Cation Dynamics and Diffusion in Lithium Orthosilicate: Two-Dimensional Lithium-6 NMR

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Many geological and technological processes depend on diffusion in crystalline silicates and oxides, but models of the dynamics of diffusion have only rarely been based on relatively direct microscopic information on the rates and energetics of the hopping of cations from site to site. Two-dimensional nuclear magnetic resonance (NMR) exchange spectra for lithium-6 in lithium orthosilicate (Li_4SiO_4) provided a detailed picture of the hopping rates of Li^+ ions among structurally distinct sites and helped to define the diffusion pathway. Rates and activation energies depended measurably on site geometry, and bulk electrical conductivity was accurately predicted.

The diffusion of cations in crystalline oxides and silicates controls a wide range of geochemical and technological processes, such as the homogenization of zoning profiles of crystals formed in magma chambers, the exsolution of immiscible phases during the cooling of materials formed at high temperature, and the intergrowth and adhesion that bond grains together to make useful ceramics. In most ionic conductors, which are of interest as solid-state electrolytes, cation diffusion controls electrical properties. Understanding of the mechanisms of diffusion has largely been based on theoretical treatment of macroscopic measurements of diffusion, conductivity, and NMR spin-lattice relaxation times. This has generally resulted in microscopic models that include parameters describing the frequency, direction, distance, and energetics of the hopping of cations from site to site. However, relatively direct observations of cation hopping dynamics have usually not been obtainable. In particular, in complex materials with multiple cation (and vacancy) sites, and thus multiple pathways for diffusion, it has been difficult to connect processes at the local and the bulk scale. For example, apparent activation energies for NMR spin-lattice relaxation are often much less than those observed for diffusion, in part because the former may sample local, within-site, as well as through-going, cation motion.

Stebbins *et al.* have recently reported one-dimensional (1D) ^6Li magic angle spinning (MAS) NMR spectra for lithium orthosilicate (Li_4SiO_4) in which the exchange of Li^+ ions among multiple sites was observed as a collapse of multiple peaks to a single averaged line (*1*). This ceramic material has been extensively studied as an ionic conductor and as a high Li refractory for fusion reactor blankets (*2–4*). Using a simple random walk model, we found that the average cation-exchange rate deduced from the NMR spectrum at 90°C was equal to that derived from extrapolation of higher temperature conductivity data. However, because the structure of Li_4SiO_4 is complex (*5, 6*), many questions have been raised about the details of cation hopping. All of the Li^+ ions could be involved in diffusion, or perhaps only a subset of cations in particular sites is important. A diffusion pathway characterized by a single activation energy could dominate, or perhaps multiple energetically distinct barriers need to be considered. The 2D, high-resolution, NMR exchange experiment is one of the few techniques that can provide details of exchange rates among multiple sites. This approach has been widely used to study dynamics in organic polymers (*7*) and in structured liquids, including molten halides (*8*) and silicates (*9*), but applications to crystalline inorganic materials have been very limited. In this report, we discuss how we have applied 2D NMR, as well as a more detailed analysis of 1D spectra, to cation motion in Li_4SiO_4, in order to explore some of these dynamical complexities.

Figure 1A shows 1D spectra collected at a series of temperatures (*1, 10*). At ambient and lower temperatures, these spectra show four partially resolved peaks corresponding to LiO_3, LiO_4, LiO_5, and LiO_6 polyhedra (*1, 11*). These peaks are motionally averaged at higher temperatures, requiring Li^+ hopping among all sites and not just local within-site motion or self-exchange. These spectra have been simulated with a simple four-site exchange model (Fig. 1B) similar to that used in a recent study of species exchange in a silicate liquid (*12*). The resulting average hopping rates are in good agreement with those expected from conductivity data (*13*), indicating that all Li^+ ions participate in conduction. However, the derived activation energy of 54 kJ/mol is somewhat lower than that for conductivity at 200° to 300°C (Table 1) (*3*). This difference might be due to differences in the actual hopping frequencies among different sites. At lower temperature, the difference in hopping frequencies is small and most exchange events contribute to the total peak shape. At higher temperature, hopping rates among some sites with higher activation energies are so fast that they have already been fully averaged to a single peak, which is thus no longer sensitive to temperature changes. In this case, the 1D peak shape simulation will underestimate the real hopping rate, leading to an apparent activation energy that is lower than the true mean value.

