Magnesium and Calcium Aluminate Liquids: In Situ High-Temperature ^{27}Al NMR Spectroscopy

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The use of high-temperature nuclear magnetic resonance (NMR) spectroscopy provides a means of investigating the structure of refractory aluminate liquids at temperatures up to 2500 K. Time-averaged structural information indicates that the average aluminum coordination for magnesium aluminate ($MgAl_2O_4$) liquid is slightly greater than for calcium aluminate ($CaAl_2O_4$) liquid and that in both liquids it is close to four. Ion dynamics simulations for these liquids suggest the presence of four-, five-, and six-coordinated aluminate species, in agreement with NMR experiments on fast-quenched glasses. These species undergo rapid chemical exchange in the high-temperature liquids, which is evidenced by a single Lorentzian NMR line.

Refractory oxide liquids help form a wide range of technologically important materials. They also form the primary constituents of natural magmas. Knowledge of the structures and dynamic processes that occur in these high-temperature liquids on an atomic scale is necessary for an understanding of their physical properties and also of their vitrification and crystallization behavior. Most structural models for such high-temperature liquids are inferred from known crystal structures or are extrapolated from the results of experiments on glasses. However, as more structural information on the liquids has become available from recent spectroscopic experiments, these approaches seem to have limited validity, and it has become increasingly obvious that it is necessary to study the structures of liquids directly (*1*).

Calcium and magnesium aluminates form two important series of refractory oxides. The structure of crystalline $CaAl_2O_4$ is related to that of the SiO_2 polymorph tridymite, with Ca^{2+} ions occupying cavities within a fully polymerized network of AlO_4 tetrahedra (*2*). Earlier spectroscopic studies have indicated that $CaAl_2O_4$ glass has a similar structure (*3*), and this observation may be extrapolated to the melt as a first approximation. In contrast, $MgAl_2O_4$ does not vitrify, and so its liquid must be studied directly.

We used ^{27}Al nuclear magnetic resonance (NMR) spectroscopy to investigate the Al environment in $MgAl_2O_4$ and $CaAl_2O_4$ liquids at temperatures up to approximately 2500 K. We used a recently developed NMR technique (*4*) that involves laser-heating a sample in aerodynamic levitation within the bore of the NMR magnet. Using Born-Mayer pair potentials, we also carried out ion dynamics simulations of these two liquids at temperatures comparable to those of the NMR experiment (*5*) in order to understand the short-range structural characteristics of the liquids (*6*) (in particular the aluminum coordination distribution) and to help interpret the NMR results. The isotropic chemical shifts obtained from the NMR experiments provide information on the averaged Al environment in the liquids and are especially sensitive to the nearest neighbor coordination number.

At approximately 2500 K, the ^{27}Al NMR spectrum for each of the two liquids (Fig. 1) consists of a single, narrow (full width at half maximum = 100 to 200 Hz) Lorentzian-shaped line. From earlier NMR experiments and vibrational spectroscopic measurements on rapidly quenched glasses and ion dynamics simulations on aluminate liquids, we know that multiple Al sites (four-, five-, and six-coordinate, noted as ^{IV}Al, ^{V}Al, and ^{VI}Al, respectively) are present in these liquids (*1*, *6*, *7*). The observation of a single line in the liquid NMR experiments indicates that these species are averaged by rapid chemical exchange at a rate faster than that defined by their separation in chemical shift (greater than 5 kHz) (*8*). In addition, ^{27}Al NMR lines in solids are split and broadened asymmetrically by first- and second-order quadrupolar interactions whose energy is determined by the value of the quadrupole frequency (ν_Q) (1 to 10 MHz in solids). The observation of a single Lorentzian line indicates that motional averaging in the liquids is occurring faster than this rate. In this case, the averaging could occur by chemical exchange or by reorientation of molecular aluminate groups in the liquid or by both (*7*).

