pressure (Castle and Surman, 1967). Diffusion in all these systems is characterized by low activation energies (typically 30 kcal mol^{-1}) and comparatively high diffusion rates, especially for the feldspars (e.g. Giletti et al., 1978). In contrast, oxygen exchange experiments under essentially dry conditions, between silicate minerals and dry O_2 or CO_2 (e.g. Muehlenbachs and Kushiro, 1974; Reddy et al., 1980), yield higher activation energies, and diffusion coefficients which are generally several orders of magnitude slower than results from hydrothermal experiments would predict. The differences are believed to arise from variations in the oxygen exchange and transport mechanisms. Dry experiments may represent volume diffusion predominantly, but there must be some additional water-mineral interaction in the wet (i.e. $P_{H_2O} = P_{total}$) experiments, e.g. hydrolysis (Yund and Anderson, 1978; Graham, 1981), surface exchange and solution-reprecipitation (Matthews et al., 1980). These processes may be pressure-dependent, and may occur to varying degrees in any given situation.

Solid-state diffusion experiments under dry conditions show that the effect of increasing pressure is to lower diffusion coefficients (e.g. Lazarus and Nachtrieb, 1963; Misener, 1974). Considerably less

data are available for the rate of diffusion as a function of pressure in the corresponding hydrothermal experiments, but Giletti and Tullis (1977) were unable to detect any significant change in the diffusion of Ar in phlogopite between 2 and 15 kbar. However, Yund and Anderson (1978) reported that oxygen diffusivity in adularia at 650 °C *increased* by a factor of 10 as water pressures increased from 125 to 4000 bar. This unusual 'reverse' effect was explained in terms of the increased activity of the 'water' in the feldspar, and was taken to support some form of hydrolysis reaction mechanism.

In order to try to contribute to the understanding of oxygen exchange processes in rock-forming minerals, oxygen diffusion rates have been determined in a variety of minerals as a function of temperature, and also of pressure. Prepared fragments of albite, rutile, garnet, and quartz were partially exchanged with water enriched in ^{18}O, and the resulting ^{18}O penetration profiles measured by ion microprobe. The minerals exhibit a wide range of oxygen diffusion coefficients. In addition, the specimen preparation was varied to demonstrate selected features and problems associated with oxygen diffusion studies under hydrothermal conditions.

Two principal types of exchange experiment are in common use for oxygen diffusion studies. Both have their relative merits and disadvantages. To facilitate easier comparison between data obtained by the two methods, and provide background for subsequent discussions, the techniques are briefly outlined in the next section.

In common with the practice of Giletti *et al.* (1978) we frequently employ the term *oxygen diffusion* whilst we accept that the transport mechanism is poorly understood.

Techniques for the measurement of oxygen diffusion rates in minerals

The bulk exchange technique

The bulk exchange (or integration) technique, so called because it is based on the total amount of isotopic exchange which has occurred between a mineral powder and a fluid during an experiment, has frequently been used for diffusion studies in silicate minerals. Although the technique has severe limitations with regard to the information which may be extracted from the measurements, the experiments are in principle straightforward to perform (Giletti and Anderson, 1975; Yund and Anderson, 1974).

For oxygen isotope exchange experiments, crystalline material is usually ground to a powder, sieved to give a limited range of grain size, and then allowed to react (under conditions of controlled pressure and temperature) with a liquid or gas whose oxygen isotopic content need only differ from that of the solid by a few permil. The oxygen isotope ratio of the powder, and in some instances the fluid, is then analysed by conventional mass spectrometry (Clayton and Mayeda, 1963). The only requirement of the technique is that the isotopic exchange must attain at least several per cent (usually $\geqslant 10$) of the equilibrium value in order to demonstrate that more than merely superficial exchange has occurred. This represents typical experimental run times of 14–30 days for diffusion coefficients of $\simeq 10^{-14}$–10^{-15} cm^2 s^{-1}, although this is strongly dependent on grain size.

By assuming that the exchange processes may be approximated to diffusion from a well-stirred reservoir into particles of known geometry, the diffusion coefficient may be calculated (Crank, 1975). For this it is usually necessary to assume a suitable geometrical model for the grains, e.g. sphere, cylinder, or sheet, and define their effective 'diffusion radius'. The errors arising from such procedures are discussed by Lin and Yund (1972). In addition to the variety of estimates and assumptions required for the analysis, the technique suffers from the disadvantage that anisotropic diffusion can not always be investigated (the micas are an obvious exception), and because of the integration procedure no information is obtained about surface reactions, solution-reprecipitation phenomena, or detailed diffusional behaviour. However, the technique does allow a check on the existence of true volume diffusion by performing experiments in which there is a large amount of isotopic exchange (Giletti *et al.*, 1978).

Single crystal exchange

Recent developments in physical analytical chemistry have enabled the determination of ^{18}O concentration gradients in materials over a depth range of 25 nm to 5–10 μm. This covers the region of immediate interest to the experimental petrologist, with the measurement of diffusion coefficients in the range 10^{-11} to 10^{-20} cm^2 s^{-1} following exchange anneals of 10 hours to one one-month duration respectively. Direct determination of the form of the ^{18}O concentration distribution offers distinct advantages over the bulk exchange method, and allows (within one experiment) the possible interpretation of: (*a*) surface exchange kinetics; (*b*) solution-reprecipitation phenomena; (*c*) dislocation- and damage-enhanced diffusion; (*d*) diffusional anistropy; and (*e*) non-fickian type behaviour.

The two most important analytical techniques are (i) nuclear activation analysis and (ii) secondary

ion mass spectrometry (SIMS). In both methods oriented single-crystal fragments of the material under study are reacted with a fluid or gas phase whose oxygen isotope composition, 10–40% $^{18}O/$ ($^{18}O + {}^{16}O$), differs markedly from that of the solid. Partial approach to isotopic equilibrium is achieved under controlled laboratory conditions, and the degree of approach to equilibrium is considerably less than 1%, as opposed to minimum values $\simeq 10\%$ for the bulk exchange methods. After the exchange both analytical methods provide an ^{18}O concentration gradient with depth beneath the oriented crystal surface:

Nuclear activation analysis. The most important reaction for the study of ^{18}O depth distribution is $^{18}O(p,\alpha)^{15}N$, which occurs with a significant cross-section at proton energies less than 800 kev (Amsel and Samuel, 1962). It has been used in a variety of modes for the determination of oxygen diffusion coefficients in silicates (Choudhury *et al.*, 1965; Reddy *et al.*, 1980; Jaoul *et al.*, 1980).

Analysis is non-destructive, relying on determination of the emitted α-energy spectrum during bombardment with protons of less than 800 kev energy. This spectrum is a function of the ^{18}O concentration distribution, the stopping powers for protons and α-particles in the material being studied, the straggling functions for the stopping power terms, and the variation in the cross-section of the nuclear reaction $^{18}O(p,\alpha)^{15}N$ with proton energy. Knowledge of the atomic interaction terms allows direct determination of the ^{18}O distribution beneath the sample surface in the depth range $\leqslant 0.1$–$2.0\,\mu m$ (Robin *et al.*, 1973; Reddy *et al.*, 1980; Jaoul *et al.*, 1980). These methods have largely superseded earlier variations in the use of the $^{18}O(p,\alpha)^{15}N$ and the $^{18}O(p,n)^{18}F$ reactions at higher proton energies (Choudhury *et al.*, 1965; Schactner and Sockel, 1977).