We observed 2D pure-absorption exchange spectra at 33° and 59°C and a range of mixing times (*14*). Typical data are shown in Fig. 2. In spectra of this type, if exchange is slow relative to the selected mixing time, the normal 1D spectrum appears on the diagonal and other peaks are absent. As exchange between any pair of sites becomes more rapid or mixing time becomes longer, cross peaks appear at the coordinates of the corresponding two peaks. The cross-peak intensities scale with the probability of exchange during the mixing period. We examined the potential complication of spin diffusion (as opposed to actual physical diffusion of cations) by varying the dilution of the ^6Li and thus the extent of homonuclear dipolar coupling. The similar cross-peak intensities for 20% and 95% ^6Li-enriched samples observed under the same experimental conditions clearly showed that spin diffusion was negligible. The large variation of the cross-

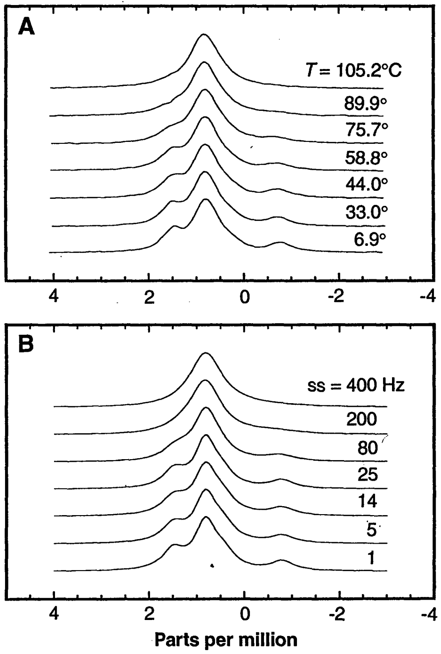

Fig. 1. (**A**) Series of 1D ^6Li MAS NMR spectra of Li_4SiO_4 acquired at the temperatures shown. (**B**) Simulated peak shapes, assuming exchange among four sites at a single mean exchange frequency (ss) as shown. Peaks correspond to Li in sites with a varying oxygen coordination number (see Fig. 2).

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peak intensity with temperature supports this conclusion.

The effect of exchange can be most clearly seen in 1D slices through the 2D spectra taken at the position of the LiO_6 peak (Fig. 3, A and B). All types of LiO_n polyhedra are involved with the exchange process at 33° and 59°C, and there is not a distinct population of nonexchanging Li^+ ions, as suggested previously (*15*). An exchange process among sites with the same coordination number ("self-exchange"), which will lead to broadening of the on-diagonal peaks with longer mixing times, seems to be negligible at the time scales and temperatures of our experiments.

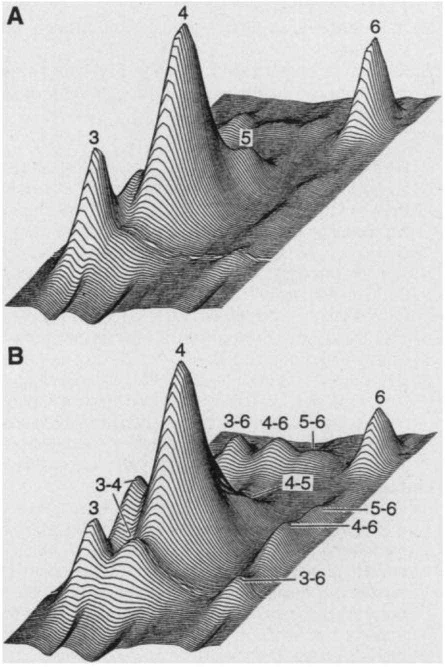

Fig. 2. Two-dimensional pure-absorption exchange NMR spectra of Li_4SiO_4 at 33°C with mixing times of (**A**) 47 ms and (**B**) 188 ms. Coordination numbers for Li sites, and exchange peaks (most clearly visible for the longer mixing time), are labeled. The ω_2 axis is horizontal.

