Constraints on aluminum and scandium substitution mechanisms in forsterite, periclase, and larnite: High resolution NMR

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ABSTRACT

The incorporation of incompatible Al in forsterite is particularly interesting due to its relevance in Al olivine-spinel geobarometry techniques as well as the proposed influence of Al on upper mantle diffusion and water storage capacity. However, determining the site preference and substitution mechanisms of aluminum in forsterite presents considerable challenge, as the incompatibility of Al in the olivine structure results in correspondingly low Al concentrations which are challenging to study. In this work we use solid state Nuclear Magnetic Resonance (NMR) to directly observe Al coordination in synthetic samples from which we can constrain site preferences. We investigate Al in MgO and clinoenstatite to confirm that the forsterite spectra do not contain contributions from these impurity phases. To better interpret our results we used the Independent Component Analysis (ICA) algorithm, SIMPLISMA, which accurately deconvoluted complex NMR line shapes, separating spectral components from known impurities and enabling the identification of unknown spectral components which in some cases we can assign to substituting Al. We additional investigate Al in larnite, which has a tetrahedral environment similar to that of forsterite and which presents an additional ICA test case, and investigate Sc in forsterite and periclase to add additionally context to our Al observations. Our $^{27}$Al and $^{45}$Sc MAS NMR spectra place additional constraints on the site preferences of Al in synthetic forsterite, clinoenstatite, periclase, and larnite as well as Sc in forsterite and periclase.
In forsterite, we identified Al in the tetrahedral site and at least three distinct octahedral environments. The overall ratio of contents of AlO$_4$ to AlO$_6$ is about 1:3; the excess of the latter suggesting that at least two substitution mechanisms are necessary for Al$^{3+}$ incorporation in forsterite. In some cases the estimated species abundance for observed features are as low as 70 μg/g Al$^{3+}$, but were readily detected by NMR. Also in forsterite, we identified Sc in a single MgO$_6$ environment. In larnite (also known as belite or C$_2$S in cement chemist notation), a single, ordered tetrahedral Al species is detected. In enstatite samples, primarily composed of clinoenstatite, $^{27}$Al NMR spectra look very similar to previous observations of orthoenstatite, likely indicating a similar coupled AlO$_6$ and AlO$_4$ substitution. In periclase, Al is observed in an undistorted MgO$_6$ site with cubic or nearly cubic point symmetry, in addition to a lower symmetry, six-coordinated site. This work provides new insight into incompatible element substitutions mechanism in minerals, in forsterite’s case indicating complex behavior involving multiple species despite compositional simplicity.

**Keywords**: Forsterite, periclase, enstatite, larnite, belite, independent component analysis, nuclear magnetic resonance, trace elements, SIMPLISMA

**INTRODUCTION**

Aluminum is an abundant element in Earth’s mantle, but scarce in olivine, a major mineral component of the upper mantle and a common phase in mafic rocks. Despite aluminum’s low concentrations in olivine (typically less than 400 μg/g), the incorporation of incompatible Al$^{3+}$ into olivine has drawn considerable interest due to its relevance to a geobarometry technique (where Al$^{3+}$ concentrations in olivine and spinel are used to predict the equilibration pressure) (Wan et al. 2008; Coogan et al. 2014), its proposed role in creating diffusion pathways for small ions, and its potential to generate sites that could accommodate water in the upper mantle (Berry et al. 2007; Zhang and Wright 2012).

In forsterite (Mg$_2$SiO$_4$), the magnesium rich end member of olivine, the preferred lattice site of incorporated Al$^{3+}$ is not obvious. The ionic radius of Al$^{3+}$ (39 to 53 pm) and its charge are between those of tetrahedral Si$^{4+}$ (26 pm) and octahedral Mg$^{2+}$ (72 pm)
(Shannon and Prewitt 1969). Due in part to this mismatch, the solubility of Al\(^{3+}\) in forsterite is limited, with experimental work indicating a practical solid solution around 500 μg/g at temperatures between 1475 and 1390 °C (Grant and Wood 2010). This low concentration limits the usefulness of diffraction methods to determine structural effects, and can pose challenges of sensitivity for spectroscopic approaches. Many prior studies of aluminum in forsterite have involved multi-dopant systems, and suggest a wide variety of Al\(^{3+}\) incorporation mechanisms that are likely influenced by the presence or absence of additional elements (Bershov et al. 1983; Purton et al. 1997; Berry et al. 2007; Evans et al. 2008; Neuville et al. 2009; Zhang and Wright 2010). For example, Electron Paramagnetic Resonance (EPR) measurements indicate charge balancing pairs of Cr\(^{3+}\) and Al\(^{3+}\), with the latter on the Si site (Bershov et al. 1983). From compositional measurements, Al\(^{3+}\) was suspected to occupy both Si and M sites (Evans et al. 2008), and later thought to be principally incorporated by disassociated charge balancing Si and M site substitutions (Grant and Wood 2010). Computational atomistic simulations referenced to previous vibrational spectroscopy have indicated that the site preference for Al\(^{3+}\) is sensitive to both pressure and the charge balance mechanism, and can involve both Si and M sites (Berry et al. 2007; Zhang and Wright 2010).

To investigate this question, we apply solid state nuclear magnetic resonance to otherwise pure forsterite samples with trace Al\(^{3+}\). Solid state NMR can have excellent sensitivity, is selective to specific nuclides, and is capable of distinguishing coordination, nearest and next nearest neighbors, deviations in symmetry, and/or changes in localized charges, for favorable nuclides at concentrations as low as 0.01 to 0.1% (on an atomic basis) (MacKenzie and Smith 2001; Stebbins and Xue 2014). At high Al concentrations, \(^{27}\)Al NMR can distinguish distinct Al octahedral sites with various Al or Si second neighbors as well as detecting distorted and or disordered tetrahedral sites, as demonstrated recently on Ca-Tschermak clinopyroxene, in which Al occupies a variety of sites, as is likely in forsterite (Flemming et al. 2015). Although requiring longer experimental acquisitions, NMR’s capabilities persist at concentrations at or below 5 wt% Al\(_2\)O\(_3\), as demonstrated by work that concluded that Al substitutes into orthoenstatite via a Tschermak mechanism (Kohn et al. 2005).
Experimental challenges

Investigating an “incompatible” cation, such as Al\(^{3+}\), by a bulk spectroscopic method such as NMR can present a considerable challenge, in that Al\(^{3+}\) preferentially partitions into other phases, which can mask detection of low concentrations of Al\(^{3+}\) in the phase of interest. Equilibrating samples at high temperatures increases solubility, the rate of diffusion, and decreases the time necessary to reach equilibrium, and thus is advantageous. However, even when syntheses are carried out well below the minimum melting temperature of the bulk system, trace impurities can induce localized melting. If present, impurity phases, such as pyroxene or melt, can preferentially incorporate Al\(^{3+}\), and only a small proportion of an Al\(^{3+}\) rich phase is necessary to overwhelm the spectra.