The main disadvantages associated with the technique are: the lack of accurate data for the atomic interaction parameters; it is sensitive to ^{18}O determination only, thus not allowing determination of chemical equilibrium of the sample throughout the diffusion profile, and it has yet to be demonstrated that the method is suitable for small hydrothermal charge samples rather than large (1 cm diameter) discs. These factors could lead to systematic but important errors in determination of diffusion coefficient.

Secondary ion mass spectrometry (SIMS). In secondary ion mass spectrometry, SIMS, a *primary* beam of energetic heavy ions sputter-erodes the uppermost surface of the sample under study, while positive and negative *secondary* ions produced in the sputtering process are mass analysed and detected. As such it is a destructive analytical

technique capable of providing isotopic and chemical composition information with depth beneath the oriented sample surface and ideally suited to determining diffusion profiles.

In conjunction with focused *primary* ion beams (diameter $< 100\,\mu m$) of reasonable current density (>0.1 mA cm^{-2}), it is possible to provide detailed concentration profiles from $0.025\,\mu m$ to 5–$10\,\mu m$ depth beneath the sample surface for small experimental samples.

The basic concept of SIMS analysis allows a direct determination of $^{18}O/^{16}O$ sample composition with depth, *provided* the analyst be aware of the many instrumental and analytical parameters that can affect the absolute depth calibration. Consequently, the accuracy of SIMS data is strongly instrument-dependent, and operational parameters must be borne in mind in interpreting data (Zinner, 1980). Giletti *et al.* (1978) have provided a thorough investigation of many of these effects and provided they are minimized, SIMS should provide the most sensitive method for determining diffusion coefficients in geological materials.

The main advantages of SIMS over all other methods are: (i) The direct determination of true $^{18}O/^{16}O$ composition profiles with depth below the sample surface. This depth can be physically measured by optical interferometry or mechanical means. (ii) The simultaneous determination of multi-element profiles to ensure chemical homogeneity throughout the diffusion zone. (iii) Depth profiles from 25 nm upwards. (iv) Microbeam and imaging facilities are available to ensure lateral homogeneity of diffusion throughout planes oriented perpendicular to the diffusion direction.

Experimental

Samples and sample preparation

Natural crystals of feldspar, garnet, quartz, and rutile were used in this reconnaissance study. The feldspar was pure albite (from Syros, Greece) in the form of clear colourless single crystals. From well-developed (001) faces, slices up to 1.5 mm thick were cleaved. These were broken into smaller pieces of the same thickness. Smooth-faced fragments, typically 2×2 mm, were selected for experiments.

The quartz was a good quality single crystal from Brazil (sample BR5 of Jones, 1978) having a low concentration of impurities (Al 70 ppm, Co 7 ppm, Fe 3 ppm, Na 40 ppm, and H 25 ppm). Basal sections, approximately 1 mm thick, were cut from the oriented crystal. Individual sections, typically 2×2 cm, were ground on SiC to 12 μm, alumina to 8 μm, and diamond paste to 0.1 μm. The resulting polished surfaces were optically flat and exhibited a variable density of 'pitting', but no scratches. Satisfactory sections were broken into 2×2 mm fragments, and those free of pits and scratches were chosen for the experiments.

A number of silicate garnets, predominantly grossular, were analysed by electron microprobe, and a sample of hessonite (British Museum specimen: BM 1966, 257) from Asbestos, Richmond Co., Quebec, Canada, was chosen. The crystals were pale orange in colour, and close to end-member grossular in composition, approximately $Ca_{2.92}Fe_{0.10}Al_{1.96}Si_{3.00}O_{12}$. Several pieces were mounted at random orientation and polished using SiC and diamond paste down to 1 μm.

Specimens of rutile (British Museum sample BM 34730) from Orenburg (USSR) were in the form of dark-red single crystals, up to 8 mm long, having 'FeO' (0.81 wt. %), SiO_2 (0.27) and 'MnO' (0.12) as the principal impurities. Slices were cut perpendicular to the c-axis, and then polished on SiC and diamond paste to 1 μm. Prepared faces of both the rutile and the garnet were typically 2×2 mm.

Hydrothermal experiments

For the diffusion experiments with albite, rutile, and garnet, prepared crystals of each type were cleaned and then sealed individually in 3 mm *O.D.* platinum tubes with approximately 8 mg of water enriched in ^{18}O, $(^{18}O/(^{18}O + ^{16}O) = 44.5\%)$. Sealed charges were run in internally heated, gas-medium pressure vessels at temperatures up to 1050 °C and pressures up to 8 kbar. Experimental charges for quartz normally consisted of 1–2 single crystal fragments loaded together with 2–4 mg of water enriched in ^{18}O, $(^{18}O/(^{18}O + ^{16}O) = 24\%)$ in 2.8 mm *I.D.* gold tubes. The high solid:fluid weight ratio (2.5–5:1) was used to minimize solubility problems in the SiO_2–H_2O system (see later discussion). Charges were run in externally-heated, cold-seal pressure vessels at temperatures of 600 and 750 °C and 1 kbar total pressure. Oxygen fugacity in all quartz experiments was near the Ni–NiO buffer of the vessels.

Studies with all minerals were performed in the same manner, except that the quartz crystals were subjected to a 'pre-anneal' with distilled water, under identical conditions to and prior to the oxygen isotope exchange runs, for times up to 10 days. Heating and cooling periods were kept to a minimum in all runs. Reported temperatures are believed to be accurate to ± 3 °C, and pressure to ± 50 bar. At the termination of the runs the crystals were removed, usually intact, and prepared for analysis by ion microprobe.

Ion microprobe analysis

Oxygen isotope composition as a function of depth beneath the sample surfaces was determined by ion microprobe analysis. The instrument used in this study was an *Atomika A-DIDA II quadrupole-equipped ion microprobe (Wittmaack, 1978). Significant differences exist in the analytical methods employed by our laboratory compared with those of other researchers (Giletti *et al.*, 1978; Jaoul *et al.*, 1980) that warrant discussion below. During the preliminary work, several techniques were modified in conjunction with instrument development resulting in a range of analytical methods that illustrate the problems inherent in SIMS analysis of oxygen diffusion profiles (Kilner *et al.*, 1981).

* Atomika GmbH, Munich.

Single crystal fragments of quartz and grossular were mounted, polished face outwards, in thick epoxy mounts (Giletti *et al.*, 1978). Vapourization led to a deterioration in the residual gas pressure during analysis from less than 2×10^{-8} torr to 2×10^{-7} torr. To overcome this, feldspar fragments were mounted, (001) cleavage faces oriented outwards, on to glass slide cover slips using small drops of epoxy resin. Four samples could be mounted on one cover slip (1×1 cm) in this manner. The rutile samples were mounted in a similar fashion, but on to a piece of platinum foil (1×1 cm), using silver dag, as a fixing medium, in order to maintain good electrical contact between the sample holder and the electrically conducting rutile. The specimens were then carefully cleaned with acetone and finally washed in de-ionized water before being dried in a desiccator. Unlike previous SIMS studies of geological materials, the insulating samples (albite, grossular, and quartz) were not coated with a thin film of Au, Al, or C to provide an electrically conducting surface (e.g. Coles and Long, 1974; Hofmann *et al.*, 1974; Giletti *et al.*, 1978; Jaoul *et al.*, 1980).

