LETTER

Cation distribution in Mg-Zn olivine solid solution: a ^{29}Si MAS NMR and first-principles calculation study

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In order to clarify cation distributions in the M1 and M2 sites of $(\text{Mg,Zn})_2\text{SiO}_4$ olivine solid solution, ^{29}Si MAS NMR spectroscopic measurement and first-principles NMR parameter calculation were conducted. The ^{29}Si MAS NMR spectra of $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$ and $(\text{Mg}_{0.90}\text{Zn}_{0.10})_2\text{SiO}_4$ olivine samples revealed three new peaks at relative chemical shift differences of 0.2, 1.1 and 2.3 ppm from the main peak of forsterite (-61.8 ppm). These shifts can be attributed to changes in the second-nearest-neighbors of Si due to substitution of Mg by Zn. Based on first-principles calculations, these peaks can be assigned to the following three groups of local Si environments in the order of increasing shift from the main peak of forsterite: i) Si tetrahedra with one corner-shared Zn in M1 or M2 octahedron, ii) Si tetrahedra with one edge-shared Zn in M2 octahedron, and iii) Si tetrahedra with one edge-shared Zn in M1 octahedron. Since the last two peaks are well separated from the others, the relative abundances of Zn in the M1 and M2 sites can be quantified using these peaks. Preference of Zn for M1 site over M2 site was inferred from the observed peak intensities. The present study demonstrated the usefulness of ^{29}Si MAS NMR spectroscopy for quantitatively studying cation distributions in solid solutions.

Keywords: Olivine, Cation distribution, NMR, First-principles calculation, $(\text{Mg,Zn})_2\text{SiO}_4$

INTRODUCTION

Cation distribution in the octahedral (M1 and M2) sites of olivine is an important factor affecting its physical properties. Diffraction techniques have been used to determine occupancies of cations in the M sites (e.g., Brown, 1982). Mössbauer spectroscopy has also been used (e.g., Virgo and Hafner, 1972), but is limited to iron-bearing systems. Although solid-state NMR spectroscopy is known to be a sensitive probe of local structures, and has been applied extensively for studies of cation (e.g., Si, Al) distributions in tetrahedral sites, there have been not many studies for M sites (Stebbins and Xue, 2014). For olivine samples containing paramagnetic elements in the M sites (Fe^{2+} , Co^{2+} , Ni^{2+} etc.), many small peaks (4 to 26) were observed in the ^{29}Si MAS NMR spectra (McCarty et al., 2015). Assignment of these peaks has relied on empirical interpretation. In order to better understand the origin of NMR peaks due to cation substitutions, it would be useful to first establish the relationship between local structure and chemical shift for olivine solid solutions without para-

magnetic interactions. We have applied ^{29}Si MAS NMR together with first-principles calculation to gain new insights into cation (Mg, Zn) distributions in the $(\text{Mg,Zn})_2\text{SiO}_4$ olivine solid solution, as well as the correlation between ^{29}Si chemical shift and local structures associated with cation distributions. Zn^{2+} was selected because it is an element with closed 3d orbitals (i.e., no paramagnetic effect). There is no published diffraction study on the distribution of Zn in the M sites in this system to date. Brown (1982) mentioned M1 site preference of Zn in the $(\text{Mg,Zn})_2\text{SiO}_4$ solid solution in his review article as a personal communication.

EXPERIMENTAL AND CALCULATION PROCEDURES

$(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$ and $(\text{Mg}_{0.90}\text{Zn}_{0.10})_2\text{SiO}_4$ olivine samples (natural ^{29}Si isotopic abundances) were synthesized from oxide mixtures of reagent-grade MgO , ZnO and SiO_2 with nominal molar ratios. The mixtures were pelleted, and heated in a platinum crucible at 1400°C for 12 to 24 h. After cooling, the pellets were ground and pelleted again, and annealed at 1400°C for 24 h, and cooled down to room temperature in 1 h. A ^{29}Si -enriched

$(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$ sample was also prepared as follows: A ^{29}Si -enriched Mg_2SiO_4 sample was first synthesized from a mixture of reagent-grade MgO and 99.88% ^{29}Si -enriched SiO_2 (from ISOFLEX USA). The resultant enriched Mg_2SiO_4 was mixed with natural isotopic abundance Zn_2SiO_4 (willemite) with appropriate ratio, and the pelleted mixture was treated at 1500 °C for 40 h, and rapidly quenched by dipping the bottom of the platinum crucible in water.

The two synthesized natural isotopic abundance olivine samples were characterized by powder X-ray diffraction (after NMR measurements). The samples were mixed with Si (NIST SRM 640d) as an internal angle standard. Diffraction patterns from 10 to 120° in 2θ were collected using a SmartLab diffractometer (Rigaku Co.). The voltage and current of the X-ray tube were 40 kV and 30 mA. An incident monochromator was used to select $\text{CuK}\alpha_1$ radiation. The obtained patterns were analyzed using a Rietveld refinement program RIETAN-FP (Izumi and Momma, 2007), and lattice parameters of the olivine solid solutions were determined. Occupancies of Zn in the M1 and M2 sites were not refined in the Rietveld refinement, because of insufficient quality of the obtained powder patterns.