Despite the challenges of detecting low amounts of impurity phases, careful characterization with Electron Probe MicroAnalysis (EPMA), X-ray mapping, and \(^{29}\)Si NMR, is useful to confirm sample quality, and to select materials for detailed investigation by \(^{27}\)Al NMR. The low Al\(^{3+}\) concentrations in olivine can require lengthy NMR acquisitions, sometimes lasting 2-4 days.

Additional minerals investigated

We investigated Al containing periclase (MgO), because we intentionally added excess MgO in our forsterite syntheses to prevent the formation of enstatite. Since enstatite is known to incorporate low concentrations of Al, we also investigated Al containing enstatite (MgSiO\(_3\)), enabling a direct comparison, and ruling out the possibility of mistakenly assigning enstatite peaks as forsterite peaks.

To better understand the context of the resulting spectra of Al-containing forsterite we also investigated similar systems. Al\(^{3+}\) in larnite (Ca\(_2\)SiO\(_4\)) was examined as a system where Al occupies only tetrahedral sites. Similar to forsterite, larnite tetrahedra are isolated from each other, linked only by divalent cations. Additionally, the maximum concentration of Al in larnite is known to be much higher than that in forsterite, providing an additional and higher concentration setting to more clearly demonstrate the effectiveness of the SIMPLISMA algorithm discussed below. Lastly, we investigated Sc\(^{3+}\) in forsterite and MgO. The charge of Sc is identical to that of Al, however the larger
ionic radius of Sc (octahedral Sc$^{3+}$, 73 pm) limits it to octahedral sites (Shannon and Prewitt 1969).

**METHODS**

**Sample syntheses**

Unless otherwise noted, samples were synthesized by hand milling oxide powders in isopropyl alcohol in an agate mortar, pressing dried material into a pellet, and heating the material with intermittent additional milling and pellet pressing. All samples were heated in platinum crucibles in air. Although equilibrium in a strict thermodynamic sense is difficult to demonstrate in these types of experiments, we did confirm in most cases that heating times were sufficient so that no further changes in Al speciation were detectable, i.e. at least a steady state was obtained. With forsterite and periclase, we found that the same Al speciation was reached, starting with Al in different initial phases such as gibbsite, corundum, or spinel. Given the long, high temperature annealing times, we assume that H$_2$O (and H$^+$) contents of the silicate phases are negligible in comparison to Al concentrations. Minor, post-synthesis water or CO$_2$ absorption in MgO or CaO would not be expected to affect the results reported here. For the most informative samples whose spectra are described here, synthesis conditions and nominal compositions are given in Table 1.

**Al$^{3+}$ doped forsterite.** Al$^{3+}$ doped forsterite was synthesized using various reagents, with 1-3 wt% excess MgO to reduce the chance of formation of enstatite. We mixed SiO$_2$ (Baker AR silica gel or quartz at 99.995% purity) and MgO (Baker AR MgO, MgO at 99.99% purity, or MgO at 99.998% purity) with previously synthesized spinel (MgAl$_2$O$_4$, made by sintering mixtures of MgO and alumina) or γ-Al(OH)$_3$. We hand milled reagents in an agate mortar, the effects of which were undetectable, an alumina mortar, which added unacceptable concentrations of alumina, or a zirconia mortar, which added zirconia particles and contributed to glass formation. Several dozen samples were heated at 1500 to 1650 °C for 72 to 240 hours, interrupted by 2 to 6 intermediate milling steps. The most homogeneous samples as determined by EPMA and NMR are those made by mixing forsterite with spinel, as in the spectra shown here. NMR spectra indicated that most samples had reached a state of chemical equilibrium, or at least that
no further changes were occurring, before 200 hours at temperature. Forsterite samples
were difficult to crush and mill due to a relatively high fracture toughness of the heated
material. Intended Al$^{3+}$ concentrations were 570 to 2700 μg/g.

**Al$^{3+}$ doped periclase.** Al-periclase was synthesized from mixtures of 99.99% purity MgO with small amounts of 50 nm particles of Al(OH)$_3$ (Nanostructured &
Amorphous Materials, Inc.) or spinel. Reagents were milled, pressed into pellets, and
heated, producing a dense ceramic that was difficult to subsequently mill. The nano-
Al(OH)$_3$ + MgO synthesis route reached steady state with respect to Al speciation in
approximately half the time required for the spinel + MgO route. Intended Al$^{3+}$
concentrations were 480 to 2100 μg/g.

**Al$^{3+}$ doped clinoenstatite.** This phase was synthesized from Baker AR MgO,
dehydrated silica gel, and γ-Al(OH)$_3$, with excess SiO$_2$ (2 wt%) to avoid forsterite
formation. Synthesis temperatures were 1300 °C for 96 to 144 hours with 1 to 3
intermediate milling steps. In subsequent firings, clinoenstatite grain growth was
minimal, and the samples crushed and milled easily.

**Al$^{3+}$ doped larnite.** Larnite was synthesized from mixtures of CaCO$_3$, SiO$_2$, and
γ-Al(OH)$_3$. Reagents were sintered for 90 minutes at 1450 °C after milling, reground, and
sintered for 60 hours at the same temperature. After a number of preliminary
experiments, impurity phases were found to be minimized (although still present) when
Si was replaced by Al on an equimolar basis, with nominal bulk Al contents of 0.15 and
0.53 wt%.