Typical operating parameters during analysis were selected as follows: to avoid primary beam dilution effects (Giletti *et al.*, 1978), the primary ion beam was mass filtered $^{40}Ar^+$, accelerated to 10 keV, with a total maximum current of 250 nA, focused to a spot size on the sample surface of 60 μm (primary ion current density > 8 mA cm^{-2}); to ensure flat-bottomed craters and improved depth resolution, by eliminating contributions to the determined profile from the crater edge, the beam was rastered over an area up to 400×400 μm, with the data acquisition electronics gated to accept secondary ions from the central 18 % of the area of the crater (Colby, 1975; Wittmaack, 1977). This rastered area was increased to 1500×1500 μm for the quartz and garnet analyses to provide improved depth resolution. Typical sputter rates ranged from 4 Å s^{-1} for the albite samples to 0.3 Å s^{-1} for the quartz specimens.

In the absence of a conducting layer on the sample surfaces, charge compensation of the primary ion beam was achieved by use of an electron flood gun operated at 250–500 eV energy and 10–20 mA total current. In all cases charging of the sample surface was minimal (< 2 V) and the ion beam remained stable during the analysis.

Residual gas pressures during analysis were always better than 2×10^{-8} torr, with the exception of quartz and garnet samples where it ranged from $(0.4–2) \times 10^{-7}$ torr, due to vapourization of the epoxy mounts.

For the quartz and garnet analyses, positive secondary ions at m/e (mass/charge) of 16, 18, and 28 were pseudo-simultaneously monitored after energy and mass filtering by rapid peak switching of the mass spectrometer (< 5 msec peak to peak switching). These correspond to the species ^{16}O, ^{18}O, and ^{28}Si. The monitoring of three masses allows determination of the chemical homogeneity of the sample through the diffusion profile by giving a cation:total-oxygen ratio which should remain constant.

Due to the low secondary ion yield of oxygen in the positive spectra (Giletti *et al.*, 1978; this study) low mass

resolution $(M/\Delta M = 100)^*$ and optimum energy settings were used to maximize the detected particle count rate $(2.5 \times 10^3$ cps for total oxygen). This resulted in H_2O spectral interference with ^{18}O equivalent to $^{18}O/(^{18}O + {}^{16}O)$ of 0.6% for a background vacuum of 2×10^{-7} torr, improving to 0.4% for a vacuum of 4×10^{-8} torr. Recorded data were corrected for this background interference.

In contrast, negative secondary ions at m/e equal to 16, 18, and 28 were detected for the albite samples and 16, 18, and 47 for the rutile samples, corresponding to the oxygen isotopes plus silicon, and the oxygen isotopes plus titanium respectively. In addition the $(OH^- + O^-)$ signal at m/e equal to 17 was monitored in one of the feldspar samples (OX42). The use of negative secondary ions in oxygen diffusion studies in silicates and oxides is unique to this laboratory, but offers several distinct advantages over the use of positive secondary ions (Kilner et al., 1981):

(i) The secondary ion yield is 10^2–10^3 times greater than the positive ion yield for oxygen species. Typical maximum count rates for total oxygen, under nominally identical operating parameters are 1×10^6 cps for the negative secondary ions compared to 2.5×10^3 cps for the positive secondary ions.

(ii) There is no observable H_2O spectral interference with ^{18}O, even at very low mass resolution $(M/\Delta M \simeq 40)$. Natural ^{18}O abundances are recorded in the tails of most profiles.

(iii) High secondary ion yields result in improved counting statistics, shorter count times and improved depth resolution (cf. figs. 1 and 2).

After each analysis craters were routinely measured for depth, d_t. In common with other workers (Giletti et al., 1978; Arita et al., 1979; Zinner, 1980) it was found that for silicates and oxides there is a linear correlation between sputtering time and depth. The extent of sputter-induced microroughness (Wilson, 1973) was checked by interference contrast microscopy. In all cases crater bottoms were found to be no rougher than the original polished or cleavage surfaces, and analysed areas are flat to within the resolution of the interferometer $(\pm 0.015 \ \mu m)$.

Crater depth measurement

Depths of sputtered craters were measured with a 'Nomarski' dual-beam interferometer attached to a conventional reflecting-light microscope (Herzog, 1962). To improve reflectivity, all samples of quartz, grossular, and albite were sputter-coated with gold. For depths less than 1.5–2 μm white light provided an adequate degree of accuracy, with the exception of the quartz profiles where a monochromator of 580 nm wavelength was used. Photomicrographs of interference patterns were taken and depths determined from these. The interference band displacement between the dual images gives a direct measurement of the depth of the sputtered crater.

For the quartz, grossular, and rutile samples, the

accuracy of the measurement depends on the flatness of the original surfaces which in general is good. Under these optimum conditions the crater depths are believed to be accurate to $\pm 0.02 \ \mu m$. For the albite samples cleavage steps around the crater make measurements more difficult, and depths may be only reliable to $\pm 0.15 \ \mu m$ in the worst cases.

Computation of diffusion coefficients

In all experiments, self-diffusion of the oxygen isotope may be modelled by transport into a semi-infinite medium from a fluid phase held at constant isotopic composition.

The general solution to Fick's first law for these boundary conditions is given by (Crank, 1975):

$$\left(\frac{C_x - C_1}{C_0 - C_1}\right) = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) - \exp(hx + h^2Dt).$$
$$\text{erfc}\left(\frac{x}{2\sqrt{Dt}} + h\sqrt{Dt}\right) \quad (1)$$

where C_x, C_0, and C_1 are respectively the ^{18}O concentration at a distance x from the crystal surface, in the fluid phase, and at $x = \infty$ in the crystal (0.002, i.e. the natural $^{18}O/(^{18}O + {}^{16}O)$ composition); t is the hydrothermal run time; D is the diffusion coefficient, and $h = k/D$ where k is the rate constant of the phase boundary exchange reaction. For high-pressure experiments $(P_{H_2O} \geqslant 1$ kbar) it is generally found that $h(Dt)^{\frac{1}{2}} \geqslant 3$, and so equation (1) may be approximated to

$$\left(\frac{C_x - C_1}{C_0 - C_1}\right) = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right). \quad (2)$$

Under these conditions the reaction at the phase boundary is fast enough so as not to significantly distort the diffusion profile. Plots of $\text{erfc}^{-1}[(C_x - C_1)/(C_0 - C_1)]$ vs. depth (x) give a straight line with slope $1/2\sqrt{Dt}$. Such a plot is illustrated with the experimentally determined diffusion profile in fig. 1 (a) and (b) for albite (annealed at 600 °C and 4 kbar).

At low pressure (i.e. $P_{H_2O} < 1$ kbar), where $h(Dt)^{\frac{1}{2}} < 3$, equation (1) is necessary and may be solved by the method of Arita et al. (1979).

Error estimation

A full error analysis of the data was not performed since (i) the grain to grain reproducibility of results is probably no better than $\pm 100\%$, and (ii) the largest single error in the determination of D from equations (1) and (2) is the uncertainty in the crater depth (d_t). For samples of albite, quartz, rutile, and garnet, d_t measurements are reliable to 12, 10–20, 2, and 2% respectively. Since $D \propto x^2$, then (neglecting errors in t) the uncertainty in the diffusion coefficients range from $\pm 5\%$ for garnet and rutile, to $\pm 25\%$ for albite, to $\pm 40\%$ for quartz. Whilst these values may be representative for individual experiments, the results for each mineral species may only be reliable to a factor of 2 or 3.