We extracted the Li^+ hopping rates by fitting the areas of cross peaks in the 1D slices (I_{ij}) as a function of the mixing time (τ_m) with the equation

$$I_{ij} = M^0_j \exp(-K_{ij}\tau_m)$$

to derive the first-order rate constant for exchange from site j to i (K_{ij}) (*16*). Here, M^0_j is the intensity at $\tau \approx 0$ for site j. The requirement that $I_{ij} = I_{ji}$ is satisfied with an average deviation of 10%. The derived rate constants shown in Table 1 agree reasonably well with 1D simulation results and the extrapolation of conductivity data, if we again assume a random walk model and the participation of all cations in through-going diffusion (*13*). In materials in which there is an excess of lattice sites over conducting ions, such as in Li_4SiO_4, where 56 Li^+ ions are distributed among 126 sites, the concentration of vacancies is expected to be only very weakly temperature-dependent. Because the vacancies necessary for conduction are already present, in Li_4SiO_4 it is also likely that all, or at least a large fraction of, Li^+ ions contribute to the conductivity (*17*). Our NMR results support this suggestion. Activation energies were calculated from the effect of temperature on rates and are uncertain by about ±10%.

The most interesting result of these observations is that both hopping rates and activation energies are different for different pairs of Li^+ sites, giving direct evidence for a distribution of energy barriers for diffusion. Diffusion of Li^+ in Li_4SiO_4 probably involves the jump of a cation into a vacant site, then the jump of another ion into the newly emptied site. This suggestion is supported by the observation that in the Al-substituted phase $Li_{3.7}Al_{0.1}SiO_4$, where many extra vacancies are introduced, both the conductivity and the NMR-observed exchange frequency increase by about two orders of magnitude (*1*). Because we do not know the coordination number in temporarily occupied vacancies and there are multiple crystallographic sites for each LiO_n polyhedron type, we cannot yet work out the detailed diffusion pathways in Li_4SiO_4. However, any future modeling of diffusion in this material should take into account its real energetic complexities. In particular, the close agreement of the LiO_3-to-LiO_4 activation energy with that for conductivity allows the speculation that this kind of jump is a required step in conduction but that hops involving LiO_6, less frequent at higher temperatures, may be actually rate-limiting.

Because there is no face-sharing of LiO_n polyhedra in Li_4SiO_4, there has been speculation that edge-shared Li polyhedra might provide the easiest diffusion pathway and might have the lowest activation energy for

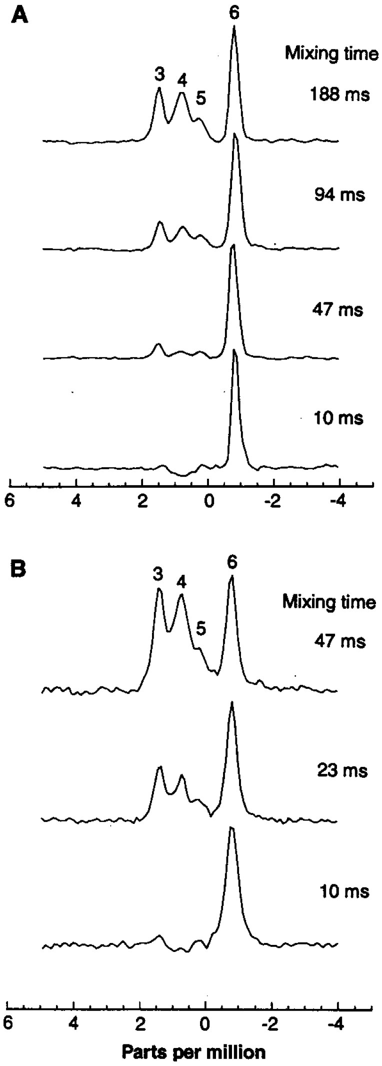

Fig. 3. Slices parallel to the ω_2 axis at the position of the LiO_6 diagonal peak in 2D exchange NMR spectra at (**A**) 33°C and (**B**) 59°C with different mixing times as indicated.

