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TRACER DIFFUSION IN GRANITIC MELTS:
EXPERIMENTAL RESULTS FOR NA, K, RB, CS, CA, SR, BA, CE, EU
TO 1300°C AND A MODEL OF CALCULATION

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Abstract. Tracer diffusivity of Na, K, Rb, Cs, Ca, Sr, Ba, Eu, and Ce has been measured in natural and dehydrated obsidians in the range 300°-1300°C, 0-4 kbar, using radiotracers and an etching technique. The results complement and extend previous results on similar material. Diffusivity ranging from 10^{-16} to 10^{-7} cm²/s have been observed. An Arrhenius law is observed for all species, with activation energies *E* ranging from 20 to 120 kcal/mol. A strong correlation of *E* with ionic radius and squared formal charge (*Z*²) offers guidelines for model calculation of the activation energy. A mechanistic model of transport through an elastic medium is adapted to the present data. It permits a fair prediction of the activation energy as a function of *r* and *Z* according to $E = 128(r-1.34)^2 + 33 Z^2/(r+1.34) + 8$ kcal/mol, with a misfit comparable to the experimental uncertainty. The correlation between *E* and the preexponential factor *D*₀ (compensation law) is discussed within the framework of the proposed model. The major conclusion is that local configuration (size, charge, coordination, etc.) is the major control for cationic diffusivity and not the properties of the matrix, such as chemical composition, viscosity, etc.

Introduction

The understanding of kinetic problems and especially diffusion in natural melts is quite important in several petrological situations. The need for kinetic data is obvious in chemical mixing, growth from the melt, and isotopic equilibration during anatexis or partial melting. Furthermore, quantitative data for a greater number of species should provide some insight into the structure of silicate melts. Up to very recently only qualitative information was available for describing these silicate melts as a collection of more or less polymerized units [see Hess, 1971]. One can use, for example, the ratio of bridging to nonbridging oxygens to correlate any measurement with structural properties of melts [Mysen et al. 1980, and references therein]. New spectroscopic data have given some information about the local environment of some cations [see, e.g., Calas, 1980]. The radial distribution functions permit one to compare different melts and give a more accurate image of their structure

[Taylor and Brown, 1979]. The diffusion data could complement in some ways these results if the diffusion process is better understood.

Since Bowen [1921] first recognized that diffusion processes in natural melts could not be an efficient process for mass transport over significant distances, very little work had been done on this topic by earth scientists until recently. On the other hand, synthetic glasses of industrial interest have been the subject of numerous studies. It is, however, very difficult for petrologists to obtain useful data from these experiments.

In the last 10 years, several earth scientists started new studies which brought about a far better knowledge of diffusion processes in natural melts, especially for basaltic and granitic composition (see review by Hofmann [1980] and references therein). I report here data that have been obtained in the last 8 years using essentially radiotracers and mapping diffusion profiles by sequential etching, a conventional technique.

2. Description of the Samples

2.1. Starting Material

The basic material is a granitic obsidian (OIS) from a postglacial flow at Hrastinnuhraun, Rangárvallasýsla in southern Iceland. This is an exceptionally good starting material in that bubbles, crystals, and microcracks are almost absent. Under 1 mm thickness, it appears dark but still transparent. Electrical conductivity [Carron, 1968; Abélard and Calès, 1980] and viscosity measurements [Carron, 1969] have been performed on the same starting material. Some diffusion experiments have been reported previously for Na [Carron, 1968], He [Jambon and Shelby, 1980] and Li [Jambon and Semet, 1978]. Several wet chemical analyses have been done over the years, and the mean is reported in Table 1. Chemical homogeneity has been checked using an electron microprobe. Foaming occurs at 950°C, so that no experiment can be performed at higher temperatures. Jambon et al. [1978] performed diffusion experiments for Cs after hydration (5.5% H₂O) of this material.

Some experiments have also been performed using another granitic obsidian from Valles Caldera, New Mexico. This glass is of slightly lower quality than the Icelandic obsidian. Magaritz and Hofmann [1978a,b] report cationic diffusivities in this material, and Shaw [1974], Jambon [1979], and Delaney and Karsten [1981] reported on the diffusion of water in that matrix. This glass has been used here because it enables us to check for coherency of the diffusion measurements obtained in Washington and in Orléans. For this glass, foaming occurs at around 1000°C, probably because

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TABLE 1. Analyses of Starting Materials

| | OIS | OVC |
|--------------------------------|-------|-------|
| SiO ₂ | 73.01 | 76.87 |
| Al ₂ O ₃ | 12.57 | 12.20 |
| Fe ₂ O ₃ | 1.32 | |
| FeO | 1.39 | 0.94 |
| MnO | 0.05 | 0.05 |
| MgO | 0.54 | 0.05 |
| CaO | 0.41 | 0.30 |
| Na ₂ O | 5.05 | 4.38 |
| K ₂ O | 4.60 | 4.40 |
| TiO ₂ | 0.20 | 0.07 |
| H ₂ O ⁺ | 0.52 | 0.38 |
| Total | 99.86 | 99.49 |

OIS, wet chemical analysis; OVC, electron microprobe analysis (total iron as FeO). H₂O⁺ obtained after ignition at 1100°C.

of its slightly lower water content. The analysis reported in Table 1 has been obtained by microprobe analysis. This obsidian was also dehydrated at 1550°C in air, and the resulting dehydrated glass (OVD) was very clear and free of all crystallites and bubbles. This permitted the performance of high temperature measurements, as required for very slow diffusing species.

2.2. Alteration during the experiments

Water loss. At 1 atm pressure, foaming and destruction of the natural samples occurs at 950° and 1000°C for OIS and OVC respectively. Below this temperature, Jambon [1980] has shown that water loss is very slow, so that only the very surficial part of the sample is affected. The concentration profiles confirmed that this effect is negligible.

Oxidation. According to the measurements of Muehlenbachs and Kushiro [1974], oxygen diffusion corresponding to isotopic exchange is very slow. We may regard this as giving an upper limit to the diffusion of oxygen which will control the oxidation of the sample. This effect is therefore negligible considering the comparatively short duration of the experiments. Because of the somewhat low iron content of the obsidian, accurate measurement of the Fe²⁺/Fe³⁺ ratio failed.

Argon solubility. For the measurements performed under argon pressure in an internally heated pressure vessel, the question arose as to whether argon solubility could influence the diffusion results. A crude estimate shows that the solubility of argon at 4 kbars does not exceed 0.1%, which is the detection limit by weighing. Since the argon diffusivity is of the same order of magnitude as that of the cations, the conformity of the diffusion profiles shows that this phenomenon, if it exists, has no effect on tracer diffusion.

Crystallisation. In synthetic glasses, nucleation and growth of crystallites frequently occurs when the melting point is approached. Because of the volume change, this introduces stress and dislocations. The melt-crystal interfaces could also be an easier pathway for diffusion; some of the tracer might also be trapped in crystallites. For OIS, OVC and OVD no significant crystallization ever occurred. Even after 10 days of annealing at 850°C, X ray diffraction

measurements do not show any characteristic diffraction peaks. Furthermore the glass samples are transparent so that any crystallization would be easily detected.

3. Experimental Techniques

Except for minor details, the experimental technique is the same as that already described by Jambon and Carron [1976]. Only the major characteristics are mentioned here, and the reader should refer to the previous paper for further details. The samples are cut and polished as thin disks of 0.5 to 5 mm thickness and 8 mm diameter. For the measurement of very slow-diffusing species in dehydrated obsidian (OVD), the results are greatly improved by firing the samples at 1100°C for about 15 min. The surficial melting of the sample permits healing of all the microcracks and imperfections that result from sample preparation, without deforming the disk significantly. This special preparation allowed us to measure diffusivities down to 2×10^{-16} cm²/s or profiles extending to no more than 0.5 μm.

For fluid samples, e.g., OVD above 1100°C, Pt tubes were used as containers. Some of these samples have been subsequently sectioned according to the technique described by Magaritz and Hofmann [1978 a]. All other samples have been sectioned by successive etching in dilute HF. Only one single tracer has been studied in each experiment. This permitted the optimization of the penetration of the tracer. Magaritz and Hofmann [1978a] showed that for obsidian there is no significant time dependence. Reproducibility of the measurements was checked for the diffusion of Cs and found to be satisfactory. Linearization of the activity profiles was routinely done, and all the calculated diffusivities have been taken from linear plots. All nonlinear profiles have been discarded. There were very few of them, generally due to irregularity of the sample surface (especially on the edges). A similar effect is observed for very short profiles if the surface is not healed before experiment. This effect precludes the measurement of the diffusivity of Ce in OIS and OVC because of its exceedingly low value at 900°C.