Results

Oxygen diffusion as a function of temperature

Albite. Ion microprobe analysis of an albite sample (run at 600 °C and 1 kbar) produced an

* Mass resolution $(M/\Delta M)$ is defined as $(M/\Delta M) = (S/\Delta S) \times (M_1 + M_2)/[2(M_2 - M_1)]$ where S is the distance between two peaks of masses M_1 and M_2, and ΔS the width of the peak at 50% of its intensity.

^{18}O profile (similar to fig. 1a) which obeyed the standard error function (equation 2). The calculated diffusion coefficient (Table I) is in good agreement with the value of 8.22×10^{-15} cm^2 s^{-1} reported by Giletti et al. (1978) for diffusion in albite (Ab$_{97}$, from Amelia Co.) under the same experimental conditions. Previous hydrothermal studies of oxygen diffusion in albite (Merigoux, 1968; Anderson and Kasper, 1975), using the bulk exchange technique, obtained diffusion coefficients which are in satisfactory agreement with the present data at 600 °C, but deviate from that of Giletti et al. (1978) at other temperatures.

Quartz. Oxygen penetration profiles in quartz (‖c) for diffusion at temperatures of 600 and 750 °C were only 0.084 μm and 0.15 μm in length respectively. It is possible that the true isotope distributions in these profiles may have been distorted by atomic mixing caused by the knock-on of specimen atoms by the primary ion beam, the so-called 'knock-on' effect (Ishitani and Shimizu, 1975;

Giletti et al., 1978; Zinner, 1980). However, preliminary analyses of samples using a 6 keV ^{40}Ar$^+$ primary beam indicate little detectable difference from the 10 keV ^{40}Ar$^+$ analyses, and are within the over-all grain-to-grain reproducibility of results. These findings are in qualitative agreement with other workers in that a primary beam of high mass to charge (^{40}Ar$^+$) produces less knock-on effects than a beam of low mass to charge (^{16}O$^-$) of equivalent energy (Zinner et al., 1976). The calculated diffusion coefficient at 600 °C, 1.4×10^{-19} cm^2 s^{-1}, is close to the lowest attainable value with the present analytical facilities and experimental methods.

In terms of an Arrhenius relation, the data for the diffusion of oxygen in quartz (‖c) at 1 kbar (Table I) may be described by $D = 1.08 \times 10^{-11}$ exp$(-31.5$ kcal/$RT)$ cm^2 s^{-1}.

Garnet. Experiments were performed at elevated pressure, to maintain garnet stability in the presence of water (Perkins et al., 1977). Crystals of
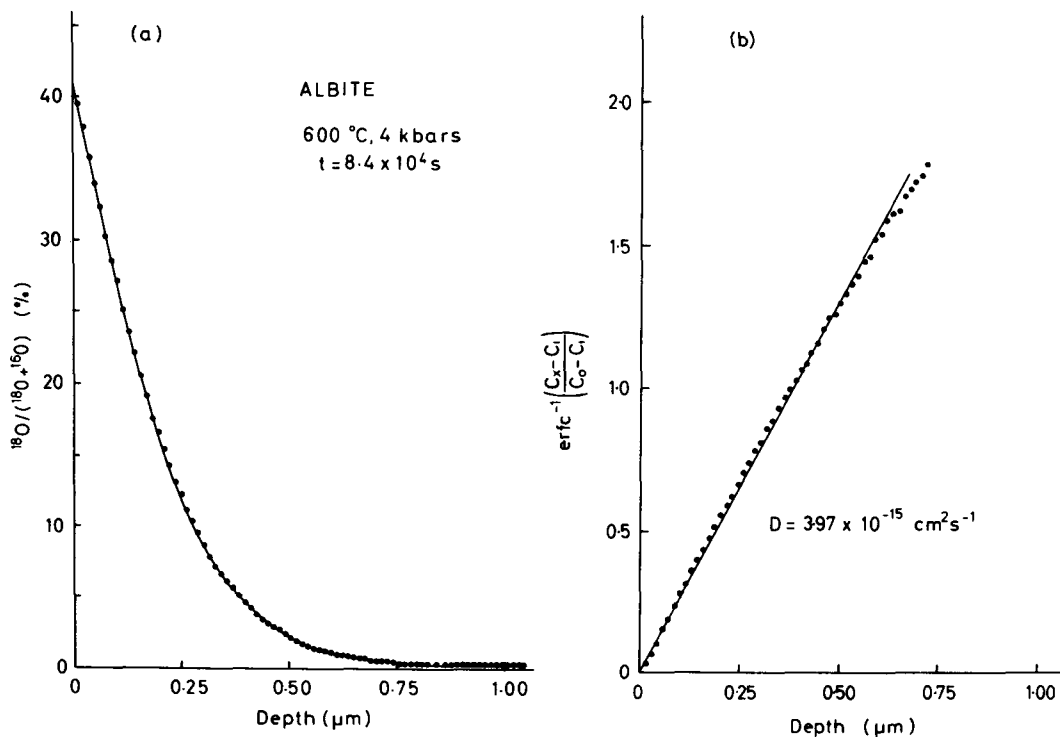

FIG. 1. Oxygen isotope ratios, ^{18}O/(^{18}O + ^{16}O), as a function of depth in an albite crystal after hydrothermal exchange at 600 °C and 4 kbar for 8.4×10^4 sec. Measured ratios are shown by dots, and the solid line is a fit to the data by the diffusion equation (Equation 2), using the diffusion coefficient determined from the inverse error function (fig. b)—see text for analytical details. Points of interest are (i) the low degree of scatter in the data, (ii) the natural isotopic concentration (0.2 %) attained without background subtraction in the tail of the profile, and (iii) the extremely good fit of the theoretical profile to the experimental data indicating volume diffusion (cf. fig. 2a, b).

grossular from runs at 850 and 1050 °C (Table I) retained their prepared, clean polished surfaces, but were deeply incised by several 'scratches' up to 1 μm deep. This damage is believed to result from selective dissolution of regions of the garnet surface damaged by grinding and polishing. Ion micro-probe analyses were performed on regions remote from the 'scratches', and ^{18}O penetration profiles were in excess of 1 μm in length at both tempera-tures. Long tails were observed on the profiles and these were probably caused by diffusion from the scratched surface, and H_2O spectral interference with ^{18}O during analysis (see section on ion microprobe analysis).

Plots of inverse error function (isotope ratios) against penetration distance (equation 2), did not follow a single linear relation, as in the case of albite and quartz, but exhibited two distinct linear portions (e.g. fig. 2b). The near-surface segment yields a 'slow' diffusion coefficient, and the deeper