The observed peak maxima correspond to the average chemical shifts of Al in the liquid: 76 ppm and 69 ppm for $CaAl_2O_4$ and $MgAl_2O_4$, respectively (*9*). These chemical shifts can be compared to the isotropic chemical shifts determined by ^{27}Al magic angle spinning (MAS) NMR spectroscopy for Al in different coordination environments in the crystalline and glassy phases (*10*). For $CaAl_2O_4$, both the crystal and glass (Fig. 1, C and D) show a single peak flanked by spinning side bands. The crystalline phase contains six different aluminum sites, which are all four-coordinate sites with similar Al–O distances. These give rise to a single, unresolved NMR peak (*11*). Isotropic chemical shifts for these sites range from 80 to 83 ppm in the crystal and 83 ppm for the glass, which are typical values for fourfold-coordinated

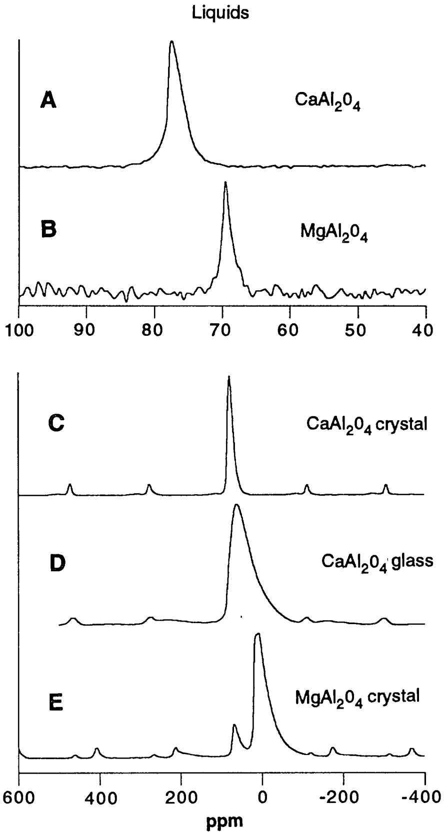

Fig. 1. High-temperature ^{27}Al NMR spectra of (**A**) $CaAl_2O_4$ liquid and (**B**) $MgAl_2O_4$ liquid. A total of 64 free induction decays (FIDs) were accumulated per sample with a $\pi/6$ flip angle, a 0.5-s recycle time, and a spectral width of 125 kHz. (**C** through **E**) ^{27}Al MAS NMR spectra of crystalline $CaAl_2O_4$ (C), glassy $CaAl_2O_4$ (D), and crystalline $MgAl_2O_4$ spinel (E) obtained at room temperature with a MAS probe at a spin rate of 15 kHz. A large sweep width (1 to 2 MHz), small pulse angle, and 1- to 2-s recycle times were used. All spectra were obtained on a Bruker MSL300 spectrometer (Karlsrühe, Germany) [external magnetic field strength (H_o) = 7.4 T; Larmor frequency (ν_L) = 78.21 MHz for ^{27}Al]. Chemical shifts are in parts per million and referenced to $Al(NO_3)_3/HNO_3$.

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Table 1. Ion dynamics simulation results for $MgAl_2O_4$ and $CaAl_2O_4$ liquids at 3000 K showing the proportions of four-, five-, and six-coordinate aluminum species. These three species account for more than 99% of all Al species for both liquids (small amounts of three- and seven-coordinate Al were observed). The average Al coordination corresponds to a weighted sum of the three major species.

Liquid	Species (%)			Average Al coordination
	^{IV}Al	^{V}Al	^{VI}Al	
$MgAl_2O_4$	40.44	49.31	9.74	4.67
$CaAl_2O_4$	57.60	38.30	3.67	4.44

Al atoms. The similarity between these values and that measured for $CaAl_2O_4$ liquid suggests that the average Al coordination in $CaAl_2O_4$ liquid is close to four.

In contrast, the NMR spectrum of the $MgAl_2O_4$ spinel phase exhibits two Al resonances associated with different coordination environments: a strong peak at 14 ppm due to ^{VI}Al and a smaller peak at 70 ppm due to ^{IV}Al (Fig. 1E). The occurrence of the two peaks indicates that the crystal has a small amount of inverse spinel structure (*12*). The isotropic chemical shift observed for the $MgAl_2O_4$ liquid is closer to that of the tetrahedral site in the spinel phase, and this result implies that the average Al coordination number in the liquid is lower than in the crystal. This observation is generally consistent with the notion that the Al site distribution in the crystal changes as a function of temperature. Earlier ^{27}Al MAS NMR studies of $MgAl_2O_4$ spinels have shown that the tetrahedral Al site (inverse spinel) is more abundant at higher temperatures (*12*).