**Sc$^{3+}$ doped forsterite.** As for Al-forsterite, Sc-forsterite with excess MgO (3
wt%) was synthesized from Baker AR MgO, Baker AR silica gel and 99.95% pure
Sc$_2$O$_3$. Mixed reagents were heated for a total of 192 hours at 1500 °C, with two
intermediate milling steps. Intended Sc$^{3+}$ concentrations were 1350 to 3350 μg/g.

**Sc$^{3+}$ doped periclase.** Several syntheses resulted in samples containing periclase
with NMR-observable Sc contents. In one approach, 99.99% purity MgO and 99.95%
purity Sc$_2$O$_3$ were mixed in a 50/50 ratio by weight and heated at 1300 °C to 1500 °C for
24 to 72 h, yielding only Sc-doped periclase and Sc$_2$O$_3$. Heated samples formed dense
ceramics that were difficult to subsequently mill. A second type of sample resulted from
a Sc-doped forsterite mixture with a bulk Sc$_2$O$_3$ content of 1.6 wt% and a large excess in MgO (70 wt%), heated at 1280 °C for 72 h.

**Electron Probe Microanalysis (EPMA)**

Electron probe microanalysis characterizations were performed using a JEOL JXA-8230 instrument. X-ray intensities were routinely standardized to a synthetic single crystal forsterite (Mg and Si), corundum (Al), kyanite (Al) and Sc metal (Sc). Additionally San Carlos olivine (Mg, Si, and Fe), spessartine garnet (Al), wollastonite (Ca and Si), albite (Na, Al and Si), and hematite (Fe), were intermittently used as secondary standards. A voltage of 15 kV, 20 nA current, 2 μm spot size, and count times of 4 minutes were used. Reference material of synthetic, Al-free forsterite was used to determine background noise levels when analyzing low Al concentrations. Water sensitive MgO and CaO samples were encapsulated in an epoxy round, cured, dry polished on silicon carbide sand papers down to 2000 grit, and then stored with desiccant in a vacuum; exposure to air was limited to 10-15 minutes.

Backscattered electron (BSE) images with high contrast ratios, energy dispersive spectroscopic (EDS) and wavelength dispersive spectroscopic (WDS) maps were used to locate sample heterogeneities, such as scarce aluminum-rich glass and crystalline impurities, when present. Major element concentrations were generally within experimental error of nominal values for the analyzed phases and are thus not reported. Element totals were typically within ± 0.03 wt%, and the largest individual major element variation we identified was ± 2 wt% of the expected value.

For high concentration elements, we determined that the observed variations in composition (Mg or Si) were randomly distributed and not correlated to sample trace concentrations. Data were rejected when low totals indicated problems with the carbon coating, focus, polish, or other difficulties.

**NMR Spectroscopy**

Samples were prepared for solid-state MAS NMR by crushing into 2-20 μm powders. A single 3.2 mm ZrO$_2$ rotor with a low $^{27}$Al background signal was used for the entirety of the project and was spun at 20 kHz. There was no detectable $^{45}$Sc background.
signal. Packed sample mass was typically 30 to 40 mg. Spectra were collected with a 14.1 Tesla Varian Unity/Inova 600 MHz spectrometer (27Al at 156.25 MHz, 45Sc at 145.98 MHz) and an 18.8 T Varian Unity/Inova 800 MHz spectrometer (27Al at 208.40 MHz, 45Sc at 194.64 MHz) using Varian/Chemagnetics “T3” MAS probes. For 27Al spectra, 0.1 M aqueous Al(NO3)3 was referenced to 0 ppm and was used for power level determinations. Effective radiofrequency power of 103 kHz was determined by measuring the 360˚ tip angle for the liquid standard. A 0.28 μs pulse, ideally a 30˚ tip angle for this nuclide in solids with significant quadrupolar coupling, was used. Referencing was reproducible to within ± 0.13 ppm. 45Sc spectra were referenced to a dilute aqueous solution of ScCl3. Effective radiofrequency power of 125 kHz was determined by measuring the 360˚ tip angle for the liquid standard. A 0.163 μs pulse, ideally a 30˚ tip angle for this nuclide in solids with significant quadrupolar coupling, was used.

Short pulse delays of 0.1 s for 27Al or 0.2 s for 45Sc were preferred to maximize the signal to noise ratios and minimize data collection times. Spectra shown here are typically not fully relaxed, but in general, differential spin-lattice (T1) relaxation among spectral components was not noticeably different in noisy spectra collected with longer delay times. Despite incomplete characterizations of relaxation, we still believe these peak areas to be meaningful, as species within the same material (i.e. tetrahedral and octahedral Al in forsterite) are expected to relax at equal rates, and approximate peak area ratios between intended and impurity phases are sufficient for our discussion.

27Al NMR rotor background signal was removed when needed by subtracting a simulated (noiseless) background spectrum based on modeling of multiple experimental spectra of the rotor, a procedure that reduces the noise of the difference spectrum considerably. Simulated background corrections agree within the noise level with background corrections based on subtraction of experimental FID’s.

Additional sample characterization

Sample homogeneities and phase identities were also investigated on powdered samples using a Rigaku Geigerflex powder X-ray diffractometer and 29Si MAS NMR collected with a 9.4 T Varian Infinity Plus 400 MHz spectrometer (29Si at 79.42 MHz).
NMR data Analysis

To help interpret our NMR data, an independent component analysis (ICA) was used, which determines statistically independent subcomponents to describe a larger parent data set. ICA techniques, although relatively uncommon in solid state NMR, are more commonly used with liquid state NMR and other spectroscopic techniques, such as IR/Raman, fluorescence, and UV-vis. Similar algorithm-based analysis techniques, such as evolving factor analysis (EFA) and principal component analysis (PCA), have even wider spread spectroscopic applications, including interpreting NMR spectra of inorganic materials (Mason et al. 2012, 2016), deconvolution of liquid state NMR spectra (Stoyanova et al. 1995; Stoyanova and Brown 2001), and analyzing Raman spectra of alkali silicate glasses (Zakaznova-Herzog et al. 2007). We also tested both EFA and PCA methods for our spectra but they did not produce reasonable components to describe known quadrupolar peak shapes.