^{29}Si MAS NMR spectra were obtained for all three samples using a Varian 9.4 T Unity-Inova NMR spectrometer and a 1.6 mm T3 MAS probe at a spinning speed of 20 kHz. The ^{29}Si spin-lattice relaxation time constant (T_1) for the natural isotopic abundance $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$ and $(\text{Mg}_{0.90}\text{Zn}_{0.10})_2\text{SiO}_4$ olivine samples were found to be 6000 ± 990 s and 2400 ± 700 s, respectively, and that of the ^{29}Si -enriched $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$ sample was 460 ± 23 s, from saturation-recovery measurement. The reported ^{29}Si MAS NMR spectrum for the natural isotopic abundance $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$ olivine sample was acquired using a pulse length of 1.0 μs (45° tip angle) and a recycle delay of 3000 s with 114 transients averaged. Those of the natural isotopic abundance $(\text{Mg}_{0.90}\text{Zn}_{0.10})_2\text{SiO}_4$ and the ^{29}Si -enriched $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$ olivine samples were each acquired using a pulse length of 2.0 μs (90° tip angle) and a recycle delay of 2000 s, with 143 and 159 transients averaged, respectively. No differential relaxations for different peaks were observed for spectra obtained with shorter (half) or longer (twice or more) recycle delay times for all three samples.

In order to relate experimentally observed ^{29}Si MAS NMR spectra and local structures, first-principles density functional theory calculation of NMR parameters is indispensable. The calculation was conducted using the QUANTUM ESPRESSO (ver. 5.1.1) package (Giannozzi et al., 2009). PBEsol functional and PAW-type pseudopotentials (Mg.pbesol-n-kjpaw_psl.0.3.0.UPF, Zn.pbesol-

dn-kjpaw_psl.0.2.2.UPF, Si.pbesol-n-kjpaw_psl.0.1.UPF, O.pbesol-n-kjpaw_psl.0.1.UPF) from the PSLibrary (Dal Corso, 2014) were used for all calculations. In order to set the Zn concentration to that comparable to the experimental compositions, a $2 \times 1 \times 2$ olivine supercell containing 16 formulae was used. Two substitution models were considered: one Zn in M1 site (Zn1 model hereafter), and one Zn in M2 site (Zn2 model) in the supercell. These models correspond to a composition of $(\text{Mg}_{0.97}\text{Zn}_{0.03})_2\text{SiO}_4$. These substituted structures were then relaxed at 1 atm. After structural optimization, the electronic structure was calculated. The kinetic energy cutoffs for wave functions and charge density, and scf energy convergence threshold were set to 60, 300 and 10^{-12} Ry, respectively. The Brillouin zone was sampled using the Monkhorst-Pack scheme with a $2 \times 2 \times 2$ grid. For NMR chemical shift tensor calculation, the Gauge Including Projector Augmented Waves (GIPAW) method (Pickard and Mauri, 2001) implemented in the QE-GIPAW package (ver. 5.1) was used.

RESULTS AND DISCUSSION

Powder X-ray diffraction patterns of the two natural isotopic abundance samples are both composed mostly of olivine peaks with a few very weak peaks that can be explained by clinoenstatite. The refined lattice parameters from the Rietveld method are $a = 4.75693(3)$, $b = 10.20216(5)$, $c = 5.98275(3)$ Å for $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$; and $a = 4.75956(3)$, $b = 10.20725(5)$, $c = 5.98460(3)$ Å for $(\text{Mg}_{0.90}\text{Zn}_{0.10})_2\text{SiO}_4$. Syono et al. (1971) reported cell parameters of $(\text{Mg,Zn})_2\text{SiO}_4$ olivine solid solutions up to 75% Zn_2SiO_4 . They noted that the cell volume changes linearly with Zn_2SiO_4 content. Therefore, the compositions of the present samples were estimated using a linear fit to their volume data. The calculated compositions are as follows: 4.1% for the nominal $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$ sample, and 10.1% for the nominal $(\text{Mg}_{0.90}\text{Zn}_{0.10})_2\text{SiO}_4$ sample, with an estimation error of about 0.6%. Both are in reasonable agreement with the expected compositions.

It is instructive to quickly review the local structure of olivine before discussing structural details. In olivine, each SiO_4 tetrahedron is linked to two M1 and one M2 octahedra by edge sharing, and to two M1 and four M2 octahedra by corner sharing. Each M1 octahedron is, in turn, linked to two Si tetrahedra by edge sharing, and to two Si tetrahedra by corner sharing, and each M2 octahedron is linked to one Si tetrahedron by edge sharing, and to four Si tetrahedra by corner sharing. Thus, the M1 and M2 local environments are not identical in terms of connectivity to Si tetrahedra.

