

OXYGEN DIFFUSION IN VITREOUS SILICA — UTILIZATION OF NATURAL ISOTOPIC ABUNDANCES

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ABSTRACT

Oxygen diffusion coefficients were determined in vitreous-SiO₂ fibers by monitoring the rate of ¹⁸O exchange between O₂ gas and SiO₂ glass. In the temperature range 1150 to 1430°C, the diffusion coefficient can be expressed by

$$D = (4.4 \pm 1\frac{1}{3}) \times 10^{-11} \exp[-(19.7 \pm 4) \times 10^3/RT] \text{ cm}^2/\text{s}.$$

The calculated activation energy of oxygen diffusion in the silica-glass fibres is about 20 kcal/mole, a value much lower than that observed in complex silicate melts. The difference in activation energies indicates that the oxygen atoms move by two different mechanisms.

SOMMAIRE

Les coefficients de diffusion de l'oxygène dans des fibres de silice (SiO₂) vitreuse ont été déterminés en contrôlant le taux d'échange de ¹⁸O entre O₂ gazeux et le verre de SiO₂. Le coefficient de diffusion pour l'intervalle de température 1150 à 1430°C peut être exprimé par:

$$D = (4.4 \pm 1\frac{1}{3}) \times 10^{-11} \exp[-(19.7 \pm 4) \times 10^3/RT] \text{ cm}^2/\text{s}.$$

L'énergie d'activation calculée de diffusion de l'oxygène dans des fibres de silice est d'environ 20 kcal/mole, valeur beaucoup plus faible que celle observée dans les fondus complexes de silicates. La différence des énergies d'activation indique que les atomes d'oxygène se déplacent par deux mécanismes différents.

(Traduit par la Rédaction)

INTRODUCTION

A knowledge of the rate and the mechanism by which atoms move in silicates is needed to

understand a variety of phenomena in geology, such as crystallization kinetics, mechanisms of phase transformations, high-temperature creep in solids, and mass transport in magmas. It is especially useful to know the rate of movement of oxygen, because it is the largest ion as well as the most abundant element in silicates. Despite their potential usefulness, relatively few oxygen diffusion coefficients have been determined in silicates of geological importance (Yund & Anderson 1974; Giletti & Anderson 1975; Muehlenbachs & Kushiro 1974). The lack of data reflects the difficulty of undertaking diffusion studies with an element that lacks a suitable radio-isotope that could be used as a tracer.

One experimental technique frequently used to determine the mobility of oxygen in oxides and glasses is to monitor by mass spectrometry the rate at which ¹⁸O atoms, artificially enriched in a gaseous phase, exchange with ¹⁶O atoms of a condensed phase (gas/solid exchange method, Haul & Just 1958). If certain conditions are met (to be discussed in the text), diffusion coefficients can be calculated from the rate of isotope exchange. The gas/solid exchange experiments are performed either at atmospheric pressure or lower. On the other hand, oxygen diffusion coefficients in feldspar and phlogopite have been determined by high-pressure water-mineral exchange techniques (Yund & Anderson 1974; Giletti & Anderson 1975). In all these methods the use of isotopically enriched materials is required and, usually only one phase is analyzed; the composition of the other is calculated from mass-balance considerations. Experimental difficulties associated with the earlier gas/solid experiments were air leaks into the experimental system and isotopic exchange between the gas reservoir and the apparatus. Thus the exchange runs are usually of short duration such that only a small fraction of oxygen of

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the solid is exchanged. Difficulties arise with the interpretation of the high-pressure (1 to 2 kbar) water-mineral exchange experiments because water participates in the exchange mechanism (O'Neil & Taylor 1967) and, at water pressures of $P > 8$ kbar, the exchange rate between silicates and water increases radically (Matsuhisha *et al.* 1976).

The gas/solid isotope exchange experiments adopted in this study are designed to avoid some of the above difficulties by utilizing the techniques of stable-isotope geochemistry to analyze both the isotopic composition of the silicate and gas. The techniques are sufficiently sensitive that natural variations of the $^{18}\text{O}/^{16}\text{O}$ ratio can be exploited in diffusion experiments, thereby avoiding the need for isotopically enriched material.