segment a 'faster' diffusion coefficient. There may have been some genuine variation in water–mineral interaction with depth, but in addition to analytical artifacts, the situation is probably complicated by experimental procedures. Some of these will be discussed later. However, in view of the facts that (i) the recast theoretical diffusion profile (isotope ratios deduced from equation (2) using the calcu-lated diffusion coefficient) based on the 'slow' component are almost indistinguishable from the actual data over most of the total range (fig. 2a), (ii) initial segments of erf^{-1} plots extend to values of 1.35–1.50, and (iii) small errors in isotope ratios at low secondary ion count rates (i.e. at greater depth) will induce large errors in erf^{-1} values, then the near-surface segments of the penetration profile are probably more reliable. These were used to determine the diffusion coefficients reported in Table I. Whilst the data are not strictly comparable, as the experiments were performed at different
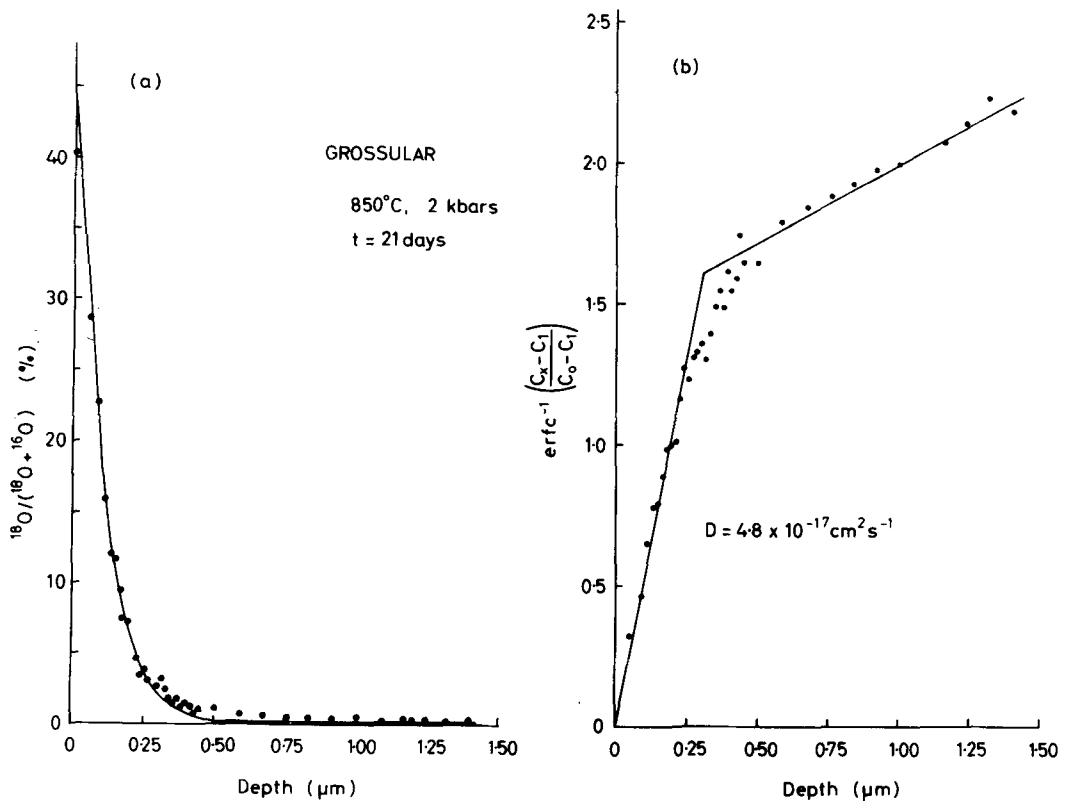

FIG. 2. Oxygen isotope ratios as a function of depth in a crystal of grossular garnet after hydrothermal exchange at 850 °C and 2 kbar for 1.823×10^6 sec. Measured ratios are shown by dots. The inverse error function plot (fig. b) exhibits two linear segments. Using the diffusion coefficient determined from the near surface region (thought to be more reliable—see text) yields a curve (by the diffusion equation) which fits the majority of the experimental data.

Table I. Oxygen isotope exchange experiments with albite, quartz, grossular and rutile.

Specimens	P/kbar	T/C	run duration t (secs)	bore depth d_t (μm)	$\frac{D}{cm^2s^{-1}}$
Albite (⊥001)	1	600	8.67 x 10⁴	1.11(±0.15)	4.2(±1.0)x10⁻¹⁵
Quartz (//c)	1	600	3.89 x 10⁶	0.08(±0.02)	1.4(±0.6)x10⁻¹⁹
	1	750	2.592 x 10⁶	0.15(±0.02)	2.1(±0.8)x10⁻¹⁸
Grossular	2	850	1.823 x 10⁶	1.40(±0.02)	4.8(±0.3)x10⁻¹⁷
	8	1050	2.813 x 10⁵	1.05(±0.02)	2.5(±0.1)x10⁻¹⁶
Rutile (//c)	1	600	6.009 x 10⁵	1.44(±0.02)	1.7(±0.1)x10⁻¹⁶
	1	1050	2.646 x 10⁵	2.10(±0.02)	3.2(±0.2)x10⁻¹⁵

Table II. Oxygen isotope exchange experiments with albite* at 600°C.

Run No	P/kbar	run duration t (secs)	bore depth d_t (μm)	$\frac{D}{cm^2s^{-1}}$
OX42	0.5	156840	1.05(±0.15)	2.0(±0.5)x10⁻¹⁵
OX9	1.0	86700	1.11(±0.15)	4.2(±1.0)x10⁻¹⁵
OX44	3.0	91200	1.10(±0.15)	3.4(±0.9)x10⁻¹⁵
OX43	4.0	84000	1.13(±0.15)	4.0(±1.0)x10⁻¹⁵
OX49	5.0	86400	0.86(±0.15)	6.4(±1.6)x10⁻¹⁵
OX45	6.0	84120	1.30(±0.15)	4.5(±1.1)x10⁻¹⁵
OX47	8.0	86400	1.30(±0.15)	4.4(±1.1)x10⁻¹⁵

* oxygen transport was measured perpendicular to the (001) cleavage face.

pressures, and may be subject to later revision (see discussion) they indicate an activation energy of $\simeq 24.4$ kcal mol^{-1} for oxygen diffusion in grossular under hydrothermal conditions at 850–1050 °C. At present there are no other oxygen diffusion data for silicate garnets for direct comparison.

In a study of oxygen diffusion in single crystal and polycrystalline yttrium iron garnet ($Y_3Fe_5O_{12}$) Paldino et al. (1964) obtained an activation energy of 65 kcal mol^{-1} and noted comparatively fast diffusion rates ($> 10^{-11}$ cm^2 s^{-1}) at the elevated range of temperatures (1100–1400 °C). When these data ('dry') are extrapolated to lower temperatures, the diffusion coefficients are typically several orders of magnitude faster than the present ('wet') results for grossular.

Rutile. In common with grossular, the specimens of rutile were also marked by 'scratches' at the end of the diffusion experiment, but in addition there was evidence of surface discoloration and corrosion, especially in the sample run at the lower temperature (Table I). Regions exhibiting least surface damage were selected for ion microprobe analysis. For both specimens the measured isotope profiles exhibit some unusual and interesting features. The Ti/($^{18}O + ^{16}O$) profile displays a strong surface peak, whilst the total oxygen ($^{18}O + ^{16}O$) profile shows a corresponding surface depression. The oxygen diffusion profile, $^{18}O/$($^{18}O + ^{16}O$), rises to a peak (35 and 17% for runs at 1050 and 600 °C respectively) at depths of $\leqslant 0.1$ μm before reaching the standard error function curve. There is a strong suggestion of gross changes in stoichiometry and corrosion near the crystal surface, but it is not clear whether the Fe content of the rutile is primarily responsible for this behaviour. With the exception of the modified near-surface regions, the ^{18}O penetration profiles fitted a single inverse error function, and the calculated diffusion rates (Table I) are faster than those obtained for the garnet at comparable temperatures. It is of interest to note that the diffusion coefficient of oxygen in rutile at 1050 °C (hydro-

thermal) from this study is approximately two orders of magnitude slower than the value obtained by Derry et al. (1981) for oxygen diffusion in synthetic rutile ($\|c$), but because of the contrasting activation energies, the situation should be reversed at lower temperatures, possibly below 750 °C. In view of the dissolution/corrosion problems encountered with these natural crystals of rutile which may have enhanced measured diffusion rates, it would be unwise to attach too much importance to the present data.