Table 1. Rates ($K_{n,n}$) (in hertz) and activation energies (E_a) of exchange among LiO_n sites in Li_4SiO_4. Rates derived from 2D NMR data, and from simulations of 1D peak shapes, are compared with those derived from measured conductivity, based on a simple random walk model (*13*). The latter are extrapolated from above 200°C with the high and low values of E_a shown, which bracket the range of experimental results (*15*). The weighted average for E_a from the 2D NMR data is 67 kJ/mol. The 1D NMR data were collected at all temperatures shown; 2D data were collected at 33° and 59°C only. We extrapolated other 2D values using the E_a values shown.

Data source	Temperature (°C)							E_a (kJ/mol)
	7	33	44	59	76	90	105	
2D exchange								
K_{3-6}	0.74	5.4	11.3	25.3	75	151	312	54
K_{4-6}	0.85	6.1	12.7	28.4	81	168	345	54
K_{5-6}	0.58	4.7	10.2	24.0	73	158	272	57
K_{4-3}	0.35	5.3	14.6	44.0	187	508	1372	74
1D exchange	1	5	14	25	80	200	400	54
Exchange from conductivity								
Low E_a	0.3	4.2	11.3	39	139	370	979	73
High E_a	0.1	1.1	3.4	13.6	57.8	175	527	82

hopping between them (5). The shortest Li–Li distances (as small as 0.23 nm) among edge-shared LiO_n polyhedra are between pairs with $n = 4,6$, $n = 3,6$, and $n = 4,5$. The 2D NMR results (Table 1) show that the first two of these pairs do in fact have relatively low activation energies. For the last pair, the exchange rate could not be determined by NMR because the peaks are strongly overlapping. For the $n = 3,4$ pair, the Li–Li distances average about 0.27 nm. It is thus not surprising that the activation energy for this exchange is the highest of those measured. The $n = 5,6$ activation energy is also relatively low, which does not seem to correspond well to the relatively long Li–Li distance for this pair (>0.27 nm). This discrepancy may be due to a relatively large error introduced in the cross-peak intensity measurement because of low intensities or to the inaccuracy of the Li^+ positions as determined by x-ray diffraction data. [The possibility of disorder of Li occupancy among some sites with LiO_6 and LiO_5 polyhedra has been suggested (6).] Other structural details also could have an important influence on the transition state during hopping and thus on the activation energy. Nonetheless, our 2D NMR data document the correlation between Li polyhedral linkage and the associated probability of Li^+ hopping among them.

In contrast to the results reported here, earlier NMR studies of ionic conductors have generally used low-resolution techniques and have relied on measurements of spin-lattice relaxation times (T_1) (2, 18, 19). These data can generally be collected over a much wider temperature range than can chemical exchange spectra but are sensitive to cation motion on many distance scales, not just diffusive motion from site to site. For comparison with previous work, ^7Li spin-lattice relaxation time (T_1) data were obtained for Li_4SiO_4 to 900°C (20) (Fig. 4). On a plot of $\ln(T_1)$ versus inverse temperature, the strong asymmetry of the slopes below and above the T_1 minimum is typical for fast ion conductors. The slope near ambient temperature (~19 kJ/mol) is much lower than that for conductivity (72 to 82 kJ/mol), again as is commonly observed. Although detailed interpretation of these data is complex and model-dependent, the general explanation for the low slope is that low-energy, local cation motion, which does not contribute to through-going diffusion and conductivity, is being sampled. These dynamics could include low-frequency vibrations, hopping between local energy minima within an over-sized coordination polyhedron, or even unsuccessful attempts at jumping to a new site.