In this study we used the SIMPLe-to-use Interactive Self-modeling Mixture Analysis (SIMPLISMA), which was previously found to perform well relative to other ICA’s on liquid-state NMR spectra (Monakhova et al. 2014). SIMPLISMA determines independent components on the basis of standard deviations, under the assumption that more significant independent components will have larger standard deviations than less significant components. Readers are directed to the following references for concise presentations of the theory and supporting formula of SIMPLISMA (Windig and Guilment 1991; Windig et al. 2002). Versions of the code can be readily found online and is detailed in Windig’s 1997 publication (Windig 1997; Mathworks.com 2007). A tutorial demonstrating the code on NMR data is also available (Solidstatenmr.com 2017). In our samples, differences in aluminum concentration, heating times, and other variations in sample synthesis provided sufficient variability among spectra to allow multiple different components to be obvious, but generally highly overlapped. For each mineral, we found that analyzing different combinations in subsets of all of the spectra collected was useful for determining the most accurate and chemically relevant independent components, which were persistently determined regardless of specific spectra used. We found that the number of independent components necessary to describe the spectra, a user specified
value, was easy to determine iteratively, with excessive components typically making
very small contributions or describing only noise or differences in phasing, as was
previously reported (Monakhova et al. 2014).

As discussed in detail later, for our spectra, SIMPLISMA was capable of deriving
components identical to spectra for known impurity phases, such as spinel. SIMPLISMA
most accurately determined known impurity phases when the spectra were windowed to
exclude spinning sidebands and the intensity of all spectra were individually normalized
to their maximum and minimum values. When sidebands were included, the algorithm
correctly associated sidebands with central peaks; however, the overall accuracy of
determining components typically suffered as the window width increased.

Fitting of spectra with quadrupolar line shapes was done using DMFit2015
(Massiot et al. 2002).

RESULTS

Aluminum in forsterite (Mg$_2$SiO$_4$)

In our samples, EPMA showed that aluminum is present in both the forsterite
crystals and in an intergranular glass phase. In the forsterite grains, EPMA compositions
(in the range of 120 to 1800 μg/g) were consistently only 20 to 35% of the intended,
weighed-in Al$^{3+}$ concentrations, suggesting that significant Al was present in Al-rich
impurity phases of low abundance. However, across all samples, analyzed forsterite Al
concentrations were observed to vary systematically with intended bulk composition. Al
contents typically varied by about 18% (relative) among different forsterite grains in a
given sample, but individual grains were typically homogeneous within the noise level.
The measured Al$^{3+}$ concentrations are above our $^{27}$Al NMR detection limit which we
estimated to be about 25 μg/g in a typical 35 mg forsterite sample, based on assumptions
of a peak with a FWHM less than 8 ppm, 80% relaxation with a pulse delay of 1 s and a 6
day acquisition.

A scarce glass phase was also detected in many samples, located along grain
boundaries or at triple junctions, as visible for a relatively glass-rich sample in Figure 1.
The abundance of glass and its composition corresponded somewhat with the purity of
reagents used, but was present in small amounts even in the highest purity experimental
products. Analysis of the glass was challenging, as such regions were typically smaller than the EPMA beam size, but indicated highly varied compositions rich in Si, Al, Mg, and Ca, with Al$_2$O$_3$, concentrations between 1.1 to 12.4 wt%. The glass compositions did not correspond to that of any known mineral. Despite its low abundance, the glass is expected to produce a sizeable feature in the $^{27}$Al NMR spectra due to its high Al concentration relative to the forsterite.

Small amounts of spinel were detectable in samples heated for shorter durations. In one sample out of 18 studied by EPMA, we also detected grains with enstatite composition, and correspondingly, the $^{27}$Al NMR spectra of this particular sample resembled a mechanical mixture of Al-doped forsterite and Al-doped enstatite. Despite all samples being synthesized with excess MgO, periclase was never detected by EPMA, possibly because it retained a similar small grain size to pure MgO samples and/or was hydrated and subsequently removed during the wet polishing process.

In the $^{29}$Si NMR spectra of our most completely reacted samples, we could detect only forsterite, and spectra were identical to the aluminum free material, i.e. the signal from any glass that was present was too low in intensity to be detected. Powder XRD of the samples detected only forsterite.

The $^{27}$Al NMR spectra contained multiple narrow AlO$_6$ features between 11 and -3 ppm with possible underlying broader components, and broad AlO$_4$ features between 95 and 20 ppm with smaller AlO$_5$ components at the lower end of this range. Some features were clearly identifiable, such as unreacted spinel when present, which produced an AlO$_4$ peak centered at about 69 ppm and an AlO$_6$ peak centered at about 12 ppm in a roughly 1:8 intensity ratio. Other features, such as the broad AlO$_4$ and AlO$_5$ components, appear to be composed of at least three aluminum species; however, determining the relative contribution of each component was difficult. Examples of typical spectra are presented in Figure 2, Figure 3, and the 1500 °C sample in Figure 4.

As detailed below, the spectra for the Al-doped forsterite samples are unique and distinct from those for MgO and for enstatite. The characteristic very narrow AlO$_6$ peak for Al-MgO is absent, and while some of the data do resemble those for enstatite (Fig. 2), comparisons between carefully referenced spectra indicate unique AlO$_6$ components for each material. This is especially obvious in 18.8 T spectra, where the enstatite peak
maximum (at -1.1 ppm) appears at a peak minimum in the forsterite samples, between
peaks at 2.0 and -2.2 ppm.

SIMPLISMA consistently determined that there are only three significant,
independent components in these spectra (Fig. 3). Inputs included background subtracted
spectra from 14.1 or 18.8 T, with as few as 6 and as many as 21 spectra. The specific
input spectra used influenced the edges of peaks and neighboring baselines, but
minimally affected the derived component peak areas and shapes. The easiest to interpret
result is component 2, which conforms to known spectra for spinel. The deconvolution of
a spinel component, which was known to be present as incompletely reacted starting
material in some of our samples, is a testament to the effectiveness of the SIMPLISMA
algorithm. Component 3 has a peak shape, width, and position containing AlO$_4$ and AlO$_5$
components that closely resemble those typical of Ca- and Al-containing silicate glasses
at compositions known by EPMA measurements to be present in our samples (Neuville et
al. 2008). In comparisons among samples, the relative peak area of this glass-like feature
approximately correlates with the abundance of Al-rich intergranular phases observed in
EPMA when measured Al concentrations were taken into account.