Two replicate measurements at 1100°C on OVD by both grinding and etching yielded diffusivities of 3.5 and 4.4×10^{-10} cm²/s, identical within analytical uncertainty. Including all significant sources of error (run duration, activity counting, weighing of slab), one can estimate a theoretical uncertainty of ± 0.3 on log D (or a factor of 2 on D). The deviations from Arrhenius lines give a mean standard deviation (log D), $\sigma = 0.6$. This larger deviation includes temperature uncertainty, which is especially significant when temperature dependence is large (of the same order as all other analytical uncertainties). The overall accuracy does not seem very good when compared to other diffusion studies on synthetic glasses. This is partly due to the use of a single technique for diffusivities ranging over 8 orders of magnitude and the comparatively small size of the natural samples. The measurements for Eu, Ce, Pb as well as all the measurements in dehydrated glass (OVD) have been performed at the Department of Terrestrial Magnetism, Carnegie

TABLE 2. Results of the Diffusion Experiments

| Species | D, cm ² /s | T, °C | t, s | Matrix |
|---------|--------------------------|-------|------------------------|--------|
| Cs | 3.3 × 10 ⁻¹⁴ | 602 | 2.50 × 10 ⁵ | OIS |
| Cs | 3.0 × 10 ⁻¹⁴ | 604 | 2.50 × 10 ⁵ | OIS |
| Cs | 1.1 × 10 ⁻¹³ | 650 | 4.23 × 10 ⁵ | OIS |
| Cs | 5.2 × 10 ⁻¹³ | 690 | 1.0 × 10 ⁵ | OIS |
| Cs | 8.6 × 10 ⁻¹³ | 700 | 9.0 × 10 ⁴ | OIS |
| Cs | 6.5 × 10 ⁻¹³ | 704 | 8.41 × 10 ⁴ | OIS |
| Cs | 8.6 × 10 ⁻¹³ | 708 | 7.34 × 10 ⁴ | OIS |
| Cs | 1.2 × 10 ⁻¹² | 760 | 5.52 × 10 ⁴ | OIS |
| Cs | 1.0 × 10 ⁻¹¹ | 802 | 1.44 × 10 ⁴ | OIS |
| Cs | 6.7 × 10 ⁻¹² | 804 | 1.69 × 10 ⁴ | OIS |
| Cs | 1.05 × 10 ⁻¹¹ | 812 | 1.44 × 10 ⁴ | OIS |
| Cs | 2.3 × 10 ⁻¹¹ | 860 | 1.44 × 10 ⁴ | OIS |
| Cs | 4.7 × 10 ⁻¹¹ | 915 | 1.56 × 10 ⁴ | OIS |
| Cs | 8.3 × 10 ⁻¹³ | 752 | 1.4 × 10 ⁴ | OIS* |
| Cs | 4.1 × 10 ⁻¹² | 806 | 7.2 × 10 ³ | OIS* |
| Cs | 3.4 × 10 ⁻¹¹ | 855 | 3.6 × 10 ³ | OIS* |
| Cs | 5.6 × 10 ⁻¹¹ | 907 | 9.0 × 10 ² | OIS* |
| Cs | 7.84 × 10 ⁻¹² | 875 | 8.5 × 10 ⁵ | OVC |
| Cs | 9.54 × 10 ⁻¹³ | 790 | 1.48 × 10 ⁵ | OVD |
| Cs | 6.30 × 10 ⁻¹² | 875 | 8.5 × 10 ⁵ | OVD |
| Cs | 1.19 × 10 ⁻¹¹ | 930 | 8.32 × 10 ⁴ | OVD |
| Cs | 3.78 × 10 ⁻¹¹ | 995 | 1.55 × 10 ⁵ | OVD |
| Cs | 1.71 × 10 ⁻¹⁰ | 1050 | 9.0 × 10 ³ | OVD |
| Cs | 3.54 × 10 ⁻¹⁰ | 1097 | 1.86 × 10 ³ | OVD |
| Cs | 4.40 × 10 ⁻¹⁰ | 1100 | 4.21 × 10 ⁵ | OVD** |
| Cs | 3.80 × 10 ⁻⁹ | 1300 | 5.4 × 10 ⁴ | OVD** |
| Na | 2.2 × 10 ⁻¹³ | 138 | 5.04 × 10 ⁵ | OIS |
| Na | 1.7 × 10 ⁻¹¹ | 230 | 3.31 × 10 ⁵ | OIS |
| Na | 1.1 × 10 ⁻⁹ | 345 | 7.56 × 10 ⁴ | OIS |
| Na | 4.2 × 10 ⁻⁹ | 407 | 1.44 × 10 ⁴ | OIS |
| Na | 3.0 × 10 ⁻⁸ | 502 | 9.0 × 10 ² | OIS |
| K | 9.0 × 10 ⁻¹² | 372 | 4.34 × 10 ⁴ | OIS |
| K | 2.4 × 10 ⁻¹⁰ | 495 | 3.6 × 10 ³ | OIS |
| K | 1.3 × 10 ⁻⁹ | 612 | 1.0 × 10 ³ | OIS |
| K | 1.2 × 10 ⁻⁸ | 735 | 1.0 × 10 ³ | OIS |
| K | 4.2 × 10 ⁻⁸ | 845 | 1.0 × 10 ³ | OIS |
| Rb | 5.3 × 10 ⁻¹³ | 420 | 2.5 × 10 ⁵ | OIS |
| Rb | 2.1 × 10 ⁻¹¹ | 562 | 5.76 × 10 ⁴ | OIS |
| Rb | 3.5 × 10 ⁻¹⁰ | 705 | 1.44 × 10 ⁴ | OIS |
| Rb | 2.0 × 10 ⁻⁹ | 832 | 9.0 × 10 ² | OIS |
| Rb | 6.8 × 10 ⁻⁹ | 945 | 1.0 × 10 ⁴ | OIS |
| Ca | 8.5 × 10 ⁻¹⁴ | 632 | 1.81 × 10 ⁵ | OIS |
| Ca | 5.0 × 10 ⁻¹⁰ | 896 | 1.8 × 10 ³ | OIS |
| Ca | 7.2 × 10 ⁻¹⁰ | 920 | 9.0 × 10 ² | OIS |
| Ca | 9.8 × 10 ⁻¹⁰ | 933 | 9.0 × 10 ² | OIS |
| Ba | 1.67 × 10 ⁻¹³ | 632 | 1.81 × 10 ⁵ | OIS |
| Ba | 6.05 × 10 ⁻¹¹ | 810 | 1.81 × 10 ⁴ | OIS |
| Pb | 1.62 × 10 ⁻¹⁰ | 950 | 1.54 × 10 ⁵ | OVD |
| Eu | 2.61 × 10 ⁻¹⁵ | 700 | 3.59 × 10 ⁵ | OVD |
| Eu | 6.14 × 10 ⁻¹⁴ | 800 | 1.76 × 10 ⁵ | OVD |
| Eu | 1.68 × 10 ⁻¹² | 912 | 6.48 × 10 ⁴ | OVD |
| Eu | 4.00 × 10 ⁻¹² | 950 | 3.44 × 10 ⁵ | OVD |
| Eu | 2.90 × 10 ⁻¹¹ | 1050 | 3.60 × 10 ⁴ | OVD |
| Ce | 2.5 × 10 ⁻¹⁶ | 875 | 8.5 × 10 ⁵ | OVD |
| Ce | 4.6 × 10 ⁻¹⁵ | 950 | 3.44 × 10 ⁵ | OVD |
| Ce | 5.1 × 10 ⁻¹⁴ | 995 | 1.55 × 10 ⁵ | OVD |
| Ce | 2.5 × 10 ⁻¹³ | 1050 | 9.0 × 10 ³ | OVD |
| Ce | 9.45 × 10 ⁻¹³ | 1100 | 1.86 × 10 ³ | OVD |
| Ce | 8.1 × 10 ⁻⁸ | 1300 | 5.4 × 10 ⁴ | OVD |
| Ce | 9.3 × 10 ⁻⁸ | 1300 | 5.4 × 10 ⁴ | OVD |

All data obtained using etching technique.
 *Argon pressure of 3 kbar
 **Use grinding technique.

Institution of Washington. All other results were obtained at the University of Orléans.