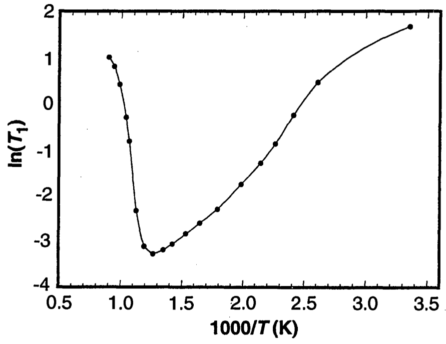

Fig. 4. Plot of $\ln(T_1)$ of ^7Li versus inverse temperature for Li_4SiO_4.

Over limited temperature ranges and in samples that have clearly resolvable, multiple peaks in high-resolution NMR, direct measurements of site-exchange frequencies can make an important contribution to understanding microscopic mechanisms of cation diffusion. Two-dimensional exchange spectroscopy can provide much greater detail and can sample much lower exchange rates than can approximations based on 1D data (1, 21). The ability to sample rates and energetics independently for different sites, or for at least different types of sites, and to link such results with structure has great potential for the design and control of the transport properties of a variety of materials.

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10. Several samples of Li_4SiO_4 with various $^6Li/^7Li$ ratios were synthesized as described in (*1, 11*) and were characterized by powder x-ray diffraction and ^{29}Si NMR. Minor proportions of other lithium silicates (mainly Li_2SiO_3) were found in some samples but do not influence the data reported here. All samples were dried at 800° to 900°C before NMR experiments and were loaded into MAS rotors in an N_2-filled dry bag. This step was important because absorption of water was found to decrease Li^+ hopping frequencies by a factor of 3 to 4 and to increase T_1 by about 40%. High-resolution NMR data were collected with a modified Varian VXR 400S spectrometer at 58.8 MHz for ^6Li, and we used a Varian variable-temperature MAS NMR probe with a rotor 7 mm in diameter. Sample spinning rates were about 5 kHz. Spin-lattice relaxation times measured near ambient temperature with the saturation-recovery technique were about 30 to 60 s; delay times between radio frequency (rf) pulses for 1D experiments were chosen to be comparable to T_1, and pulse lengths of 2 μs (rf tip angle of about 30°) were used. We calibrated the temperature by using the relation between the ^{207}Pb chemical shift in $PbNO_3$; this calibration is believed to be accurate to about ±1°C, although the calibration depended strongly on spinning rate (A. Bielecki and D. P. Burum, paper presented at 36th Rocky Mountain Conference on Analytical Chemistry, Denver, CO, 29 July 1994). Uncertainties in the average exchange frequencies derived by 1D peak shape simulations were about ±20%.
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$$1/\tau = 6k_BT\sigma/(cfpe^2d^2)$$
Here, k_B is Boltzmann's constant, T is absolute temperature, e is the charge on the electron, c is the concentration of the conducting cation, and d is the average hop distance (*19*). The fraction of ions participating in conduction, p, is taken as 1, as discussed in the text. The correlation factor, f, is also set equal to 1 because of the large number of available Li ions and vacancies [P. G. Shewmon, *Diffusion in Solids* (McGraw-Hill, New York, 1963)]. In a structure with a large number of empty sites or intrinsic vacancies (such as Li_4SiO_4) as well as significant site disorder, the probability of a return hop to the original site may be no higher than that of a hop to a new site, resulting in $f = 1$. This approximation is supported by the agreement of conductivity and NMR results in this study but must be tested more exactly in studies of other materials.
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22. Supported by NSF grant EAR 9204458. We thank three anonymous reviewers for insightful comments on the original draft.

29 June 1995; accepted 19 September 1995