In contrast, component 1 is unique to the forsterite samples, and indicates that the
area of the higher frequency AlO$_4$ feature is correlated to that of the AlO$_6$ peaks,
suggesting that they are indeed all part of the same phase. The relative peak area of
component 1 averages 20-40% of the total area, which approximately agrees with the
EPMA-measured forsterite composition and the intended bulk sample composition (20 to
35% of the total Al in forsterite and the remainder in other phases). Relative peak areas
from component 1 determined from 14.1 and 18.8 T spectra indicate that approximately
25 to 27% of the Al$^{3+}$ incorporated into the forsterite structure is tetrahedral and 72 to
75% is octahedral.

The AlO$_6$ contribution to the derived component 1 is complex, typically with
three or four peak maxima even in samples that are free from AlO$_6$ containing impurity
phases, such as spinel. The line shapes are different for spectra collected at 14.1 and 18.8
T, because of the reduced effects of quadrupolar coupling at the higher magnetic field.
Quadrupolar coupling can produce split peaks with two maxima when both the coupling
constant C$_Q$ is large enough and the asymmetry parameter η is small enough,
complicating data analyses. Using quadrupole line shapes generated in DMFit2015 we
were able to fit original datasets from both fields with multiple quadrupolar line shapes
that reproduced the spectra reasonably well (Massiot et al. 2002). But, due to limited
fitting constraints, in part because of overlapping peaks and noise, we could not derive a
set of unique parameters or relative peak areas. We are confident, however, that a
minimum of three distinct types of AlO₆ sites are required to explain the spectra.

We also conducted a preliminary investigation of the effect of temperature on
Al⁴⁺ site occupancies in forsterite. Sample material that had been heated for 168 hours at
1500 °C and quenched (which produced typical spectra as in Figs. 2 and 3) was then
heated for an additional 72 hrs at 1200 °C. The lower temperature sample (Fig. 4) shows
a decreased amount of the glass phase (at least as represented by its contained Al),
indicating some crystallization, and increased intensities for both the higher frequency
tetrahedral component (at about 75-95 ppm) and the higher frequency octahedral peak (at
about 10 ppm). In other samples, the changes in the glass peak area with temperature are
often minimal, with the most obvious changes among the various octahedral components.

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Aluminum in periclase (MgO)

EPMA measurements of Al-doped MgO samples indicate concentrations within
one standard deviation of the intended values. No glass or other impurity phases were
detected, possibly because of the small grain size of less than about 3 μm.

The ²⁷Al NMR spectra contain a remarkably narrow (FWHM 0.14 ppm), fast
relaxing peak near the high frequency extreme of the known AlO₆ region (about 16 ppm),
a neighboring lower frequency AlO₆ peak (shoulder at 14.2 ppm), an underlying broad
AlO₆ feature, and a broad four coordinated resonance(s) between 90 and 40 ppm (Fig. 5).
Time-temperature studies indicated that equilibrium, or at least steady state, was reached
by 68 hours at 1500 °C. Samples heated for shorter durations or heated at lower
temperatures had obvious spinel peaks in the spectra, as well as an unexpected
intermediate phase Gaussian shaped peak centered at 82 ppm. This intermediate feature
was only detected, and was always detected, when both spinel and Al in MgO were both
present in the sample. Figure 5 illustrates the ²⁷Al NMR spectra of an equilibrated MgO
sample.
Due to its fast relaxation of the remarkably narrow peak, this feature should be easily identifiable if present in spectra of Al-forsterite and other minerals. The area of the narrow peak typically represents 8 to 18% of the total octahedral intensity; its width requires a very small quadrupolar coupling parameter $C_Q$ no larger than 0.45 MHz (Table 2). The $C_Q$ is likely less than this value, as the observed 180° radiofrequency pulse width of 5.0 μs is nearly the same as that for the liquid standard, which also requires a very low $C_Q$ value. In solids, the small $C_Q$ is indicative of a high symmetry with a cubic or nearly cubic point symmetry, which we believe is due to Al$^{3+}$ in the Mg$^{2+}$ site, undistorted by nearby vacancies or additional Al/Mg substitutions. Its high frequency peak location also implies relatively short bond lengths for octahedral aluminum, likely an effect of localized charge compensation and the Al$^{3+}$ cation in an Mg$^{2+}$ site. The other AlO$_6$ and AlO$_4$ features in the spectra, which must originate from lower symmetry chemical environments, are discussed in more detail in McCarty (2016), as are additional observations on Al in periclase.

**Aluminum in enstatite (Mg$_2$Si$_2$O$_6$)**

We attempted to avoid formation of enstatite in our forsterite samples by adding excess MgO to all, and quenching some from temperatures above those at which enstatite is stable. However, to directly compare our forsterite spectra to that of a potential enstatite impurity, we synthesized Al-enstatites with mixing and milling procedures identical to those for our most fully-reacted forsterites, although with different proportions of reagents and lower temperatures.

$^{29}$Si NMR indicated that about 70 to 80% of each sample was composed of clinoenstatite. The remaining materials included mixtures of protoenstatite, orthoenstatite, and minor amounts of cristobalite (SiO$_2$). Glass was not detected in these spectra. EPMA analysis indicated sparse, unreacted SiO$_2$ in a matrix of fine-grained (< 20 μm) enstatite containing Al at concentrations 15 to 60% below the intended syntheses. We noted large heterogeneities in Al concentration, with the majority of values clustered around the mean but some concentrations at twice the mean value. Additional heating led to minimal increases in homogeneity, implying slow intergranular Al transport relative to that in our forsterite experiments at higher temperatures. We were not confident that
detecting intergranular glass by EPMA was possible due to the small grain size and
difficulties with polishing the grain mounts.

$^{27}$Al NMR spectra of Al-doped enstatite (one example in Fig. 2), contain a broad
AlO$_4$ peak with narrow AlO$_6$ components, as well as signal from unreacted spinel. Our
spectra are similar to those in previous investigations of anhydrous orthoenstatites with
much higher Al contents, with AlO$_6$ peaks nearly identical (Kohn et al. 2005). The four
coordinated regions of our spectra also appear to contain a glass peak similar to the
forsterite component 3 and to previously studied aluminosilicate glasses (Neuville et al.
2008): it is not clear how much, if any, of this component is actually in the pyroxene.