4. Experimental Results

All the experimental results are reported in Table 2 with temperatures and run durations. The experimental technique permitted measuring diffusivities ranging from 10⁻¹⁶ to 10⁻⁷ cm²/s. The results for sodium are interesting because they can be compared to previous measurements (Figure 1) by Carron [1968] on OIS, Magaritz and Hofmann [1978a] on OVC, and Sippel [1963] on an obsidian of unspecified composition. All the results are in very good agreement, which is very satisfactory since different techniques were used in these studies.

4.1. Temperature Dependence

All measured diffusivities conform to Arrhenius laws within the limits of uncertainty:

$$D = D_0 \exp -E/RT$$

which yields straight lines in the conventional log D : 1/T plots (Figure 1 and 2), where T is the absolute temperature in °K, and R the gas constant (1.987 cal/mol-°K). D₀ (cm²/s) and E (kcal/mol) are therefore characteristic parameters, called the frequency factor and activation energy, respectively. They have been calculated by least squares fit of the data to the equation:

$$\log D = \log D_0 - 0.434 E/RT$$

They are reported in Table 3 with standard deviation and temperature range. The decrease of D with temperature is strong especially for highly charged cations and heavy alkalis (about 1 order of magnitude for 100°C). For the smaller alkalis Na and K, this effect is far less significant.

The range of activation energy variations (a

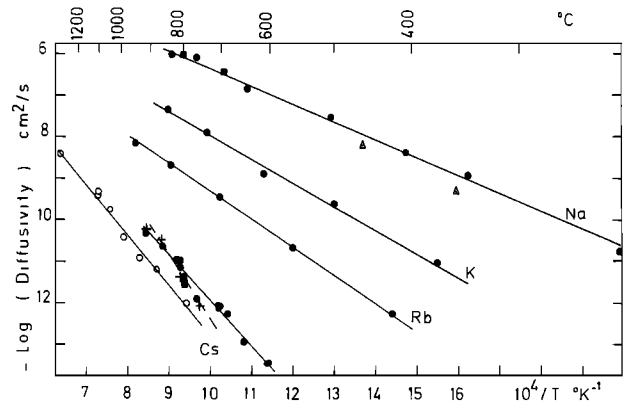


Fig. 1. Arrhenius plot for the alkalis in obsidians. Dehydrated obsidian (OVD), open circles, this study. Natural obsidians (OVC), (solid squares), Magaritz and Hofmann [1978a] for two Na points and four Cs points at 800°C; (OIS) (solid circles), all this study except three measurements for Na by Carron [1968] above 600°C; (crosses), Cs in (OIS) 3 kbar, this study; also figured are previous measurements by Sippel [1963] for Na in an unspecified obsidian, triangles.

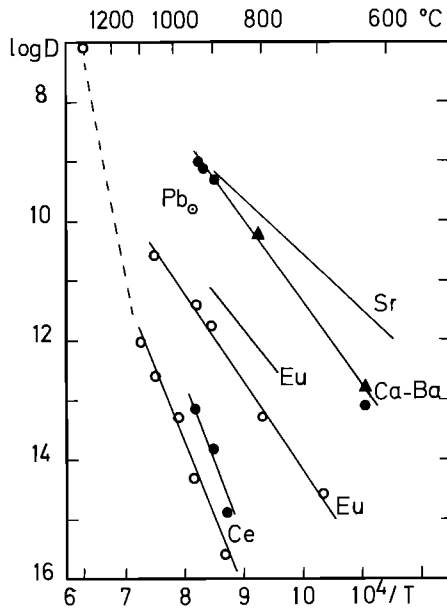


Fig. 2. Further results in obsidians. All this study. Also reported as straight lines are the results of Magaritz and Hofmann [1978a, b] for Eu and Sr in (OVC). It may be noticed that results for Ce and Eu in natural obsidian (OVC, solid circles and line) lie significantly above the corresponding lines in dehydrated obsidian (OVD, open circles). The same is observed in Figure 1. The differences between Eu and Sr are interpreted as an effect of charge (see text). Also plotted, Ca (dots), Ba (triangles) and one Pb result.

factor of 5 between sodium and cerium) makes it a useful parameter in understanding the variations of diffusion rates in these systems. The generally greater uncertainty in D_0 (or $\log D_0$) is the major reason why it has been disregarded in most previous studies. It corresponds to the intercept at the value $1/T = 0$. In the present experiments, the total range of $10^3/T$ is 0.7 - 1.2, with an even more restricted interval for a single Arrhenius line; this restricted temperature interval creates uncertainties when the slope is not accurately determined. Because the range in D_0 is more than 10 orders of magnitude, it is still a possible tool for understanding diffusion processes.

4.2. Discussion of the Temperature Dependence

No discontinuity was ever observed in the Arrhenius plots, in contrast with those described previously in synthetic glasses [see, e.g., Johnson et al., 1951]. In the previous section it was assumed that the temperature dependence follows the Arrhenius equation:

$$D = D_0 \exp - E/RT \quad (1)$$

This law is observed for diffusion in diverse materials such as metals, salts, oxides, and glasses as long as a single diffusion mechanism is effective. Lacharme [1976] has shown that over a restricted temperature range ($\approx 300^\circ\text{C}$), the overall experimental accuracy is generally insuffi-

cient to reveal significant deviations from linearity that would imply the existence of more than one mechanism. The above expression (1) can be derived from the theory of absolute reaction rate [Glasstone et al., 1941]. Application of this expression to glasses has been challenged by several authors who have proposed instead equations such as

$$D = D_0 T^{1/2} \exp - E_1/RT \quad (2)$$

$$D = D_0 T \exp - E_2/RT \quad (3)$$

$$D = D_0 \exp - E_3/RT \exp - (\sigma/2RT)^2 \quad (4)$$

In the case of diffusion of He in silica glass, Shelby and Keeton [1974] have shown that (3) or (4) provided a significantly better fit of the data. The present data are not of sufficient accuracy to choose statistically between equations. Adding more data on other natural and synthetic material [Jambon and Carron, 1976, 1978; Jambon and Shelby, 1980; Jambon, 1980], i.e. 218 points, also does not allow resolution of this question. The usual form of the Arrhenius equation was therefore retained as adequate to describe the present data.

4.3. Pressure dependence

The only measurements I have made of the effect of pressure, are for Cs in OIS. The diffusivity at 3 kbar is very close to that at 1 bar. At first sight the activation energies, 69.8 and 49.8 kcal/mol seem to be significantly different; However, the standard deviations of 9.3 and 2.0, respectively, make this difference rather uncertain. Watson [1979a] has shown for the diffusion of Ca in a $\text{Na}_2\text{O} : \text{CaO} : \text{Al}_2\text{O}_3 : \text{SiO}_2$ melt, that tens of kilobars are necessary to see significant variations. If there is an effect of pressure, it

TABLE 3. Arrhenius Parameters

| | E, kcal/mol | $\log D_0$ cm^2/s | Temperature Matrix range, $^\circ\text{C}$ | Ref |
|----|----------------|--------------------------------------|---|-----|
| He | 8.01(0.32) | -3.23(0.15) | OIS 200- 280 | 3 |
| Li | 21.5 (0.9) | -1.75(0.25) | OIS 300- 900 | 4 |
| Na | 20.2 (0.3) | -1.91(0.18) | OIS 140- 850 | 2 |
| K | 25.4 (0.9) | -2.46(0.24) | OIS 350- 850 | 1 |
| Rb | 30.4 (0.2) | -2.86(0.05) | OIS 400- 950 | 1 |
| Cs | 49.8 (2.0) | -1.04(0.44) | OIS 600- 920 | 1 |
| Cs | 69.8 (9.3) | 2.83(1.9) | OIS* 750- 900 | 1 |
| Ca | 67.8 (1.1) | 3.31(0.22) | OIS 630- 930 | 1 |
| Ba | 64.5 (-) | 2.1 (-) | OIS 630- 810 | 1 |
| He | 8.56(0.25) | -2.86(0.11) | OVC 190- 270 | 3 |
| Sr | 42.7 (0.8) | -1.26 | OVC 670- 950 | 5 |
| Ba | 45.1 (1.5) | -1.42 | OVC 700- 950 | 5 |
| Eu | 59.1 (-) | -0.26(-) | OVC 800- 950 | 6 |
| Ne | 14.1 | -4.54 | ** 100- 400 | 7 |
| Cs | 48.1 (2.9) | -2.01(0.45) | OVD 790-1300 | 1 |
| Ce | 117.2 (5.7) | 6.72(0.99) | OVD 875-1100 | 1 |
| Eu | 69.0 (1.2) | 0.89(0.22) | OVD 700-1050 | 1 |

References are (1) this work, (2) this work and Carron [1968] (3) Jambon and Shelby [1980], (4) Jambon and Semet [1978], (5) Magaritz and Hofmann [1978a], (6) Magaritz and Hofmann [1978 b], (7) Reynolds [1960]. Numbers in parantheses are one σ error.