Results from our ion dynamics simulations for the two liquids at 3000 K (Table 1) show that the calculated average Al coordination number for $MgAl_2O_4$ liquid was 4.67; this number was 4.44 for $CaAl_2O_4$ liquid (*13*). The larger average Al coordination number calculated for $MgAl_2O_4$ liquid was qualitatively consistent with the more shielded isotropic chemical shift observed from the high-temperature NMR experiment (*14*).

The ion dynamics simulations also provided information about the distribution of Al sites in the liquids (Table 1). This cannot be obtained from the high-temperature NMR data because of the rapid chemical exchange between these species. The simulations indicate that significant amounts of four- and five-coordinated Al are present in both $CaAl_2O_4$ and $MgAl_2O_4$ liquids at a given temperature. However, the $^{IV}Al/^{V}Al$ ratios were very different for the two liquids: 1.51 for $CaAl_2O_4$ and 0.82 for $MgAl_2O_4$ at 3000 K. The simulations also indicate that both liquids contained relatively small amounts of six-coordinated Al (10 atomic percent ^{VI}Al in $MgAl_2O_4$ and 4 atomic percent in $CaAl_2O_4$) and that only negligible amounts (less that 0.1%) of oxygen are not bound to aluminum.

Recent ^{29}Si NMR studies on silicate glasses have shown the presence of ^{V}Si (*15, 16*). The abundance of this species increases with a faster quench rate or higher fictive temperature, and it has been proposed that this species acts as an intermediate during the process of viscous flow in silicate melts by chemical exchange (of O^{2-}) between different silicate polymer species (*16, 17*). The function of ^{V}Al in aluminate liquids could be similar (*7*). Comparison of solid-state ^{27}Al NMR spectra of $CaAl_2O_4$ glasses quenched at different rates shows a greater abundance of ^{V}Al in the faster quenched glasses (*18*).

Our results demonstrate that high-temperature NMR studies combined with ion dynamics simulations provide a powerful tool for the elucidation of the structural properties of refractory oxide liquids. Our observations indicate that substitution of Mg^{2+} for Ca^{2+} in aluminate liquids causes an increase in the average coordination number of Al. A simple explanation for this can be provided by a consideration of the difference in size of the two metal cations. Ca^{2+} is larger and can accommodate a greater number of oxygen anions than can Mg^{2+}. If the coordination of $(M^{2+} + Al^{3+})$ around oxygen is essentially the same for the two liquids (*19*), then the average coordination of oxygen about aluminum must be greater in the $MgAl_2O_4$ liquid. Such effects will be important in the determination of the coordination behavior of Al^{3+} and other network-forming cations in natural magmas and glass-forming batches.