Although the enstatite spectra look similar to those of our forsterite samples, at
18.8 T, the enstatite AlO$_6$ peak maximum is clearly in between those of the forsterite, as
visible in Figure 2. This is further supported by spectra acquired at 14.1 T, where the
enstatite peak maximum is consistently 2 ppm higher than the forsterite peak maximum.
In the forsterite spectra used for our analyses of Al components, we thus believe that
there is little to no enstatite component.

Aluminum in larnite ("belite," $\beta$-Ca$_2$SiO$_4$)

Synthesis of Al-doped samples of larnite without significant Al-rich impurity
phases was not successful. The most interpretable data were for samples made by
replacing Si with Al on an equimolar basis with total bulk Al contents of 0.15 or 0.53
wt%. In the latter sample, EPMA imaging detected rounded, 40 to 60 μm grains that
contained 40% of the intended total Al. Thin regions of intergranular glass (42 wt%
Al$_2$O$_3$, 44 wt% CaO, and 12 wt% SiO$_2$) were common. X-ray diffraction, optical
microscopy and $^{29}$Si NMR data indicated that the crystalline components of these
samples were nearly all larnite, with a few percent of the $\gamma$-Ca$_2$SiO$_4$ phase.

The $^{27}$Al spectra of our samples contain peaks only for AlO$_4$ species (Fig. 6).
Most of the components of the spectra are relaxed using a 0.1 s delay time, with a small
amount of additional intensity related to the highest frequency peak present in 1 s delay
time spectra. Using both 14.1 and 18.8 T spectra of our samples we determined the
parameters for the prominent, high frequency peak with a clear quadrupolar lineshape
(Table 2, Fig. 6).
SIMPLISMA analysis of multiple spectra of larnite samples determined 4 components. Component 1 describes the high frequency quadrupolar lineshape, component 2 is very similar to data on Al\(^{3+}\) in alite (Ca\(_3\)SiO\(_5\)), component 3 resembles a typical calcium aluminosilicate glass, and component 4 is the expected rotor background signal which was subsequently subtracted and is not shown. Because components 2, 3 and 4 can be attributed to impurity phases, it can be concluded that component 1 originates from Al in ordered tetrahedral sites in larnite. Using a least squares regression to fit component 2, component 3, and our simulation of component 1 to the spectra of the “larnite 0.53%” sample, we determined that 41% ± 4 of the total intensity was from Al in the larnite, in good agreement with our EPMA measurements (40%).

As reported by Skibsted et al. (1994), we confirm that only AlO\(_4\) species are necessary to accommodate Al\(^{3+}\) in larnite. For unknown reasons, our observed peak is about half the width of that previously reported, resulting in different derived parameters. Due to the good agreement between the EPMA-determined concentrations and the relative area of the well-defined quadrupolar doublet, we suspect there is minimal, if any, disordered AlO\(_4\) in larnite.

**Scandium in forsterite**

EPMA on our Sc-doped forsterites indicates homogeneous samples with no other mineral or glass phases detected by BSE imaging, EDS, or WDS mapping. Point analyses indicated higher homogeneity within individual grains (sample standard deviations of 45 to 70 μg/g Sc) and lower homogeneity between grains (sample standard deviations of 130 to 270 μg/g Sc). Despite the apparent homogeneity, the observed concentrations were below the expected synthesis values by an average of 14%.

In the \(^{45}\)Sc NMR spectra of Sc-forsterites, a single, well-defined quadrupolar peak shape is present in the range typical for ScO\(_6\) sites (Fig. 7). This peak and the parameters derived from both 14.1 and 18.8 T data (Table 2) do not resemble previously reported spectra for known scandium phases, such as the Sc\(_2\)O\(_3\) synthesized at the same temperature (Sc\(_2\)O\(_3\) has two distinct Sc octahedral sites and its spectrum correspondingly has two overlapped quadrupolar powder patterns) (Kim et al. 2006). The spectra for forsterite samples containing both lower and higher Sc concentrations are identical except...
for amplitude. The calculated peak shape agrees well with the experimental spectra and also accurately reproduced observed spinning sidebands (not shown).

**Scandium in periclase**

In reacted mixtures of MgO and Sc$_2$O$_3$, we detected a peak which is clearly different than Sc in forsterite, appearing as a low intensity, narrow feature at 210 ppm due to a high symmetry site, with a FWHM peak width of only 0.4 ppm, and thus a maximum $C_Q$ of $<1.5$ MHz (Fig. 8). On the basis of the similarly narrow peak width of AlO$_6$ in MgO and its relatively high frequency, we assign this peak to Sc$^{3+}$ in an MgO$_6$ site with cubic or nearly cubic point symmetry. A similar peak was seen in a mixed periclase-forsterite sample (“Sc-MgO 1.6%”), the spectrum of which also showed Sc in the forsterite as described above. All Sc-MgO samples contained a large excess of the Sc$_2$O$_3$ phase, whose NMR peak intensity served as a rough internal standard for rough estimates of the concentration of Sc in the periclase, as noted in Table 1.

A MgSc$_2$O$_4$ phase was reported to form at temperatures above 2000 °C (Muller-Buschbaum 1966), but our synthesis conditions yielded only mixtures of Sc$_2$O$_3$ and MgO containing trace amounts of Sc$^{3+}$.

**DISCUSSION**

The identification of a spectral component that is clearly Al in forsterite provides new and unique constraints on Al$^{3+}$ site preference and substitution mechanisms. These results also demonstrate the possible complexity of even this “simple”, single-element substitution into olivine. Spectral component 1 (Fig. 3) does contain both AlO$_4$ and AlO$_6$ peaks, indicating Al$^{3+}$ substitution into both Si and M sites, and suggesting that a conventional Tschermak’s mechanism (Evans et al. 2008; Grant and Wood 2010) ($^{IV}$Si$^{4+}$ + $^{VI}$Mg$^{2+}$ = $^{IV}$Al$^{3+}$ + $^{VI}$Al$^{3+}$) does play an important role. However, the roughly 1/3 ratio of tetrahedral to octahedral Al peak areas suggests that one or more additional mechanisms are also operating, to allow substitution of excess Al as AlO$_6$. Such mechanisms have been proposed, and in the absence of other substituting cations, it is generally thought to involve charge compensation with one Mg$^{2+}$ vacancy for every two incorporated Al$^{3+}$. Our results do not yet allow all such details to be refined, but the clear
presence of multiple AlO$_6$ sites does suggest important complexity. Furthermore, preliminary studies indicate that the proportions of different Al$^{3+}$ species may be influenced by temperature.