*Pressure of 3 kbar.

**Tektite glass

is small over a pressure variation of a few kilobars. For smaller species, the effect of pressure is expected to be even less significant because of presumably smaller activation volumes.

4.4. Effect of the Chemical Composition of the Matrix

In this particular study no attempt was made to estimate the effects of varying composition. Several previous studies on feldspar glasses (Na, K, Rb, Cs) and basaltic glass (Na, K, Rb, Cs, Sr, Ba) [Jambon and Carron, 1976, 1978] and measurement for sodium in synthetic glasses of various compositions (Frischat [1975] for SiO_2 and Winchell and Norman [1969] for $\text{CaO} : \text{Al}_2\text{O}_3 : \text{SiO}_2$, among others) permit discussion of this aspect of the problem. The first striking feature (Figure 3) is the similarity of Arrhenius lines for a given species in all the glasses. In Figure 3, results for Na and Cs in six different glasses in the range $400^\circ\text{--}1000^\circ\text{C}$ are collected. The greatest deviation is observed for Na in the basaltic glass. For other species, as already noticed by Hofmann [1980], the agreement between this basaltic glass and OIS (or OVC from Magaritz and Hofmann [1978] a) would be much better. A similar agreement is observed between obsidian and albite or orthoclase glasses. Significant differences are observed, but they always fall within a very narrow range in comparison to variations that are observed with increasing temperature or between different species.

The conclusion is that for the glasses with $\text{SiO}_2 + \text{Al}_2\text{O}_3$ variations in the range 60–100%, the effect is comparatively minor. The most important

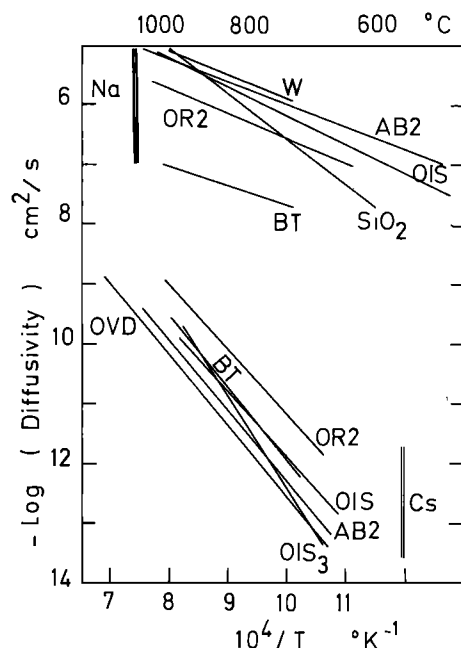


Fig. 3. Diffusion of Na and Cs in several matrices. AB2, OR2, albite and orthoclase glasses [Jambon and Carron, 1976]. BT, basalt glass [Jambon and Carron, 1978]. W, $\text{CaO}:\text{Al}_2\text{O}_3:\text{SiO}_2$ glass [Winchell, 1969]. The line for Na in SiO_2 is from Frischat [1975]. The spread in diffusivity is small compared to variations between species and even the variations with temperature.

systematic difference is found for the orthoclase glass, which has probably a much looser structure than albite and obsidian. Taylor and Brown [1979] have shown that alkali feldspar glasses and obsidian have closely related structures that may be depicted as a stuffed tridymite analog. This similarity may explain the relatively small variation in diffusivity between all compositions except for those of basaltic glass for which the structure is probably quite different. Whereas variable compositions in dry systems have a very slight effect or none at all, the addition of water changes the results drastically. This has been shown by Jambon et al. [1978] and Watson [1979b, 1981]. The results of these authors are in qualitative agreement, showing an increase of several orders of magnitude for a few percent water in the melt. The major drawback in the measurements of Jambon et al. [1978] is that the concentration profile of water in their sample was poorly known, and hence the correspondence between water concentration and diffusivity was not accurate. Whereas the diffusivity of Cs is drastically affected by water content, Watson's [1981] results show that the effect is negligible for Na and intermediate for Ca.

At this stage, it is worth noting that we have data for Eu and Ce in both OVC and OVD, and for Cs in OIS and OVD. In all three cases, the diffusivity is significantly lower in the dehydrated sample, OVD (Figures 1–2). In the case of Eu one could argue that this is due to the change of the redox state of the glass (see next section); however, for Ce and Cs, this particular effect is certainly negligible. On the average, changing the water concentration from 0.3 to 0.0 wt % decreases the diffusivity by a factor of 50 to 100. This is in qualitative agreement with the statements of Jambon et al. [1978] that most of the increase occurs between 0 and 1 wt % H_2O . Since most natural obsidians have water contents between 0.1 to 0.5 wt %, the major variations in diffusivity in these glasses for a specific species will be connected to this water abundance rather than to the chemical composition in the broader sense (SiO_2 concentration, for example). On the other hand, Arrhenius parameters show comparatively little variations.

The variation of diffusivity with water concentration is very similar to that of water itself [Shaw, 1974; Jambon, 1980; Delaney and Karsten, 1981], for which the diffusivity increases drastically between 0 and 1% water.

4.5. Effect of Diffusing Species

From the results of Figures 1–2, we can see at first glance that there is a progressive variation from small to large cations. This is particularly obvious for the alkalis. This feature can also be observed for rare gases in silica glass [Swets et al., 1961] and has been described by Jambon and Carron [1976] in feldspar glasses. This feature is not clear for alkaline earth elements, but these species are all smaller than K, and Ca is about as large as Na. Considering species of similar size, such as Na, Ca, Ce, and He [Jambon and Shelby, 1980], we observe a progressive increase in the magnitude of diffusivity as well as in the activation energies with increasing charge (Table 4 and Figure 4). No simple

TABLE 4. Activation Energy and Diffusivity in Obsidians for Species of Similar Size but Varied Charges

| | He | Na | Ca | Ce |
|-----------------------------|------------------|------------------|-----------------------|-----------------------|
| D 800°C, cm ² /s | 10 ⁻⁵ | 10 ⁻⁶ | 5 × 10 ⁻¹⁰ | 2 × 10 ⁻¹⁸ |
| E, kcal/mol | 8 | 20 | 68 | 117 |
| Ionic radius | 1.10 | 1.24 | 1.20 | 1.22 |

Data for helium are extrapolated from Jambon and Shelby [1980].

correlation with other parameters like electronegativity or ionic potential has been found.

Correlation with ionic radius r. As noted above, the correlation of diffusivity and ionic radius is most apparent for the alkalis, since they have all the same charge and their size varies considerably. We can add to the present data those of Jambon and Semet [1978] on Li diffusion in OIS. The ionic radii are those defined by Whittaker and Muntus [1970] in VIII fold coordination. There are several reasons for this choice. One is that coordination of species in glasses is not very well known, and consequently, I chose one single coordination number. The qualitative agreement would not be changed were it possible to choose more appropriate coordination numbers.

Winchell [1969] and Winchell and Norman [1969] proposed a linear correlation between E and 1/r. In their original paper, this law worked very well for alkalis, but for other cations they used an ad hoc radius, ρ defined as

$$\rho = 1.59r$$

A similar relationship has not been found in other glasses [Jambon and Carron, 1976] nor is it obeyed in obsidians. A possible explanation to this discrepancy is that the activation energies were all greater than 40 kcal/mol, in contrast to the present results.

More commonly, a relationship between E and $(r + b)^{-1}$ has been proposed, for instance in ionic crystals [see Adda and Philibert, 1966]; b and r represent the anion and the cation radius, respectively. A similar equation can be fitted to the alkali data of the present paper (r in Å and E in kcal/mol):

$$E = 16.4 - 5.6/(r - 1.9) \quad (5)$$

The validity of the correlation is quite uncertain, however (5 points for defining 3 parameters), and the negative value of b has no physical significance. A similar calculation was not applied to other species, since data exist only for three alkaline earth elements and two rare earth elements.

In summary, none of the simple correlations proposed so far can describe our results satisfactorily.