Vitreous silica was chosen as the subject of this diffusion study because previous determinations of the activation energy of diffusion range between 29 and 71 kcal/mole (Haul & Duembgen 1962; Sucov 1963; Williams 1965). The diffusion coefficients in these three studies were determined by monitoring the rate at which ^{18}O from O_2 gas exchanged with SiO_2 .

METHOD

Experimental

Oxygen diffusion coefficients were determined in silica-glass fibers* by measuring the rate of isotopic exchange between O_2 gas of known isotopic compositions and SiO_2 . The method differed from previous gas/solid (Haul & Duembgen 1962; Sucov 1963; Williams 1965) isotope exchange studies in that the isotopic composition of the gas did not change appreciably during the course of the experiment, and only the isotopic change in the SiO_2 was determined. The boundary conditions are simpler in these experiments and the diffusion coefficients can be easily calculated from the data.

In the experiments, which ranged between 1000 and 1430°C ($\pm 5^\circ\text{C}$), tufts of glass fibers were suspended by Pt wire in a 1.3 cm, vertical, mullite-tube furnace through which oxygen gas (99.99% pure) from a commercial cylinder was passed continuously at 1.03×10^4 kg/m² pressure at a rate of about 180 ml/min. The durations of the experiments were from 2 to 170 hours. The

isotopic compositions of the oxygen gas, the starting SiO_2 glass, and the exchanged SiO_2 glass were determined by mass spectrometer. The oxygen was extracted quantitatively from the silica fibers (typically 20 mg) by the BrF_5 method (Clayton & Mayeda 1963). The extracted oxygen was reacted with hot carbon to form CO_2 and analyzed for its $^{18}\text{O}/^{16}\text{O}$ ratio in a double-inlet, double-collecting, isotope ratio mass spectrometer. The isotopic compositions are reported relative to a natural carbonate in the usual delta notation, where

$$\delta^{18}\text{O}_{\text{sample}} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{standard}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \times 10^3.$$

The δ notation has the advantage of accentuating the small isotopic differences found in nature and does not require determination of absolute isotopic abundance ratios; if, for instance, the $^{18}\text{O}/^{16}\text{O}$ ratio in the sample is 1% greater than in the standard, its $\delta^{18}\text{O}$ is said to be +10‰. The difference in isotopic composition between the oxygen gas and the starting SiO_2 glass was about 16‰. The standard deviation among repeated silicate analyses has been found to be $\pm 0.13\%$.

Determination of diffusion coefficients

The diffusion coefficients can be evaluated from the isotope exchange data by using a solution of the diffusion equation for finite systems. The appropriate solution in the case of glass fibers held in flowing gas, is the solution derived for diffusion from an infinite reservoir into an infinitely long cylinder. Assuming the following initial and boundary conditions,

$$\begin{aligned} c &= c_1 \neq 0 & \text{for } 0 < r < r_0 & \text{ and } t = 0 \\ c &= c_t \neq 0 & \text{for } r = r_0 & \text{ and } t > 0 \end{aligned}$$

the solution becomes (Duenwald & Wagner 1934):

$$\frac{\bar{c} - c_t}{c_1 - c_t} = \sum_{v=1}^{\infty} \frac{4}{\xi_v} \exp\left(-\frac{\xi_v^2 D t}{r_0^2}\right), \quad (1)$$

where \bar{c} is the averaged concentration of the diffusing species in the cylinder of radius r_0 after a diffusion run of time t , c_1 is the initial uniform concentration in the cylinder, and c_t is the final concentration at the cylinder surface if equilibrium were allowed to be achieved; ξ_v are the roots of the equation $J_0(x) = 0$, where $J_0(x)$ is the Bessel function of zero order. The solution holds if phase boundary reactions are negligible.

Applying the solution to the isotopic exchange between the flowing oxygen gas, isotopic compo-

*The glass fibers, obtained from Amersil Inc., have a mean diameter of 6 μm , and are drawn from commercial grade T 08 (Type II silica glass with about 130 ppm OH).

sition of $\delta^{18}\text{O}(\text{O}_2)$, and the SiO_2 sample, starting isotopic composition of $\delta^{18}\text{O}(\text{SiO}_2)_i$, and where $\delta^{18}\text{O}(\text{SiO}_2)_f$ is the isotopic composition of the sample after exchange, the following relation holds:

$$R = \frac{\bar{c} - c_f}{c_i - c_f} = \frac{\delta^{18}\text{O}(\text{SiO}_2)_f - \delta^{18}\text{O}(\text{SiO}_2)_i}{\delta^{18}\text{O}(\text{SiO}_2)_f - \delta^{18}\text{O}(\text{SiO}_2)_i} \quad (2)$$