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5. The ion dynamics simulations were performed on systems of 300 to 350 particles at 3000 K to ensure that the systems exhibited liquid-like behavior (the melting point of $MgAl_2O_4$ is 2398 K) and to keep computing times within practical limits Equilibration times were 8000 timesteps (1 timestep = 2.0×10^{-15} s). As a result of the simulations being run at constant volume rather than constant pressure, simulation pressures fluctuated on the order of ± 0.6 GPa over the course of each run. Run densities for each liquid at 3000 K were constrained by extrapolation of existing experimental data (partial molar volumes) obtained at lower temperatures and by the maintenance of simulation pressures in the range of −1 to 1 GPa [E. F Riebling, *Can. J. Chem.* **42**, 2811 (1964), R A. Lange and I. S. E. Carmichael, *Geochim. Cosmochim. Acta* **51**, 2931 (1987)].
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8. In solids, ^{27}Al chemical shifts for the AlO_4, AlO_5, and AlO_6 groups fall in characteristic frequency ranges that are separated by 20 to 40 ppm (on the order of a few kilohertz in the magnetic field used in this study) In a liquid that consists of aluminate polyhedra with various nearest neighbor coordination numbers, chemical exchange between these species must occur at rates faster than their difference in frequency in order for a single line in the NMR spectra to be observed.
9. Because of fast motional averaging in the liquids, chemical shifts are isotropic and hence represent the average chemical shift for Al in the liquid
10. In MAS NMR experiments with solids, isotropic chemical shifts for quadrupolar nuclei such as ^{27}Al are determined from the position of the center of gravity of the central transition and the positions of the spinning side bands of the (±1/2 to ±3/2) external transitions. These spinning side bands were observed in the spectra of the solid phases in Fig. 1 [D. Massiot, C. Bessada, J. P. Coutures, F. Taulelle, *J. Magn. Reson.* **90**, 231 (1990)]
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13. We determined coordination numbers of oxygen about aluminum by counting all oxygen atoms within a radial cutoff distance for each Al atom at each timestep in the simulation. These data were accumulated over a period of 500 consecutive timesteps Cutoff distances were chosen to correspond with the first minimum following the first peak in the calculated Al–O pair distribution function of each liquid. Average Al coordination numbers for both $CaAl_2O_4$ and $MgAl_2O_4$ (normal spinel) crystals remained unchanged (four and six, respectively) if we used these cutoffs assuming the effects of thermal expansion are negligible.
14. Results from the ion dynamics simulations are qualitatively consistent with the high-temperature NMR results in that $MgAl_2O_4$ liquid, with a lower chemical shift value than $CaAl_2O_4$ liquid (69 versus 76 ppm), has a higher average Al coordination number. Quantitatively, if we assume that the isotropic chemical shift value for a tetrahedral AlO_4 group is approximately 80 ppm and that for an octahedral AlO_6 group is 10 ppm (*11*) [R. J. Kirkpatrick, in *Spectroscopic Methods in Mineralogy and Geology*, F. C. Hawthorne, Ed. (Mineralogical Society of America, Washington, DC, 1988), chap. 9], then a chemical shift difference of 7 ppm represents an average Al coordination number difference of 0.2 This is close to the difference in average Al coordination between the two liquids obtained from the simulations. It has been shown previously that ^{27}Al isotropic chemical shifts are temperature-dependent (*20*), and actual chemical shifts for ^{IV}Al, ^{V}Al, and ^{VI}Al species are not known at the temperatures of these melts The

average Al coordination numbers predicted with solid-state NMR chemical shift correlations with Al coordination number are 4.31 and 4 11 for $MgAl_2O_4$ and $CaAl_2O_4$, respectively

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19 The average coordination number of oxygen is 4 00 in $MgAl_2O_4$ spinel and 3.75 in crystalline $CaAl_2O_4$ (*2*).
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Noble Gas Partitioning Between Metal and Silicate Under High Pressures

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Measurements of noble gas (helium, neon, argon, krypton, and xenon) partitioning between silicate melt and iron melt under pressures up to 100 kilobars indicate that the partition coefficients are much less than unity and that they decrease systematically with increasing pressure. The results suggest that the Earth's core contains only negligible amounts of noble gases if core separation took place under equilibrium conditions.

The Earth's mantle, at least the upper mantle, has undergone extensive degassing during the early history of the Earth. Mantle degassing models based on the comparison of $^{40}Ar/^{36}Ar$ isotopic ratios between the mantle and the atmosphere strongly suggest that the degassing of the upper mantle was very extensive; that is, more than 80% of the primordial volatiles have been degassed (*1*). In view of this extensive degassing, it is puzzling that primordial ^{3}He and ^{20}Ne are still degassing from the Earth's interior (*2*, *3*). In particular, helium has such a high diffusivity that one would assume that this element has almost completely degassed. Davies (*4*) therefore suggested that the primordial helium is retained in the core and has been escaping slowly. The crucial assumption in this suggestion is that helium was partitioned preferentially into the iron core rather than into silicates (the mantle) under high pressure. Stevenson (*5*) also suggested that the apparent depletion of xenon in the terrestrial atmosphere might have been caused by the preferential incorporation of this element into the metallic core. To evaluate these predictions, we measured the noble gas (He, Ne, Ar, Kr, and Xe) partitioning between iron and silicates under high pressures.