The component 1 AlO$_4$ peak for the forsterite is somewhat broad and without a clear quadrupolar line shape, which could be the result of low signal-to-noise or to some disorder leading to distributions of NMR parameters. However, its location is at the high frequency extreme (left side as plotted) of the known range for such sites in minerals, with allowable isotropic chemical shifts bounded by at least 95 ppm as defined by the upper side of this component (Stebbins 1995). This result is not surprising, as SiO$_4$ groups in forsterite have one of the highest $^{29}$Si chemical shifts known for diamagnetic silicates (-62 ppm), as expected for Q$^0$ groups (no shared oxygen between tetrahedra) (Stebbins 1995).

Further insight into Al$^{3+}$ substitution can be gained by comparing forsterite to larnite, which has the same stoichiometry and similar topology, with Q$^0$ Si sites and larger M sites with distorted 6 or 7-fold coordination (Jost et al. 1977). Despite the apparent lack of substitution of Al$^{3+}$ into the too-large Ca sites in larnite, the overall solubility appears to be higher than in forsterite. AlO$_4$ sites in larnite also produce an extreme $^{27}$Al isotropic chemical shift of 96 ppm, but appear to be highly ordered with a well-defined quadrupolar line shape (Fig. 6). These differences are possibly related to the absence of octahedral Al$^{3+}$ in this mineral and its influence on the substitution mechanisms and cation distributions. In larnite, the Al$^{3+}$ species is probably either always isolated from, or always neighboring, the defect providing the charge balance, leading to the observed ordered line shape. This contrasts strongly with forsterite, where there are many more conceivable variations in nearest cation neighbors for a tetrahedral site, including Mg$^{2+}$, Al$^{3+}$, or vacancies in the M1 and/or the M2 sites. Each of these combinations would be expected to affect the chemical shift or quadrupolar parameters, producing peaks the sum of which could resemble the broad AlO$_4$ feature visible in component 1 derived from our forsterite spectra. It is also possible that due to the presence of neighboring M site occupants, the AlO$_4$ site symmetry might be distorted resulting in greater C$_Q$ values and a broader peak.
Based on attempts at lineshape fitting, the complexity of the forsterite component 1 AlO\textsubscript{6} peak shapes requires three (or more) distinct sites. The three species represent different local environments, possibly Al\textsuperscript{3+} in M1 vs. M2, or the effects of a vacancy or of Al\textsuperscript{3+} in a neighboring M site or of Al\textsuperscript{3+} in an adjacent Si site. Any of these could cause variations in the chemical shift, C\textsubscript{Q}, or quadrupolar asymmetry parameter $\eta$, leading to changes in peak shape and position.

Previous \textsuperscript{25}Mg NMR investigations of pure forsterite showed that the two M sites have distinct NMR peak parameters that can potentially be compared to our \textsuperscript{27}Al results (Table 2) (Davis et al. 2010). This provides an opportunity to consider the effects of cation substitution on site distortion. The quadrupolar coupling constant C\textsubscript{Q} is proportional to the principle value of this tensor and to the nuclide-specific quadrupolar moment Q (MacKenzie and Smith 2001). The reported \textsuperscript{25}Mg C\textsubscript{Q} values of 5.2 MHz (M1) and 4.3 MHz (M2) can thus be adjusted for \textsuperscript{27}Al by multiplying by the ratio of Q’s for the two nuclides (147/199) (MacKenzie and Smith 2001), yielding predicted values of 3.8 and 3.2 MHz. These are among the range of values that produce reasonable line shapes for the latter nuclide in forsterite.

Our \textsuperscript{45}Sc NMR results for Sc-forsterite also provide some perspective on Al\textsuperscript{3+} substitution. The much larger size of the Sc\textsuperscript{3+} cation (73 vs. 53 pm for six-fold coordination) precludes its substitution into tetrahedral sites, consistent with the observed single ScO\textsubscript{6} NMR signal with a well-defined quadrupolar lineshape. As for AlO\textsubscript{4} groups in larnite, the lack of peak broadening due to disorder suggests that all detectable Sc\textsuperscript{3+} sites in forsterite are equivalent, and thus are either uniformly associated with or uniformly disassociated from whatever defect is providing charge compensation, for example a Mg\textsuperscript{2+} vacancy.

Adapting the reported \textsuperscript{25}Mg NMR data for forsterite (Davis et al. 2010) to \textsuperscript{45}Sc again requires multiplying the C\textsubscript{Q}’s by the ratio of the magnitudes of the quadrupolar moments, which in this case is 220/199. The predicted values of 5.7 and 4.8 MHz are very different from our observed single C\textsubscript{Q} value for the ScO\textsubscript{6} site (9.4 MHz), suggesting in this case that considerable additional site distortion occurs. Again, comparison with the \textsuperscript{27}Al data for AlO\textsubscript{6} sites in forsterite highlights the complexity of the substitution.
mechanism(s) in the latter as well as the ability of NMR to identify a single trace cation substitution mechanism when such simplicity is actually present.

Our preliminary studies also suggest that octahedral site occupancies for Al in forsterite may change significantly with temperature, but further experiments will be needed at the lower temperatures to allow confirmation of re-equilibration under conditions of slow Al diffusion and/or exsolution.