The final ^{18}O concentration at the cylinder surface, $\delta^{18}\text{O}(\text{SiO}_2)_f$, is only approximately equal to the measured $\delta^{18}\text{O}(\text{O}_2)$ of the infinite oxygen gas reservoir, because differences in thermodynamic properties of isotopic molecules will cause some isotopic partitioning between phases. It can be estimated from other silicate/gas isotope exchange experiments that at equilibrium the $\delta^{18}\text{O}$ of oxygen gas is about 2% greater than that of the silica at the temperatures of interest (Muehlenbachs & Kushiro 1974); therefore, $\delta^{18}\text{O}(\text{SiO}_2)_f$ can be obtained from the measured $\delta^{18}\text{O}(\text{O}_2)$ values after corresponding corrections.

RESULTS

Table 1 lists the diffusion parameters, the isotopic compositions, and the calculated oxygen diffusion coefficients. Satisfactory convergence of the series in equation (1) was obtained using 6 or less terms when 25% or more isotopic exchange was achieved. Because the convergence becomes slow for isotopic exchanges of the order of a few percent, a computer program using 50 terms of the series in equation (1) has been applied. All diffusion coefficients given in Table 1 were calculated with this program.

The largest error in the calculation of the diffusion coefficients is introduced by uncertainty of the fiber dimension, because the fiber radius enters the formula as r^2 . An uncertainty in the radius of $\pm 10\%$ induces a scatter of $\pm 20\%$ in the diffusion coefficients. It was noted that during the experiments some of the fibers had fused, adding further uncertainty to the radius.

The diffusion data with their respective uncertainties are shown in Figure 1 as a function of reciprocal temperature in the usual Arrhenius plot. A least-squares fit produces the following temperature dependence of the diffusion coefficient,

$$D = (4.4 \pm 1.4) \times 10^{-11} \exp \left[- (19.7 \pm 4) \frac{10^8}{RT} \right] \text{ cm}^2/\text{s}$$

leading to an activation energy of diffusion of about 20 kcal/mol and a pre-exponential factor of the order of 10^{-11} to 10^{-10} cm^2/s .

The diffusion coefficient at 1012°C (2.3×10^{-17} cm^2/s) is orders of magnitude smaller than the extrapolated value from the Arrhenius plot which would yield a value of 1.9×10^{-14} cm^2/s . Possible explanations will be discussed below.

Table 1
Diffusion Coefficients Calculated From the Oxygen Isotope Exchange Between SiO_2 Fibers and Oxygen Gas

T [°C]	t [h]	$\delta^{18}\text{O}(\text{SiO}_2)$ [‰]	$\delta^{18}\text{O}(\text{O}_2)$ [‰]	R	D [cm^2/s]
1012	168.60	-11.24	+4.53	0.972	2.30×10^{-17}
1151	49.30	-3.56	+5.01	0.448	4.04×10^{-14}
1205	16.40	-5.88	+5.01	0.607	5.56×10^{-14}
1207	24.00	-5.00	+4.53	0.531	5.66×10^{-14}
1244	16.50	-5.33	+4.53	0.555	7.31×10^{-14}
1272	14.50	-5.75	+5.06	0.599	6.58×10^{-14}
1283	4.80	-7.11	+4.53	0.680	1.21×10^{-13}
1295	4.70	-7.51	+5.06	0.719	9.34×10^{-14}
1341	5.40	-7.61	+5.01	0.725	7.76×10^{-14}
1429	2.75	-8.11	+5.01	0.759	1.15×10^{-13}

Initial $^{18}\text{O}(\text{SiO}_2) = -11.64$ ‰

DISCUSSION

Data

Phase-boundary reactions, the glass transition temperature, or devitrification of the SiO_2 glass must be considered before the oxygen diffusion data of Table 1 are accepted.