Oxygen diffusion as a function of pressure

Albite. Crystals of albite recovered from hydrothermal exchange experiments at 600 °C (Table II) over the pressure range 0.5–8.0 kbar, were clean and apparently unaltered in all cases, except for the run at 8 kbar where a white, fine-grained, unidentified deposit was observed. Calculated diffusion coefficients (Table II) differ by no more than a factor of 4 over the whole pressure range, and excluding the results at 0.5 and 5.0 kbar (associated with an abnormally low oxygen isotope surface concentration), the data average 4.1 (± 0.5) × 10^{-15} cm^2 s^{-1}. Although the diffusion coefficient from the run at 0.5 kbar is significantly lower than the rest of the data, it is within the expected grain-to-grain variation and there is no evidence of any significant pressure dependence for oxygen diffusion rates in albite at 600 °C between 1–8 kbar. In marked contrast, Yund and Anderson (1978) reported that oxygen diffusion rates in adularia at 650 °C (determined by the bulk exchange technique) increased rapidly with pressure between 125 and 4000 bar. Possible explanations for this discrepancy are discussed in the following section.

Discussion

In agreement with the findings of Giletti et al. (1978), the results of this study confirm that an ion microprobe may be used to determine oxygen isotope ratio gradients in silicate and oxide

minerals after hydrothermal exchange experiments. In addition, it has emphasized the advantages of using an $^{40}Ar^+$ primary ion beam and negative secondary ion data acquisition in conjunction with low residual gas pressure ($< 2 \times 10^{-8}$ torr). Perhaps more importantly, it has shown that measured oxygen penetration gradients and diffusion rates are sensitive to certain experimental and analytical factors. Some of these are examined in more detail below.

Experimental considerations

For a mineral at constant pressure, temperature, and composition, the disequilibrium variations in dislocation density, and point defect concentration, can have a pronounced effect on diffusion rates. For this reason it has become common practice in oxide diffusion studies (e.g. Atkinson and Taylor, 1978) to try to establish an equilibrium defect concentration, and eliminate those additional defects generated by sample preparation (e.g. grinding and polishing). This usually takes the form of a 'pre-anneal' under identical conditions to those of the diffusion experiment, or at least at elevated temperatures. However, the rate of recovery of surface damage varies considerably between minerals. For example, mechanical polishing of Al_2O_3 crystals damages a layer $\leqslant 1$ μm in depth, and recovery can be achieved by annealing for 4 h at 1650 °C (Reed and Wuensch, 1980). In contrast, mechanical abrasion of MgO crystals may generate dislocations to a depth of 100–700 μm (Sonder et al., 1981), and heating for short times ($\simeq 6$ h) at 1300 °C has little effect on the dislocation density. The resulting enhancement of diffusion rates by artificially high defect concentrations consequently differs for different minerals. Reed and Wuensch (1980) found that oxygen diffusion rates (dry) in single crystal Al_2O_3 were only a factor of 2 slower in the annealed specimens, but Anderson (1969) reported that ^{14}C diffusion rates in calcite were a factor of 50 slower in annealed samples. To what extent this represents the true variation in the diffusion kinetics with surface damage for each material is difficult to assess, since contrasting methods were used to prepare the samples and determine D. Unfortunately, the available information on the generation and recovery of defects in the common rock-forming minerals is limited, and thus predictions of such effects on diffusion processes can become highly speculative. Nevertheless, the present study provides some useful information.

Natural undeformed feldspars commonly have relatively low dislocation concentrations, i.e. $< 10^7$ lines cm^{-2} (Marshall et al., 1976; Yund et al., 1980), but in both natural and experimentally deformed crystals (e.g. White, 1975; Marshall et al., 1976) this

may rise to $\geqslant 10^{12}$ lines cm^{-2} in regions adjacent to grain boundaries in particular, providing easier paths for diffusion. As a consequence Yund et al. (1980) observed a significant increase in the rate of oxygen diffusion in polycrystalline albite which had been artificially strained. The act of cleaving nominally undeformed feldspar crystals should not produce an appreciable increase in the defect concentrations, and so pre-anneals should not be necessary. However, mechanical grinding of a crystal to a sized powder (as opposed to chopping, e.g. for a mica: Giletti, 1974b) for a bulk exchange experiment must, in general, increase the defect level considerably. It may therefore be expected that diffusion coefficients determined from bulk exchange experiments would always be appreciably faster than those from exchange experiments with single crystals which have been suitably pre-treated. This is not always the situation as the data for oxygen diffusion in several feldspars (e.g. Giletti et al., 1978) clearly demonstrate. The most likely explanations for the feldspars are that (i) crushing of single crystal fragments still yields powders which are relatively free of dislocations (e.g. electron microscopy mounts), and (ii) the presence of water in the hydrothermal experiments helps to heal the dislocations comparatively rapidly, and this process will be assisted if the material is first exchanged with a fluid to produce an end-member composition (Lin and Yund, 1972). It should be noted that problems can arise in bulk exchange experiments, and Anderson (1969) found a factor of 50 between diffusion coefficients obtained with annealed and unannealed powdered samples of calcite.

The quartz crystals in this study were pre-annealed in distilled water before the diffusion experiments, and there is no evidence from the appearance of the specimens, or the penetration profiles, to suggest excessive surface damage. Indeed, the pre-anneal appears to serve as a form of chemical polish, dissolving the quartz, to produce a flat damage-free surface (Vig et al., 1977, 1978). In contrast, the crystals of garnet and rutile were not pre-annealed after polishing and the selective dissolution of weakened areas suggests that damage probably extends to a depth of at least 1 μm. Since a short hydrothermal pre-anneal does not appear to be appropriate for garnet or rutile (due to dissolution/corrosion effects) the damaged layers could perhaps be removed by chemical polishing, i.e. acid dissolution (e.g. Jaoul et al., 1980), or ion milling (e.g. Ando et al., 1981). With suitably pre-treated crystals, lower diffusion coefficients may be obtained if the experiments are repeated.

Some minerals are not stable in the presence of

hydrothermal fluids and the natural rutile samples employed here suffered noticeable corrosion. The effect may have been less if the damaged surface layer had been removed or if the impurity content had been lower. In preliminary hydrothermal exchange experiments with synthetic magnetite, the crystals suffered considerably more corrosion (on both polished and sawn-cut faces) than the rutile, and there was a measurable weight loss in all the magnetite specimens. Whilst certain oxide minerals are probably affected by water more than most silicate minerals, the latter group can still suffer limited dissolution by natural weathering (e.g. Berner, 1981). However, in hydrothermal exchange experiments (under suitable P,T conditions) the effect of dissolution on the majority of silicates should be minimal, provided the material is of *good quality* and *unstrained*, and the pH of the fluid is close to 7. In this context it is interesting to note that problems of solution-reprecipitation were anticipated with the quartz experiments because of the relatively high solubility of SiO_2 in H_2O at 600–700 °C at 1 kbar (Walther and Helgeson, 1977). Since the diffusion profiles showed little or no evidence of such problems, it would appear that the faster dissolution of the sawn cut-back surfaces of the specimen buffered the system and preserved the finish on the (more stable) polished faces (Vig *et al.*, 1977; Suda *et al.*, 1978; Kennedy *et al.*, 1962).