**IMPLICATIONS**

Despite the difficulties of producing single-phase samples doped with incompatible elements and the unexpected complexity of some of the resulting spectra, we have demonstrated that spectroscopy on multiple related samples with varying phase proportions, combined with EPMA characterization and SIMPLISMA data analysis, can constrain the substitution mechanisms for Al$^{3+}$ in forsterite. Experiments that examine Al$^{3+}$ sites in other minerals with analogous tetrahedral and octahedral sites (e.g. larnite, periclase, and CaO) and the analogous but larger trivalent cation Sc$^{3+}$ are also helpful in interpreting spectra, as well as in showing that when trace element substitution does occur by a simple, single mechanism, that process can be readily and definitively observed. In line with its success for NMR spectroscopy of organic molecular liquids, SIMPLISMA can perform well at separating complex, overlapped solid state NMR spectra into components, which can then be more easily given structural significance.

Our results for Al in forsterite suggest that more than one substitution mechanism plays a role at the same time and experimental conditions, with charge compensation on tetrahedral and octahedral sites important but excess AlO$_6$ also present, necessarily accompanied by other means of charge balance. The balance of these different mechanisms may shift with temperature and compositional variables. Several of the substitutions proposed in the literature (Purton et al. 1997; Grant and Wood 2010; Zhang and Wright 2010) may well operate simultaneously, a realization supported in part by the established pressure sensitive nature of Al concentrations (Wan et al. 2008). Future work on trace element substitution and solubility should recognize the potential for multiple co-existing mechanisms. The success, albeit with long hours of spectrometer time, for samples with low Al concentrations bodes well for future studies of this and other NMR-accessible trace elements in silicate minerals. Future work at higher magnetic fields could
provide much needed gains in spectral resolution and sensitivity. Potentially, more complex NMR techniques such as Al-Al homonuclear correlation experiments may provide an additional level of understanding of trace element incorporation (Iuga 2011).

Our results for other minerals, although discussed only briefly here, have wider implications as well. The narrow NMR peak width for the undistorted Al$^{3+}$ site in MgO, paired with the simple crystal structure, provides a model system that may prove useful for studies of solid state synthesis reactions.

For larnite, our work confirmed previous findings of solely tetrahedral aluminum (Skibsted et al. 1994). Due to this mineral’s high relevance to the cement industry, our reported peak parameters, and the concept of using an ICA to determine independent components from complex spectra, may help develop tools for accurately characterizing complex multi-component cements.

Our investigations of trace contents of Sc$^{3+}$ again mark this cation as an excellent spectroscopic target representing the behavior of a trivalent cation with radius between those of Al$^{3+}$ (smaller) and the rare earth cations (larger), as previously demonstrated for Sc-doped pyrope and grossular garnets (Kim et al. 2007). Its ready detectability, wide chemical shift range, and convenient quadrupolar moment (slightly higher than $^{27}$Al) can be quite sensitive to the local atomic structure, even at low concentrations. Future work on Sc$^{3+}$ may similarly contribute to our understanding Al$^{3+}$ incorporation in other minerals and may extend to other larger rare earth elements as well.

Many of the results presented here, particularly on kinetic and temperature effects, are preliminary but suggest interesting prospects for potentially unique and useful future studies. Going beyond substitution mechanisms addressable with $^{27}$Al and $^{45}$Sc NMR, $^7$Li, $^{11}$B, $^{23}$Na, and $^{31}$P may be both particularly amenable to future NMR studies of geochemically interesting problems.

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Laboratory) for introducing us to component analysis methods. We also thank two anonymous reviewers for thoughtful responses and constructive comments.
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List of Figure Captions

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### Table 1. Labels and synthesis conditions for samples shown in figures.

<table>
<thead>
<tr>
<th>Figure label</th>
<th>Mineral of interest</th>
<th>Al or Sc source</th>
<th>Intended Al or Sc (μg/g)(^a)</th>
<th>Observed Al or Sc (μg/g EPMA)</th>
<th>% in mineral(^b)</th>
<th>Temp. (°C)</th>
<th>Hours</th>
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<td>Fo-A</td>
<td>forsterite</td>
<td>Spinel</td>
<td>910</td>
<td>320 (175)</td>
<td>35</td>
<td>1500</td>
<td>168</td>
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<td>c</td>
<td>35</td>
<td>1200 +72</td>
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<td>Fo-B</td>
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<td>(\gamma)-Al(OH)(_3)</td>
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<td>1150 (230)</td>
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<td>Spinel</td>
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<td>320 (210)</td>
<td>34</td>
<td>1500</td>
<td>205</td>
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<tr>
<td>Fo-D</td>
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<td>Spinel</td>
<td>2520</td>
<td>725 (120)</td>
<td>29</td>
<td>1500</td>
<td>60</td>
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<tr>
<td>Fo-E 225 hrs</td>
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<td>Spinel</td>
<td>600</td>
<td>160 (70)</td>
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<td>227</td>
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<tr>
<td>Fo-E 156 hrs</td>
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<td>c</td>
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<td>1550</td>
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<td>-</td>
<td>1600</td>
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<td>(\gamma)-Al(OH)(_3)</td>
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<td>-</td>
<td>30(^f)</td>
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<td>2100 (160)</td>
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\(^a\)Intended bulk composition in μg/g of Al or Sc unless indicated as wt%.

\(^b\)The estimated percentage of Al or Sc determined to be within the mineral of interest on the basis of intended synthesis composition and EPMA observed composition.

\(^c\)No significant difference in Al composition from that of the parent material (Fo-A) was detected.

\(^d\)Heated for an additional 72 hours at 1200 °C beyond that of the parent material (Fo-A).

\(^e\)This is the parent material of Fo-E 227 hrs, and was not extensively investigated by EPMA.

\(^f\)% in mineral” estimated using NMR fitting.

\(^g\)Sc in MgO roughly estimated from NMR data only.
### Table 2. NMR peak parameters derived here or reported previously.

<table>
<thead>
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<th>Mineral</th>
<th>Site</th>
<th>NMR-observed coordination</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta$</th>
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<td>AlO$_6$</td>
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<td>-</td>
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<td>periclase</td>
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<td>ScO$_6$</td>
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<td>MgO$_6$</td>
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<tr>
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<td>ScO$_6$</td>
<td>106.5 ± 1.2</td>
<td>9.38 ± 0.28</td>
<td>0.68</td>
<td>-</td>
</tr>
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</table>

$^a$Source is this work or literature reference cited.

$^b$C$_Q$ and $\eta$ determined from simulating a MAS spectra at 18.5 T (Davis et al. 2010).
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