Haul & Just (1958) were the first to point out how a gas/solid exchange mechanism has to be treated mathematically if volume diffusion and phase-boundary reactions simultaneously control the exchange process. The existence of diffusion control is indicated when the calculated diffusion coefficient is independent of exchange time. Sucov (1963) concluded that volume diffusion is operative in O_2/SiO_2 exchange experiments, because straight lines passing through the origin were obtained when plotting, from his data, Dt as a function of t itself for temperatures at 1006 and 1150°C. However, the range of diffusion times was limited to only 200 min. Measurements by Williams (1965), which were carried out over longer exchange times of up to 150 hours, indicate that for shorter times at lower temperatures (950 and 1100°C) the presence of a phase-boundary reaction is noticeable. Volume diffusion becomes predominant for diffusion times greater than 10 hours. Phase-boundary effects seem to become increasingly negligible with increasing temperature and exchange time. According to the above studies, no phase-boundary effects are to be expected in this study because long diffusion times and high temperatures were used. Moreover, the high degree of exchange, of 25-55% at temperatures

greater than 1150°C (see Table 1) immediately suggest volume diffusion control. Therefore, a systematic study of the possible time dependence of the diffusion coefficient was not undertaken. Two diffusion runs near 1200°C did yield the same diffusion coefficient although the exchange time differed by 50% (Table 1).

The control mechanism for oxygen diffusion at 1012°C, where only 3% isotopic exchange was observed, is unsolved. The exchange time, 168 hours, would suggest a negligible control by phase-boundary reactions according to the data of Williams (1965). However, a substantial phase-boundary reaction is suggested by the fact that the diffusion coefficient at 1012°C is 3 orders of magnitude smaller than the extrapolated value from the high-temperature Arrhenius plot. A more likely alternative interpretation of the low diffusivity at the lower temperature may be that the 1012°C experiment is the only one conducted below the glass transition temperature of SiO₂ (1100-1150°C). A drastic decrease of oxygen mobility has been reported by Oishi *et al.* (1975) in the glass transition region for CaO-Al₂O₃-SiO₂ and Na₂O-CaO-SiO₂ glasses. However, no indication of this decrease in mobility was detected in the previous studies (Haul & Duembgen 1962; Sucof 1963; Williams 1965).

Finally, the effect of devitrification during the diffusion run has to be discussed. Microscopic examination of the fibers after the diffusion runs did not reveal the presence of crystals; however, incipient crystallization could be

observed in the higher temperature (1341 and 1429°C) experiments. From studies (Wagsfaff 1968) of the growth of α -cristobalite (high-temperature modification) in SiO₂, it can be predicted that crystallization of no greater extent than $5 \times 10^{-2} \mu\text{m}$ would occur during the experiments below 1300°C. During those experiments at least 30% of the oxygen was exchanged, clearly indicating that the exchange reaches far beyond the possibly crystallized surface layer, and therefore reflects the diffusion properties of the silica glass.

At the two higher temperatures, crystallized layers up to 0.5 μm and more are to be expected; i.e., the crystallized layers may be the same size as the penetration depth of the isotopic exchange. Further experiments of short duration could resolve the ambiguity of devitrification affecting oxygen diffusion in SiO₂. The high-temperature experiments have nevertheless been included in the Arrhenius plot (see Fig. 1) because no pronounced change in diffusion could be observed within them. Apparently, oxygen mobility in α -cristobalite, whose density is very close to that of SiO₂ glass (2.21 compared to 2.20 g/cm³ for vitreous silica) resembles that in SiO₂ glass. Structural similarity between silica glass and α -cristobalite has been pointed out before (Oberlies & Dietzel 1957).

On Figure 2 the published oxygen diffusion data in SiO₂ glass are compared with the results of this study. All previous data were obtained by the gas/solid isotope exchange method, but in which only the decrease of the isotopic ratio