Cationic charge. To study conveniently the effects of the cationic charge, it follows clearly from the previous section that we have to deal with species of constant radius to remove the effects of size. Fortunately, He, Na, Ca, and Ce having similar radii can be used to investigate charge effects (Figure 4). As far as we know, no

empirical relationship has been proposed for the effect of charge on diffusion in silicate melts except by Hofmann [1980] for diffusivity in a molten basalt. He proposed at 1300°C, the empirical equation

$$\log D (1300^\circ\text{C}) = a \log Z^2 r + b$$

based on measurements on Na, Mn, Co, Ca, Sr, Ba, Gd, Eu, and V. Unfortunately, a similar relationship does not apply to granitic melts; a relationship between the activation energy and the square of the cation valence Z is proposed (Figure 5). This relationship has previously been proposed by Jambon and Delbove [1977] for He, Na, and Ca in an albite glass. A similar relationship holds here for four species:

$$E = 8.0 + 13. Z^2 \quad (\text{kcal/mol}) \quad (6)$$

Extrapolation to cations with a valence of four would result in an activation energy of 208 kcal/mol. Such an extrapolation is probably not reasonable, as will be shown later on.

The case of Europium (Figure 2). Europium displays the property of having two possible oxidation states in natural rocks. In their first measurements on the diffusion of Eu in obsidian, Magaritz and Hofmann [1978b] assumed that Eu had a valence of 3. This was reasonable for their basalt melt as they obtained identical results for Eu and Gd. However, the present data show a significant difference between Ce and Eu in obsidian (OVC, OVD). A possible (but unlikely) explanation is that Ce is present in our glass as Ce⁴⁺. On the basis of the results of Schreiber et al. [1980] on the oxidation state of Ce in silicate melts, this is not plausible. Furthermore, a few diffusion experiments done on Sm were found to be within, at most, one order of magnitude of those for Ce. They were not reported here because of their very poor accuracy. If Eu diffuses as Eu²⁺, then one would expect a diffusivity very similar to that of Sr²⁺. However, Eu

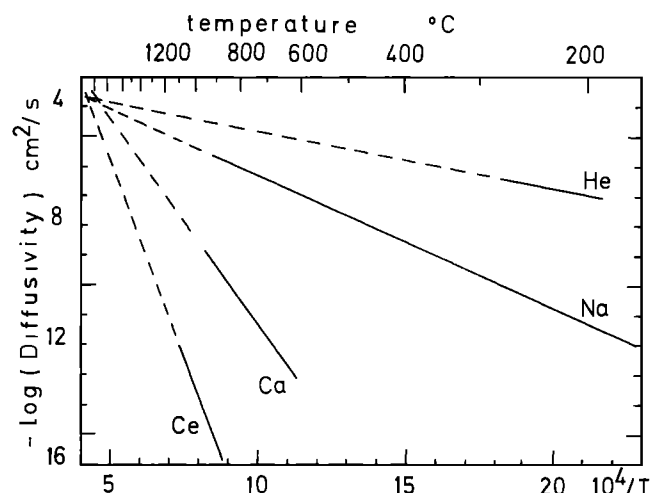


Fig. 4. Diffusivity for species with approximately similar radius. The line for He is from Jambon and Shelby [1980]. The fanning Arrhenius lines from a single point express the compensation law (see section 5.4) in contrast to Figures 1 and 2.

diffusivity is very different from both Ce^{3+} and Sr^{2+} , so an alternative explanation is needed. A possibility is that Eu is present as both Eu^{2+} and Eu^{3+} , with the Eu^{3+}/Eu^{2+} ratio being given by an equilibrium law. The redox state of the melt is buffered by Fe^{2+}/Fe^{3+} equilibrium. In this situation, it can be shown [Crank, 1975, chap. 14] that the measured diffusivity \bar{D}_{Eu} will be related to the Eu^{3+}/Eu^{2+} ratio. Since the diffusivity of Eu^{3+} (similar to that of Ce^{3+}) is negligible compared to that of Eu^{2+} (similar to that of Sr^{2+}), we obtain

$$D(Eu^{2+}) = \bar{D} (1 + Eu^{3+}/Eu^{2+}) \quad (7)$$

If, as a first guess, we take $D(Eu^{2+}) = D(Sr^{2+})$, we obtain, at 900°C:

$$Eu^{3+}/Eu^{2+} = 5 \times 10^2$$

This figure seems quite reasonable for a glass prepared by melting in air to allow dehydration. Further experiments conducted under controlled oxygen fugacity should confirm the present speculations. However, it is worth noticing that if this result and its interpretation are correct, this technique would permit a unique determination of the Eu^{3+}/Eu^{2+} ratio, which is very difficult to obtain when low concentrations are concerned, as is the case in natural systems.

5. Discussion of the Results and Models of Interpretation

5.1. The Melt Glass Transition and Diffusion

In the low-temperature range amorphous silicates are termed glasses. In the high-temperature range, e.g., above the transition temperature T_g , amorphous silicate systems are considered as supercooled liquids. This distinction is confirmed by the physicochemical properties of these silicates which are continuous over the melting range down to T_g . The transition temperature can be defined by measuring several properties like the viscosity ($\eta \approx 10^{13}P$), or the thermal expansion coefficient (discontinuity at T_g), each one giving a different temperature which in turn depends on the thermal history of the silicate. Roughly speaking, T_g corresponds to the temperature at which the structural change of the silicate cannot be accommodated anymore because of the exceedingly high relaxation time in comparison with the duration of feasible experiments. In the case of obsidians, the viscosity has been measured by Carron [1968] for OIS. He gives a viscosity of $10^{13}P$ at 750°C. Measuring the thermal expansion of OIS (A. Jambon, unpublished data, 1980) in reference to an albite glass standard similar to that studied by Arndt and Häberle [1973] yields a discontinuity in the thermal expansion coefficient around 650°–700°C. This was interpreted as the transformation temperature in fair agreement with the viscosity measurement. However, the diffusion measurements, show no discontinuity for OIS in the range 950°–150°C. The glass transition does not affect the diffusion properties of any of the cations measured so far. It has been shown previously on synthetic melts that nothing unusual happens to the diffusivity in the melting range [Winchell and Norman, 1969;

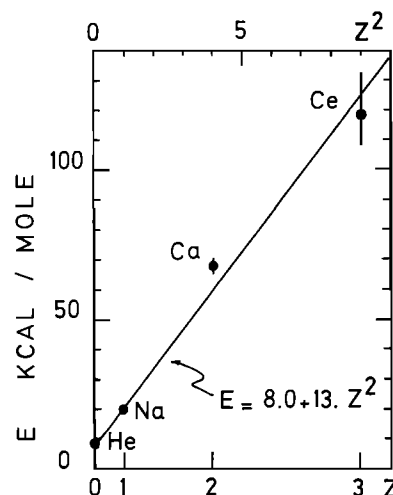


Fig. 5. Correlation between activation energy E and squared valence Z^2 . A similar trend was observed by Jambon and Delbove [1977] in feldspar glasses. He is from Jambon and Shelby [1980].

Jambon, 1980], as is also observed here (Figure 2) for Cs in OVD. We may therefore conclude that, as far as diffusion is concerned, the obsidians behave as supercooled liquids. No distinction can be made between a glass and a melt, in contradiction with some previous studies in the system $Na_2O : CaO : SiO_2$ [Johnson et al., 1951].

5.2. Stokes-Einstein law

From the above results, it follows that the two obvious parameters governing diffusion rate are ionic charge and radius. Now, I will try to reconcile the experimental results with simple theoretical models. We can roughly distinguish two kinds of models:

1. The first one considers that diffusion is comparable to the moving of a neutral sphere in a liquid; this is the well-known Stokes-Einstein law and its more sophisticated analogs.

2. The second class of models considers that the movement is one of a sphere moving in an elastic medium and thus uses elastic properties of the matrix.

The Stokes-Einstein law relates diffusivity D to viscosity according to the equation

$$D\eta = kT/6\pi r$$

where k is Boltzmann constant, T the absolute temperature ($^{\circ}K$), and r the ionic radius. As already stated by Carron [1968] and Murase [1962] and more recently in view of the many more recent data (discussed by Hofmann [1980]), this law is not appropriate in describing diffusion properties of silicate melts. However, Oishi et al. [1975] have shown that there is a good agreement between diffusivity of oxygen and viscosity in the systems $CaO : Al_2O_3 : SiO_2$, $Na_2O : CaO : SiO_2$, and $Na_2O : SiO_2$. In contrast, all the cationic diffusivities determined in obsidians are far larger than D predicted by Stokes-Einstein law. A qualitative explanation could therefore be that a more efficient mechanism for diffusive transport is effective for all the cations studied so far.