Our experiments were carried out on a mixture of basalt powder (48.7% SiO_2, 2.1% TiO_2, 16.3% Al_2O_3, 12.1% Fe_2O_3, 0.2% MnO, 5.9% MgO, 9.3% CaO, 4.0% Na_2O, 0.9% K_2O, and 0.5% P_2O_5) and Fe powder (commercial reagent with a purity of 95%, grain size <150 μm) in a ratio of about 1:3 by weight. Basalt powder, chosen because of its low melting temperature compared to that of peridotite, was ground in an agate mortar and was estimated to have a grain size of <100 μm. The basalt-iron mixture was put into a small capsule and subjected to high pressures. The porosities of the starting material were 30 to 40%. We used three types of high-pressure presses: a piston press at Kobe University (5 and 20 kbar), a cubic anvil press at Osaka University (60 kbar), and a uniaxial split-sphere press at Okayama University (100 kbar). For the 5- and 20-kbar experiments, the samples were directly loaded into a cylindrical graphite heater (0.14 cm^3) and were heated at 1600°C for 3 hours after high pressures had been attained. For the 60- and 100-kbar experiments, the samples were put into a boron nitride tube (about 0.03 cm^3), which was set in a graphite (60 kbar) or a rhenium (100 kbar) heater. For the 60-kbar measurements, the samples were held at 1600°C for 40 min after the highest pressure (60 kbar) had been attained. In the 100-kbar experiments, pressure and temperature were raised simultaneously (to a pressure above ~70 kbar), but the heater broke when the highest temperature and pressure were attained. In all cases, we were able to quench the samples from the highest temperature by turning off the heater, and then the pressure was slowly reduced to zero. All samples showed a clear segregation of a metallic phase from

Table 1. Noble gas concentrations in metal and silicate glass as measured in distribution experiments under high pressures. The noble gas concentration was analyzed with a static mass spectrometer. The reproducibility in the analysis was less than 10% in most cases. The procedural blank levels were as follows: $^{4}He = (3.0 \text{ to } 6.3) \times 10^{-11}$ cm^3 STP (standard temperature and pressure), $^{20}Ne = (0.83 \text{ to } 5.0) \times 10^{-12}$ cm^3 STP, $^{36}Ar = (0.76 \text{ to } 2.4) \times 10^{-12}$ cm^3 STP, $^{84}Kr = (1.2 \text{ to } 7.9) \times 10^{-13}$ cm^3 STP, and $^{132}Xe = (0.64 \text{ to } 6.6) \times 10^{-14}$ cm^3 STP. The blank correction was applied to the data. The data are in parentheses when the blank corrections were 20 to 90%, for which cases the concentrations have errors of up to a factor of 2 when we take blank variation into account. If blank corrections were more than 90%, upper limits are shown without blank correction. M, metal samples; G, silicate glass sample; ST, starting material.

Pressure and time	Sample	Sample weight (mg)	^{4}He	^{20}Ne	^{36}Ar	^{84}Kr	^{132}Xe
			($\times 10^{-8}$ cm^3 STP/g)			($\times 10^{-10}$ cm^3 STP/g)	
ST	Fe powder	1718.01	(0.0639)	0.0583	0.196	0.777	0.130
ST	ER-24	563.86	3.89	0.0467	0.245	1.51	0.355
5 kbar, 180 min	DIS8M	187.62	(0.260)	(0.162)	0.44	0.979	(0.0513)
	DIS8G	5.80	(6.43)	(1.81)	3.04	10.5	(1.57)
20 kbar, 180 min	DIS5M	119.95	(0.149)	(0.0699)	0.249	0.956	(0.125)
	DIS5G	3.04	(10.4)	(4.17)	8.69	48.2	15.1
60 kbar, 40 min	DIS11M	117.70	(0.567)	0.828	1.58	3.45	0.158
	DIS11G	4.80	529	781	1250	2720	82.6
100 kbar, <1 min	DIS12M	13.74	<16.5	(0.214)	(0.411)	(0.606)	<0.219
	DIS12G	2.12	(160)	624	1050	2090	50.5

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