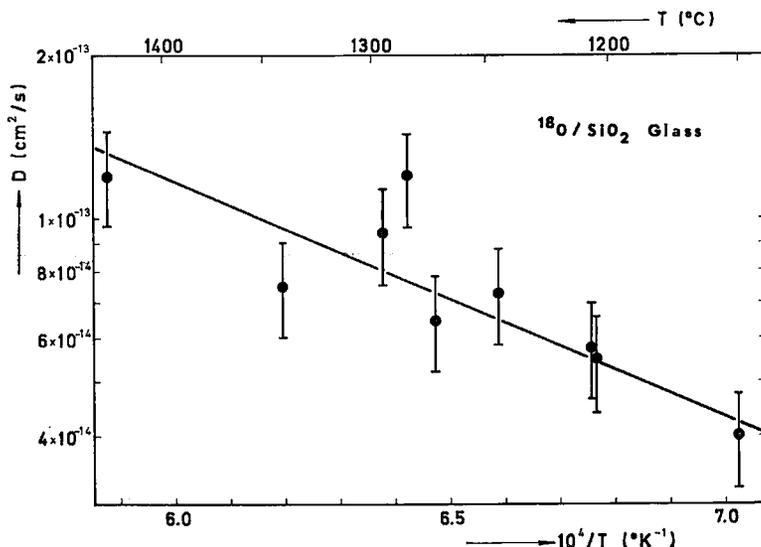


FIG. 1. Oxygen tracer diffusion coefficient in vitreous silica (Type II) as a function of temperature.

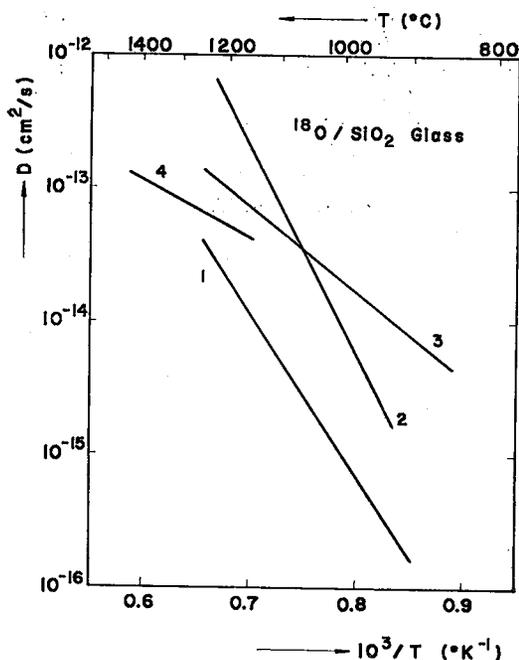


FIG. 2. Comparison of oxygen tracer diffusion coefficients in vitreous silica as a function of temperature. Data according to: (1) Haul & Duembgen 1962; (2) Sucov 1963; (3) Williams 1965; (4) present work.

in a fixed volume of gas was monitored. The reported activation energies range from 29 to 71 kcal/mole. The activation energy determined in this study, 20 kcal/mole, is closest to the 29 kcal/mole given by Williams (1965), whose absolute values of the diffusion coefficients are also closest to those reported here at comparable temperatures. Perhaps it is significant that the SiO_2 used in this study and in the one by Williams (1965) was obtained from the same manufacturer (Amersil Inc.).

Mechanism of oxygen transport

The 20 kcal/mole activation energy for diffusion of oxygen in pure SiO_2 is much less than the 50 to 100 kcal/mole activation energy observed in complex silicate glasses and melts (Muehlenbachs & Kushiro 1974; May *et al.* 1974; Oishi *et al.* 1975). The mechanism of oxygen transport must differ when network-modifying cations are present in the SiO_2 network. Further evidence for two distinct mechanisms of oxygen movement is given by the differing pressure dependences as measured in the gas/solid exchange experiments. Williams

(1965) found in SiO_2 that the diffusion rate was directly proportional to the O_2 pressures whereas May *et al.* (1974) observed in binary silicate glasses ($\text{K}_2\text{O-SiO}_2$) that the diffusion rate was inversely proportional to the square root of the O_2 pressure. The diffusion data imply that in SiO_2 the diffusion step involves dissolved molecular O_2 within the SiO_2 (see discussions in Motzfelds 1964, and Meek 1973), whereas, in the case of the complex silicates, oxygen movement occurs with Si-O bond breaking. One should also note that activation energy of permeation of O_2 gas through fused SiO_2 (22 kcal/mole; Norton 1961) is very close to the activation energy of diffusion determined in this study.

A direct consequence of the different diffusion mechanisms is obvious in comparing the activation energies of oxygen tracer diffusion with those of viscous flow; in SiO_2 glass the activation energy of oxygen diffusion is much smaller than the 150-170 kcal/mole found for viscous flow in the range from 900-1400°C, whereas for silicate glasses, a one-to-one relationship between these two properties can be established (Oishi *et al.* 1975).

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