It is quite possible that cations with high charge, like Si or Al which are believed to have very low diffusivities, follow the Stokes-Einstein law. For these elements, the mechanism that is effective for other cations will not exceed that of transport by some viscosity-related mechanism. This speculation is suggested by the quite unrealistic value obtained by extrapolation from cationic diffusivities toward species like Si.

The disjunction between properties related to the silicate network (like viscosity) and diffusion suggests that this process is correlated to properties of the cation itself (short range order) rather than the matrix (intermediate and long range order). This view confirms qualitatively the fact that the chemical composition of the matrix is only a subsidiary parameter in describing diffusion properties in silicate systems of geological interest.

5.3. Diffusion and Elastic-Electric Properties of Glasses

Frenkel [1947] first considered the relation between diffusion and elastic properties of solids. He related the activation energy to the shear modulus of the matrix. This modulus has been measured in several silicates over their melting range by Murase and McBirney [1975] using ultrasonic wave propagation. For obsidians the shear modulus is constant from 1200°C to room temperature. A model for calculating the activation energy of diffusion in glasses has been first proposed by Anderson and Stuart [1954]. They subdivide the activation energy \bar{E} into several contributions according to

$$\bar{E} = E_s + E_c + E_r + E_p + E_v \quad (8)$$

where E_s is the shear energy corresponding to the elastic repulsion of the neighbors upon jumping to the next stable position. E_c is an electric energy (called Coulombian energy) which corresponds to the electrostatic energy involved during a jump. E_r , E_p , and E_v are repulsive, polarisation, and Van der Waals energy, respectively. E_p and E_v are negligible, and E_r may be assimilated as a fraction of E_c and included therein.

One of the obvious weakness of this model is that it implies transport via insertion like positions; for transport occurring via substitution like positions, one should add one more energy term E_f , corresponding to the energy of formation of these sites. In SiO_2 and $\text{SiO}_2 : \text{TiO}_2$ glasses, activation energy for He (and other rare gases) can be fitted reasonably well using (8) [Shelby, 1972a,b]. On the other hand, for glasses of the systems $\text{Na}_2\text{O} : \text{SiO}_2$ and $\text{Na}_2\text{O} : \text{SiO}_2 : \text{Al}_2\text{O}_3$ [Shelby, 1973; Shelby and Eagan, 1976] the agreement is not as good, suggesting that the addition of an E_f term is necessary.

Determination of E_s . For an ideally close-packed liquid, Frenkel [1947] gives the expression of the shear energy involved during a jump:

$$E_s = 8 \pi g r_D (r - r_D)^2 \quad (9)$$

where g is the shear modulus, r_D the radius of a gate between oxygen anions through which the dif-

fusing cation has to jump; r is the cationic radius. For a real liquid, (9) may be modified to

$$\begin{aligned} E_s &= a g r_D (r - r_D)^2 & r > r_D \\ E_s &= 0 & r < r_D \end{aligned} \quad (9')$$

where a is a coefficient to be determined experimentally. In silica glass, when taking $E_f = 0$, a good fit for He, Ne, Ar, and Kr is obtained for $a \approx 4.8$ ($g = 17.4 \text{ kcal } \text{Å}^{-3}$) and $r_D \approx 0.8 \text{ Å}$, which is intermediate between rings of four and five oxygen atoms. For albite glass, the higher activation energy cannot be accommodated by the same values of a and r_D . Since Taylor and Brown [1979] have shown that silica, albite glass, and obsidian have closely related structures, this most likely could be reconciled by using an $E_f \neq 0$. Doing that, we obtain a much better fit for the silica glass, while taking $E_f = 6 \text{ kcal/mol}$ and $r_D = 1.1 \text{ Å}$. A new value of a is obtained from the heavy noble gases data: $a = 2.4$. These latter values should not be considered very accurate since they depend critically upon the radii used for the rare gases. These radii in silicate systems are not very well known and are quite speculative. For obsidians the value of E_f can be taken as the activation energy for He diffusion, $E_f = 8 \text{ kcal/mol}$. The coefficient a cannot be calculated independently of r . Taking the same value for a and r_D in obsidians as in silica glass yields too high values for the alkalis (see next section); therefore to obtain a better fit, we assumed $a = 5.5$ and $r_D = 1.34 \text{ Å}$, similar to the radius of oxygen. Then (9) becomes

$$E_s = 5.5 g r_D (r - r_D)^2 + 8.0 \quad (10)$$

The size of r_D corresponds to the maximum radius of a sphere moving freely through a ring of six oxygen atoms. In the stuffed tridymite structure, which is considered as a good analog for silica and obsidian glasses [Taylor and Brown, 1979] the most likely geometrical structure through which atoms have to jump would be rings of six oxygens. Therefore if there is any geometrical significance to be attributed to r_D , as in the model first proposed by Frenkel [1947], then we must admit that this value is in fair agreement with what is presently known about the structure of these glasses.

A criticism that can be made against this model is that it uses the shear modulus of the glass, whereas it has been shown that diffusion properties are mostly intrinsic properties of the cation. This apparent inconsistency could be resolved by using specific shear moduli for cations (from the calculations of Hazen and Finger [1979]). This would probably improve the fit; however, in such a model we need to know the coordination of all the cations involved and the corresponding moduli. Furthermore, what we need is not site deformation but gate deformation upon jumping. At present, there appears to be no simple way to obtain this information with any confidence, and consequently, in the absence of a better choice the shear modulus relationship was retained. Since the shear modulus variations between the compositions considered here are very moderate, most variation of E_s stems from the squared difference $(r - r_D)^2$ essentially, which is a local characteristic.

Determination of E_c . The coulombian energy for a cation with charge Z surrounded by oxygens of total charge Z_o at a distance of $(r + r_o)$ is given by

$$E_c = b ZZ_o / (r + r_o) \quad (11)$$

where b is a constant depending on dielectric properties of the matrix. This law cannot be reconciled with the experimental results that show a quadratic dependence of E_c upon Z except if cations can only enter sites with a charge equal to their own charge. This implies a strong control of site charge by charged species moving around (probably Na) and some coupling between diffusing species and regulating species. Such an interpretation could explain the striking similarity between Li and Na in obsidian (OIS) as well as in other glasses [Jambon and Semet, 1978]. Until a better explanation of this aspect of the problem is proposed, I will just consider E_c to be of the form

$$E_c = b Z^2 / (r + r_o) \quad (12)$$

where b is calculated from (6) to be $33 \text{ \AA} \text{ kcal/mol}$.

Application of the model to the present data. From (8), (10), and (12) we obtain a more general formulation for obsidians, giving \bar{E} in kcal/mol. The cationic radius r is in \AA for VIII fold coordination.

$$\bar{E} = 8 + 128(r - 1.34)^2 + 33 Z^2 / (r + 1.34) \quad (13)$$

This equation is applied to the present results, plus the results of Jambon and Semet [1978] for Li and Jambon and Shelby [1980] for He both in OIS, which yields nine data points to determine three parameters, the fourth one being forced to equal the oxygen radius, $r_o = 1.34 \text{ \AA}$ (Figure 6). No attempt of a least squares fitting of the data was made because the accuracy in all the parameters is not sufficient to allow a meaningful refinement. The average misfit is 8%, which is about twice the standard deviation observed for Arrhenius slopes. The Eu point lies very close to the $Z=2$ line, which probably means that the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio is almost constant within the temperature studied here and confirms that the diffusing species is probably Eu^{2+} because of the too low diffusivity of Eu^{3+} .

The results of Magaritz and Hofmann [1978a] for Sr and Ba in OVC fall somewhat off the $Z=2$ line, and the discrepancy remains unresolved. The measurement for Ne [Reynolds, 1960] in a tektite glass lies above the $Z=0$ line. This could be due to the particular composition of this matrix (no water at all) and the particular experimental technique (powder method).

In conclusion, I want to emphasize that the fit obtained so far is quite fair in view of all the oversimplifications introduced into the model. The next step will be to check whether diffusivity of other smaller cations confirms this semiempirical relation, which is at least a potentially powerful law.