It is concluded, that in order to avoid the generation of artificially high diffusion coefficients, the specimens should be prepared to minimize the defect concentrations and sample damage, and the experiments should be performed under conditions where the specimen is stable (Giletti, 1974*a*). Furthermore, the analytical procedures should be optimized to avoid the distortion of the data by instrumental artifacts.

Experimental data and exchange mechanisms

The temperature dependence of the present results for oxygen diffusion in quartz, garnet, and rutile are shown in fig. 3 along with a representative selection of published data for oxygen diffusion in various rock-forming minerals (for details see Freer, 1980, 1981). The most obvious general trend is the sharp division of the data into studies performed under essentially wet and dry conditions. This feature has been noticed previously by several other authors, e.g. Yund and Anderson (1978) for oxygen diffusion in feldspars. The collective data (fig. 3) indicate that oxygen diffusion rates in dry environments are characterized by high activation energies (typically 70–95 kcal mol^{-1}) and generally, comparatively slow diffusion rates, restricting measurements to elevated temperatures ($\geqslant$ 850 °C for most minerals). The highest activa-
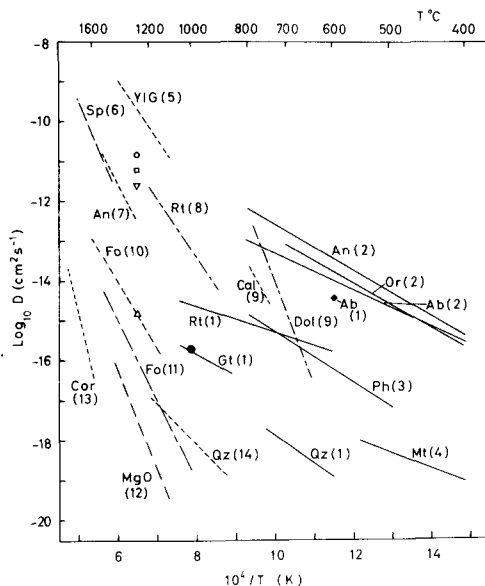

FIG. 3. Compilation of oxygen diffusion coefficients in a variety of rock-forming minerals as a function of temperature. Solid lines and solid symbols indicate exchange experiments with hydrothermal fluids. Broken lines and open symbols represent exchange with dry air, O_2 or CO_2 at atmospheric pressure. Key: Qz quartz; Gt grossular; Rt rutile; Ab albite; An anorthite; Or orthoclase; Ph phlogopite; Mt magnetite; YIG $Y_3Fe_5O_{12}$; Cal calcite; Dol Dolomite; Sp spinel ($MgAl_2O_4$); Fo forsterite; MgO periclase; Cor corundum; ● Fo-Giletti *et al.* (1979); ○ plagioclase, □ enstatite, ▽ diopside, △ zircon- Muehlenbacks and Kushiro (1975); ◆ Ab—this study. Numbered data = 1 this study (Table I); 2 Giletti *et al.* (1978); 3 Giletti and Anderson (1975); 4 Castle and Surman (1967); 5 Paldino *et al.* (1964); 6 Ando and Oishi (1974); 7 Muehlenbachs and Kushiro (1974); 8 Derry *et al.* (1981); 9 Anderson (1972); 10 Jaoul *et al.* (1980); 11 Hallwig *et al.* (1981); 12 Narayan and Washburn (1973); 13 Reed and Wuensch (1980); 14 Schactner and Sockel (1977). For details see references.

tion energy has been reported for Al_2O_3 (188 kcal mol^{-1}) and the lowest for quartz (47 kcal mol^{-1}). Conversely, the data from hydrothermal experiments are characterized by low activation energies (25–37 kcal mol^{-1}) and relatively high diffusion rates, allowing measurements down to 350 °C in some cases. With the exception of the data for magnetite (Castle and Surman, 1967), which has a very low activation energy 17 kcal mol^{-1} (possibly reflecting dissolution effects), and the present results for rutile, the majority of the wet data (both in the figure and tabulated in Freer, 1981) are remarkable for their uniformity of activation energy.

If the exchange experiments with dry gases

represent predominantly volume self-diffusion, which seems plausible from the high and varied activation energies, then in the hydrothermal experiments there must be some additional water-mineral interactions which lower the energy barrier for oxygen isotope exchange and assist transport rates. The uniformity of the activation energies in the latter case seems to show the dominating effect of the water, and possibly indicate that similar exchange mechanisms operate in most minerals. Matthews *et al.* (1980) have identified three distinct mechanisms for water–mineral exchange at pressure of 2–15 kbar: (i) initial rapid surficial exchange, (ii) exchange through solution-reprecipitation, and (iii) exchange controlled by solid-state diffusion. In any given case there may be a complex combination of all three processes, depending upon the minerals involved and the applied pressure. In studies with albite and anorthite, for example, Matthews *et al.* (1980) noted that process (i) does operate, but the bulk of the isotopic exchange occurs through a diffusional mechanism, rather than solution-reprecipitation. In general they found the effect of pressure is to increase the rate of isotopic exchange.

Yund and Anderson (1978) measured the diffusion of oxygen in adularia as a function of pressure, and examined the role of water in the oxygen exchange process. They suggested that water as molecular H_2O, OH^-, or H^+ in the feldspar structure increased the oxygen exchange rate by a form of hydrolysis mechanism. In their bulk exchange hydrothermal experiments at 650 °C, an unusual and dramatic *increase* in the oxygen diffusion rate was observed with increasing pressure to 4 kbar. This was partly explained by differences in the concentration of 'water' in the feldspar, and possibly the operation of a dissolution-reprecipitation mechanism at the higher pressures. The failure to observe any significant pressure dependence in the present oxygen diffusion experiments with albite (fig. 4) does not support the proposals of Yund and Anderson (1978) as a universal mechanism for oxygen exchange with feldspars. However, it is interesting to note that whilst the measured oxygen isotope ratios at the surface of the albite crystals were high in most specimens, they did not equal that of the hydrothermal fluid. The surface ^{18}O concentration increased with increasing pressure (fig. 5) in a non-linear manner. For albite we would therefore imply that it is the 'surface exchange' mechanism, and not the oxygen diffusion rate which varies as a function of pressure over the bulk of the range examined. It is possible that the data of Yund and Anderson may have been distorted by a surface exchange process which varied as a function of pressure, but it is also possible that
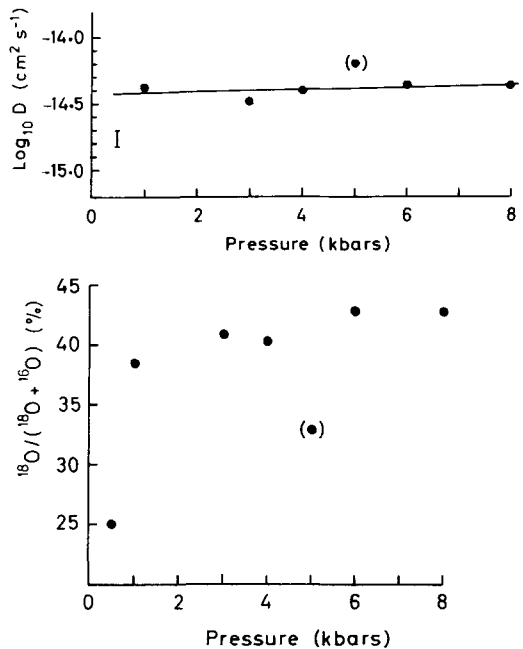
FIGS. 4 and 5. FIG. 4 (*above*). Calculated diffusion coefficients (*D*) for oxygen in albite at 600 °C as a function of fluid pressure. Uncertainties in the determined values of *D* are generally $\pm 25\%$ (see Table II for details). The line is at least squares fit of the data excluding points at 0.5 kbar and 5 kbar (see text). FIG. 5 (*below*). Surface oxygen isotope ratios, $^{18}O/(^{18}O + ^{16}O)$, in albite as a function of pressure after hydrothermal exchange experiments at 600 °C. With the exception of the run at 0.5 kbar, the uncertainties in the surface concentrations lie within the size of the symbols used. All experiments at $P \geqslant 1$ kbar were run for approximately 8.4×10^3 sec.

albite behaves differently to adularia and that some pressure-dependent, mineral–fluid exchange processes operate in adularia. A direct comparison between the two feldspars can not be made without performing oxygen exchange experiments with single crystals of adularia rather than powdered material.