The effect of water. It has been shown elsewhere [Jambon et al., 1978; Watson, 1979b, 1981] that the addition of water to obsidian increases the diffusivity especially for slow diffusing

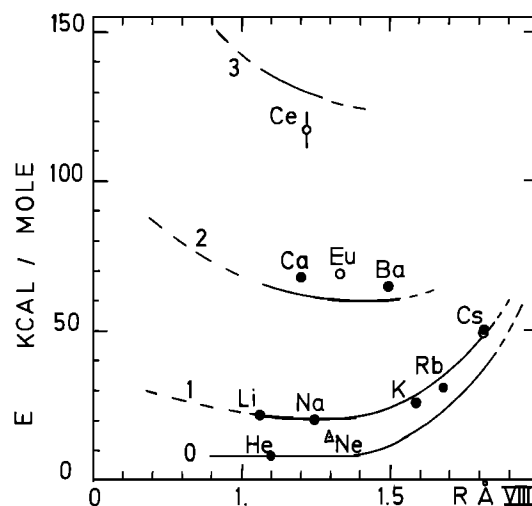


Fig. 6. Comparison between measured activation energy (OIS: solid circles; OVD: open circles) and prediction according to equation (13) (lines). Ne is from Reynolds [1960] in a tektite glass and He from Jambon and Shelby [1980] for both OIS and OVC.

species. Simultaneously, the activation energy and D_0 are decreased. The question now is, how can one explain these variations within the framework of the proposed model. The addition of water to the glass breaks bridging oxygen bonds into two OH units, and consequently, the binding energy between the SiO_4 units is drastically reduced. The jump from one position to the next will be much easier and the elastic component of the activation energy will therefore decrease. This is qualitatively observed for Cs and Na. For Cs, the activation energy decreases from 50 to 20 kcal/mol and for Na from 20 to about 16. In our model, the elastic energy for sodium is supposed to be zero; therefore if this variation is real it implies that the electric term is affected by the addition of water. Similarly, the activation energy for Ca decreases from 50 to about 25, which is far outside analytical errors. This confirms that both the elastic and electric components are affected by the addition of water. If the first contribution is readily understood, the latter is not as obvious. However, the experimental measurements of Hazen and Finger [1979] showed that there is a general relationship between bulk modulus, charge of cation, and size of cation-anion polyhedra; therefore any change in the bulk modulus is expected to be correlated to a cation-anion readjustment: changing the distance between a cation and its surrounding oxygens affects both elastic and electric contributions to the activation energy. Detailed calculation of the effect is not possible yet since the activation energies measured in hydrous melts are not very accurate and the small number of species analyzed so far do not permit an overall generalization.

Watson [1979b, 1981] suggests that the increase of diffusivity in hydrous melts is due to a greater number of potential sites, hence reducing the average jump distance for Cs. First, a decrease in D_0 and mean jump distance alone is expected to explain a decreased mobility, the

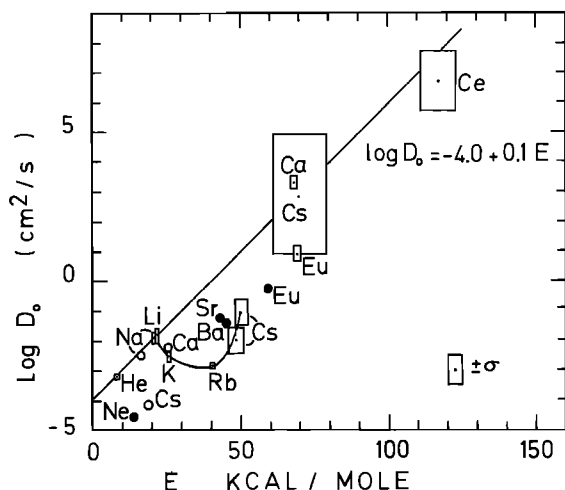


Fig. 7. Compensation plot for all species measured so far in obsidians. Li is from Jambon and Semet [1978]. Na, Ca, and Cs in hydrated obsidians (circles) are from Watson [1979b, 1980]; all others as previously mentioned; σ values are quoted for the present values and when available. The line is the visual best fit to He, Na, Ca, Ce. The alkalis in OIS are obviously not compensated (curved line).

opposite of what is actually observed. Since $D_0 \propto d^2$ (where d is the mean jump distance), the decrease of D_0 by a factor of 10^3 for Cs and 10 for Na should correspond to a decrease of d by factors of 30 and 3, respectively. For Na, Carron [1968] and P. Abélard (personal communication, 1981), using electrical conductivity data, showed that the mean jump distance accordingly yields 2 Å, which is less than one oxygen diameter. As for Cs, if the jump distance in dry obsidian is the same as for Na, then a reduction by a factor of 30 is untenable. Furthermore, we can consider the jump distance of Na as a lower bound for that of Cs in hydrous melt. Increasing this jump distance by a factor of 30 would bring activation energy to about 30 times that of sodium, i.e., several hundred kcal/mol. Therefore the variation of jump distance, if it exists, is certainly not the major source of variations in D_0 , and these variations do not explain the enhanced mobility.

The analogy of dry and hydrous obsidian compared with the solid and liquid state, respectively is also somewhat misleading. Usually, glass specialists put the difference between solid and liquid around the transformation temperature T_g . For obsidian (OIS) $T_g \approx 650^\circ\text{C}$ (A. Jambon, unpublished, 1980), which falls in the middle of the temperature range studied here. There is no indication of any variation in the diffusion mechanism at this temperature. Therefore, invoking a liquid-solid analogue to explain diffusion properties of these glasses is inadequate and will only obscure the interpretation of the diffusion mechanism.

5.4. Compensation Law for Obsidian

Winchell [1969] showed that the correlation between $\log D_0$ and E observed for many Arrhenian phenomena is also (approximately) valid in silicate melts and glasses. Before going into a

more detailed discussion, I want to emphasize that the correlation has to be very closely observed to retain any significance. If we consider an Arrhenius plot bounded by temperatures of 400° to 1700°C and diffusivities of 10^{-5} to 10^{-16} cm^2/s , it will contain all the diffusivities measured so far, essentially because of experimental feasibility. The transformation of all the lines that cross over this domain with negative slopes (i.e., positive activation energy) into a compensation plot, $\log D_0$ versus E , yields a truncated sector spreading along an apparent correlation line, with a half width of 47 kcal/mol at the mean value of 40 kcal/mol. When Winchell [1969] collected diffusion results from all kinds of silicates, including melts, glasses, and crystals of various compositions, he obtained a correlation for 134 points ($\sigma = 15$ kcal/mol); 99% of these points are expected to fall within $\pm 3\sigma$, i.e., ± 45 kcal/mol, comparable to the width of the domain previously calculated. The point is that it requires a very high correlation coefficient, or a small σ , for this correlation to have any physical significance. Such properties are observed when looking at some specific correlations, e.g., a series of glasses or a series of species in a single matrix [see Winchell and Norman, 1969; Jambon and Carron, 1978; Hart, 1981]. All the data for obsidians have been plotted in Figure 7, which deserves several comments. Even though some scatter is observed, the correlation is probably real. The second point is that species, with approximately similar radii, are 'well' correlated, the remaining scatter being of the same order as the analytical uncertainty. This effect of compensation is already clear on Figure 4, where He, Na, Ca, and Ce display Arrhenius lines fanning from a single point ($= 2000^\circ\text{C}$, 2×10^{-4} cm^2/s). This property is a corollary of the compensation law. For the species with $r = 1.2$ Å, the correlation line is approximately

$$\log D_0 = -4.0 + 0.1 E \quad (14)$$

with D_0 in cm^2/s and E in kcal/mol. It is not clear whether the data obtained for hydrous melts fall on that same line or not because of the very significant uncertainty on D_0 . All the larger species fall below the line, or in other words, for the same value of D_0 they have higher activation energy and lower diffusivity than if they were compensated according to (14). Now, looking more closely at the alkalis in dry obsidians (Figure 7), we can see that they are not compensated at all. This property is quite unfortunate because it precludes an accurate prediction by use of the compensation law. For instance, a value of $\log D_0 = -2$ corresponds to E ranging 20 to 50 kcal/mol, and this is not due to an uncertainty in the data. The feature observed here for alkalis is not an overall feature of silicate glasses, since Jambon and Carron [1978] showed that in a basaltic glass the correlation is excellent. The domain of application of the compensation law will probably remain unclear until much more reliable data become available.

The interpretation of the compensation law is not straightforward. Theories have been developed by Zener [1952], Lazarus [1955] and Rüttschi [1958], using both mechanical and quantum

mechanical formulations. In the case of melts or glasses, only classical formulations are feasible. From the present results, the compensation appears excellent for species with $r = 1.2 \text{ \AA}$. From section 5.3, it follows that for these particular species, the elastic component E_s is negligible, most of the activation energy stemming from the electrostatic component E_c , with the exception of He. Looking into Zener's [1950] theory of compensation is rather frustrating since it rests upon a formulation of the elastic energy of migration. It is possible somehow to overcome this difficulty; Hazen and Finger [1979] have shown that there exists a simple correlation between bulk modulus K_p , charge Z and anion-cation distance $(r + r_o)$. In oxides and silicates it yields

$$K_p (r + r_o)^3 = 7.5 Z \text{ Mbar } \text{\AA}^3 \quad (15)$$

When assuming that a similar law still holds in glasses and because of the simple relationship between bulk and shear modulus ($g \approx K_p/2$), we obtain for a series of cations with constant radius

$$g = \alpha Z \quad (16)$$

α being constant. This permits writing a new expression of E_c , while putting (16) into (13). It yields for cations with $r = 1.2 \text{ \AA}$:

$$E = \beta g^2 + 8 \quad (17)$$

where β , a function of the radius only, is therefore constant in the present case. Under these conditions it may be shown (see the appendix) that a compensation relation is expected under very reasonable assumptions for isoradius species:

$$\log D_o = A + B E \quad (18)$$

For smaller species, compensation could still hold because (17) remains still valid. The only species studied so far and corresponding to this case is Li, which is actually compensated. As long as no further confirmation from other species is available, this fit could be coincidental as well. For larger species, (17) cancels; there is an additional term of shear energy E_s which affects the compensation (see the appendix). The first coefficient A in the compensation equation (18) is decreased by the addition of a negative term. This corresponds qualitatively to the variations observed for the alkalis. The order of magnitude is correct too, but the exact value depends critically on the value of r_p in (9). It has been chosen more or less arbitrarily as 1.34 \AA . In addition to this we did not consider possible variations of the energy of formation of defects E_f with size. For the large cations it could be slightly different. Our conclusion is therefore that for cations with constant radius but different charge, and independently of the validity of the proposed theory, the compensation law is sufficiently well observed to be used as a predictive tool. For cations with radius of the order of 1.2 \AA and for smaller cations we predict that the compensation should be the same, whereas for larger cations the intercept should be decreased and the slope remain approximately

constant. If these predictions are correct, the approximate calculation of diffusivity becomes possible. Estimation of activation energy as explained in the previous section, combined with compensation effects, permits theoretically the calculation of both E and D_o of the Arrhenius equation. There remains, however, some doubt about the validity of the present theory for strongly covalently bonded species, like Si. Further experimental determination will permit testing the validity of the theory and increase the accuracy of the prediction. At this point we want to emphasize that only accurate determinations of Arrhenius parameters are useful in delineating the theory. More approximate determinations may be useful to obtain a good order of magnitude for petrological calculation, but such data cannot help the development of any predictive theory. At the present level of knowledge, the orders of magnitude of tracer diffusivities are quite well known. The next goal is to obtain more accurate data.

6. Conclusions

All previous considerations show that the diffusion process is controlled by short range order or local environment of the cation. Properties of the matrix on the other hand have little or no influence on transport phenomena. Even the number of defects or available sites is rather independent of the anionic framework, as is demonstrated by the continuity over the transformation range. This property may not hold for less silicic systems, since in that case, some discontinuities have been observed [see, e.g., Johnson et al., 1951; Jambon and Carron, 1978]. As a consequence, study of local environments of cations and their oxidation state will be of great interest to a better understanding of transport phenomena.

Diffusivity may also provide some insight into the structure of melts and glasses. If the jump distance for all cations is of the same order of magnitude, then the diffusivity could be a direct quantitative measurement of the stability of cations in oxygen polyhedra; it measures the number of jumps per unit time. Thus one finds that cations with high charge are very stabilized (e.g., Ce^{3+}) in contrast to cations with smaller size (Na^+ , K^+) or even rare gases. The diffusivity of Al and Si is not accurately known, but it is believed to be small in comparison with other cations. This corresponds qualitatively to the strong Si-O and Al-O bonds, a feature well known to geochemists. This way of using diffusivity permits a more elaborate classification than the traditional network-formers-modifiers. Both classifications agree with one another, of course, but there certainly exists a continuous variation from the very mobile modifiers to the strongly bonded formers, and intermediate elements should not be looked at as network freaks.

Appendix

We start from a general expression of the Arrhenius law:

$$D = D_o \exp - \frac{\Delta H_m + \Delta H_f}{RT} \quad (A1)$$

$$D_0 = a^2 \nu \exp \frac{\Delta S_m + \Delta S_f}{R} \quad (\text{A2})$$

where f and m refer to the formation of an empty site and to the migration of a cation into such a site. First, consider the thermodynamic relation:

$$\Delta S_m = - \frac{\partial \Delta G_m}{\partial T} = -\Delta G_m^0 \frac{\partial (\Delta G_m / \Delta G_m^0)}{\partial T} \quad (\text{A3})$$

where ΔG_m^0 is the free energy at zero temperature. Since the enthalpy of migration does not vary very much with temperature (constant activation energy), we can write as a good approximation:

$$\Delta G_m^0 = \Delta H_m^0 \approx \Delta H_m \quad (\text{A4})$$

From the relationship between shear modulus and migration energy, in the particular case when $r < r_D$,

$$\frac{\partial (\Delta G_m)}{\partial T} = \frac{\Delta (\beta g^2)}{\partial T} \approx 2 \beta g_0^2 \frac{\partial (g/g_0)}{\partial T} = 2 \Delta G_m^0 \frac{\partial (g/g_0)}{\partial T} \quad (\text{A5})$$

whence

$$\frac{\partial (\Delta G_m / \Delta G_m^0)}{\partial T} = 2 \frac{\partial (g/g_0)}{\partial T} \quad (\text{A6})$$

Putting (A6) and (A4) into (A3) yields

$$\Delta S_m = - 2 \Delta H_m \frac{\partial (g/g_0)}{\partial T} \quad (\text{A7})$$

In a conventional Arrhenius law, the activation energy E is given by

$$E = \Delta H_m + \Delta H_f \quad (\text{A8})$$

Since all the cations under consideration have the same size, we may assume that $\partial (g/g_0)/\partial T$, ΔS_f , and ΔH_f are the same. This seems reasonable because geochemists know that substitutions of cations are mainly governed by their size. Cations with similar radius are therefore thought to move through the same sites and therefore have similar values for the above parameters. Finally, after rearrangement we obtain

$$\left\{ \begin{array}{l} \log D_0 = A + B E \\ A = \log a^2 \nu + 0.434 \frac{\Delta S_f}{R} + \frac{0.869}{R} \Delta H_f \frac{\partial (g/g_0)}{\partial T} \\ B = - \frac{0.869}{R} \frac{\partial (g/g_0)}{\partial T} \end{array} \right. \quad (\text{A9})$$

The experimental results give the compensation equation

$$\log D_0 = - 4.0 + 0.1 E \quad (\text{A10})$$

From a comparison of (A10) and (A9) we obtain

$$\frac{\partial (g/g_0)}{\partial T} = - 2.3 \times 10^{-4} \text{ } ^\circ\text{K}^{-1} \quad (\text{A11})$$

This value comforts the assumption in (A5) that $g \approx g_0$ in regard to the accuracy of the present results. This value is also reasonable compared to what is known of the temperature dependence of shear modulus. Using (A8), we can also compute ΔH_f and ΔS_f :

$$\left\{ \begin{array}{l} \Delta S_f = - 6.2 \text{ cal } ^\circ\text{K}^{-1} \text{ mol}^{-1} \\ \Delta H_f = 8.0 \text{ kcal/mol} \end{array} \right. \quad (\text{A12})$$

Unfortunately, these quantities cannot be calculated independently so that there is no proof of the validity of the theory except that it affords no evident absurdity.

For other species with $r > r_D$, (A6) becomes

$$\Delta S_m = \frac{- 2 \Delta H_m}{\partial T} \frac{\partial (g/g_0)}{\partial T} + \alpha g_0 \frac{\partial (g/g_0)}{\partial T} \quad (\text{A13})$$

and the first term in the compensation equation becomes A':

$$A' = A - 6.4 (r - r_D)^2$$

For Cs the modification is $A - A' = 1.6$, whereas the observed variation is 2.4, surprisingly close to the predicted value.

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