Although Yund and Anderson (1978) were able to reconcile differences in published oxygen diffusion rates in adularia feldspar on the basis of the pressure effect they had determined for adularia at 650 °C, they noted that a similar pressure dependence would not account for the difference in the results for albite. Moreover, it may be seen (Giletti *et al.*, 1978: fig. 4) from a comparison of oxygen diffusion rates in albite at 250–600 bar (Merigoux, 1968), 1 kbar (Giletti *et al.*, 1978), and 2 kbar (Anderson and Kasper, 1975) that because of the range of activation energies, even a pressure

dependence which varied as a function of temperature could not explain all the disagreements. It seems likely that some of the disparity in the measured diffusion rates arises from the nature of the specimens (Giletti et al., 1978), and possibly from variations in experimental technique.

In view of the conflicting data for the effect of pressure on oxygen isotope diffusion rates in albite (this study) and adularia (Yund and Anderson, 1978), it is difficult to generalize on the behaviour of oxygen isotope exchange processes between silicate minerals and hydrothermal fluids. A realistic appraisal of the effect of pressure on oxygen diffusion rates and diffusion/exchange mechanisms will not be possible without additional data for a variety of minerals at different temperatures.

Petrological applications

Experimentally determined fractionation factors for oxygen and hydrogen isotope exchange between minerals and fluids may be used to determine the composition and origin of fluids participating in water–rock interactions, and to provide a basis for oxygen isotope thermometry (e.g. Taylor, 1974). The general assumption that oxygen isotope equilibria between minerals and fluids are frozen in at temperatures close to temperatures of formation of mineral assemblages may commonly be invalid (e.g. Javoy, 1977; Graham, 1981). The contention of Hoernes and Friedrichsen (1978) that minerals (re)equilibrate their oxygen isotopes only at the time of crystallization is in contradiction with the available oxygen diffusion data. Giletti et al. (1978) showed that oxygen diffusion rates in feldspars (wet) are sufficiently fast to permit oxygen exchange to comparatively low temperatures, and are thereby unsuitable for geothermometry. Attention has thus been directed towards establishing those minerals which do not readily exchange oxygen with water, and which have comparable diffusion parameters.

Most studies of oxygen isotope thermometry of metamorphic mineral assemblages have used calibrated mineral-pair thermometers in which quartz is one mineral of the pair. A recent experimentally superior recalibration of oxygen isotope fractionation between quartz and water (Matsuhisa et al., 1979) commonly yields considerably lower quartz-mineral temperatures than previous calibrations (e.g. Bottinga and Javoy, 1973), and these temperatures may be much closer to temperatures of effective cessation of oxygen diffusion in one mineral in the pair, than to temperatures of crystallization of the mineral assemblage (e.g. Javoy, 1977; Graham, 1981). However, these temperatures will only have any *absolute* significance if the minerals

have similar diffusion parameters and grain sizes. Oxygen isotope temperatures comparable to maximum temperatures of crystallization (e.g. metamorphism) will only be preserved if water is lost from the assemblage at this temperature, or if oxygen diffusion in a mineral pair in the presence of water is sufficiently slow. In the former case, oxygen isotope equilibrium between the constituent minerals should be preserved. Preservation of oxygen isotope equilibrium does not appear to be common in metamorphic rocks (e.g. Javoy, 1977; Deines 1977; Graham 1981).

The *relative* order of oxygen isotope temperatures calculated for mineral pairs in related metamorphic assemblages may provide a clue to the *relative* oxygen diffusion rates in the constituent minerals in the presence of water. A survey of several oxygen isotope studies of metamorphic terrains using the best available experimental calibrations (all referenced in Graham, 1981), and in particular the quartz–feldspar–water calibration of Matsuhisa et al. (1979), indicate the following general pattern of apparent temperatures:

$$T_{\text{quartz-rutile}} > T_{\text{quartz-magnetite}} > T_{\text{quartz-muscovite}} \approx T_{\text{quartz-biotite}} > T_{\text{quartz-feldspar}}$$

Oxygen diffusion data in fig. 3 are in general agreement with this order of closure temperatures, with the exception of rutile. Consistently high recalculated quartz-rutile temperatures (520–580 °C) for type-C eclogites (Desmons and O'Neil, 1978; Matthews et al., 1979) are close to those calculated by garnet-clinopyroxene thermometry. Either these temperatures have no absolute significance, as the preliminary diffusion data would suggest, or more likely the experimentally measured oxygen diffusion rates in rutile have been much enhanced by the dissolution and corrosion problems encountered in experiments. Resolution of this discrepancy awaits a more detailed experimental study of oxygen diffusion in rutile, using synthetic Fe-free rutile.

The slow oxygen diffusion rates in quartz relative to micas and feldspars (fig. 3) emphasize the caution which must be exercised in attempting to assign any absolute significance to oxygen isotope thermometry using these minerals. On the other hand, the slow and comparable oxygen diffusion rates in quartz and garnet suggest that these minerals in metamorphic rocks may freeze in oxygen isotope ratios attained at or near to temperatures of crystallization. No experimental data are currently available for oxygen isotope fractionation between garnet and water; obtaining this data would seem to be a worth-while experimental objective.

Conclusions

1. All specimens for oxygen exchange experiments, which have been mechanically prepared (ground/polished), should be treated to minimize the defect content.

2. Failure to remove damaged surface layers from specimens can result in spurious oxygen penetration profiles, and anomalously high diffusion coefficients.

3. In the presence of hydrothermal fluids, rutile and magnetite can suffer extensive corrosion. Measured oxygen isotope profiles in such damaged minerals can lead to unrealistic diffusion coefficients.

4. Oxygen isotope diffusion coefficients (D) in quartz ($\|c$) may be described by $D = 1.08 \times 10^{-11}$ $\exp(-31.70 \text{ kcal}/RT)$ cm^2 s^{-1} at 600–750°C (1 kbar). For grossular garnet, $D = 4.8 \times 10^{-17}$ cm^2 s^{-1} at 850°C (2 kbar) and $D = 2.5 \times 10^{-16}$ cm^2 s^{-1} at 1050°C (8 kbar). In rutile, D ($\|c$) $= 3.16 \times 10^{-15}$ cm^2 s^{-1} at 1050°C (1 kbar).

5. No pressure dependence was observed for the diffusion of oxygen in albite at 0.5–8.0 kbar and 600°C. For most of the pressure range $D \simeq 4.1$ $(\pm 0.5) \times 10^{-15}$ cm^2 s^{-1}.

6. Oxygen diffusion in quartz and garnet may be sufficiently slow at elevated temperatures to provide a basis for useful oxygen isotope geothermometers.

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