The ^{29}Si MAS NMR spectra of the three $(\text{Mg,Zn})_2\text{SiO}_4$ olivine samples are shown in Figure 1. These spectra all exhibit a main peak near -61.8 ppm, close to that of pure Mg_2SiO_4 forsterite (e.g., Stebbins, 1995). In ad-

Figure 1. ^{29}Si MAS NMR spectra of $(\text{Mg,Zn})_2\text{SiO}_4$ olivine solid solution samples at a spinning rate of 20 kHz. From top to bottom: natural isotopic abundance $(\text{Mg}_{0.90}\text{Zn}_{0.10})_2\text{SiO}_4$, natural isotopic abundance $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$, and ^{29}Si -enriched $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$.

dition, all of them contain a smaller peak near -59.5 ppm, an even weaker peak near -60.7 ppm and another small peak near -61.5 ppm that is partially resolved from the main peak in the spectra of natural isotopic abundance samples (top and middle spectra). Chemical shifts and full-width-at-half-maximum (FWHM) for these peaks are listed in Table 1. Comparison between the two natural isotopic abundance olivine samples revealed that the relative intensities of the three peaks with respect to the main peak near -61.8 ppm are higher for the sample with higher Zn content. Thus, these three new peaks are most likely from the olivine solid solution and represent Si sites with Zn next-nearest neighbor(s). For the two natural isotopic abundance samples, no other peaks were observed in the NMR spectra; whereas for the ^{29}Si -enriched $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$ sample, two additional small peaks near -80.6 and -83.2 ppm (outside the plotting range of Fig. 1) were also observed, and may be attributed to a small amount of clinoenstatite (Kanzaki et al. 1992).

The signal/noise ratio of the spectra for the ^{29}Si -enriched $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$ (bottom spectra) is much better than those of the natural isotopic abundance samples. However, the peak widths (~ 0.3 ppm) of the ^{29}Si -enriched sample are broader than those of natural isotopic abundance samples (~ 0.1 – 0.2 ppm) (Table 1). This is likely due to the presence of trace amount of paramagnetic elements in the ^{29}Si -enriched sample, which would explain both the larger FWHM and the shorter T_1 . ^{29}Si

Table 1. ^{29}Si NMR parameters from simulation of MAS NMR spectra *

Sample **	Chemical shift (ppm)	FWHM (ppm)	Relative intensity
n- $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$	-61.74	0.11	0.73
	-61.53	0.13	0.14
	-60.69	0.14	0.03
	-59.49	0.14	0.10
n- $(\text{Mg}_{0.90}\text{Zn}_{0.10})_2\text{SiO}_4$	-61.76	0.17	0.55
	-61.54	0.17	0.23
	-60.67	0.15	0.03
	-59.51	0.16	0.13
	-59.33	0.17	0.06
e- $(\text{Mg}_{0.95}\text{Zn}_{0.05})_2\text{SiO}_4$	-61.77	0.28	0.84
	-61.54	0.27	0.09
	-60.71	0.28	0.01
	-59.51	0.28	0.06

* Simulation results assuming Lorentzian peaks for all, because unconstrained fit with mixed Gaussian/Lorentzian line shapes resulted in Lorentzian fractions close to 1 for the stronger peaks and the qualities of spectra are not good enough to yield reliable Lorentzian fractions for the smaller peaks. Simulations with unconstrained Lorentzian fractions gave similar peak positions (within the last reported digit), FWHM and relative intensities (for the ^{29}Si -enriched sample), but the relative intensities for the natural isotopic abundance samples are less reliable. The spectrum for the $(\text{Mg}_{0.90}\text{Zn}_{0.10})_2\text{SiO}_4$ sample was simulated with two components for the peak near -59.5 ppm because of its asymmetric nature, which may be attributed to Si tetrahedra with zero and one corner-shared Zn neighbor in M1 or M2 octahedral site, in addition to one edge-shared Zn neighbor in M1 octahedral site.

** n- stands for natural isotopic abundance; e- stands for ^{29}Si -enriched.

Table 2. Calculated structural and ^{29}Si NMR parameters of forsterite and single Zn-substituted models

Model	Lattice parameters ($2 \times 1 \times 2$ cell)				Enthalpy (Ry)	^{29}Si NMR chemical shift (ppm)*			
	a (Å)	b (Å)	c (Å)	Volume (Å ³)		Edge-shared Zn		Corner-shared Zn	
						M1	M2	M1	M2
Forsterite	9.5166	10.1923	11.9629	1160.35	-4426.2135				
Zn1 model	9.5191	10.1976	11.9611	1161.10	-4634.3181	2.99		0.34	
Zn2 model	9.5188	10.1910	11.9666	1160.83	-4634.3128		1.62		0.17

* Averaged relative shift from Si sites without Zn neighbors.

1 Ry = 1312.74 kJ/mol

MAS NMR spectra measured with much shorter relaxation delay times (≤ 1 s) for this sample revealed a number of much smaller peaks that are further shifted from the main peaks, similar to those reported for forsterite doped with paramagnetic ions (McCarthy et al., 2015), consistent with this inference.

First-principles calculation results are listed in Table 2. Total enthalpies for the two models revealed that the Zn1 model (Zn in M1 site) is energetically more favored than the Zn2 model (Zn in M2 site) by 6.96 kJ/mol. This corresponds to the enthalpy change for the exchange of a single pair of Mg-Zn between M1 and M2 site out of a total of 16 pairs in the $2 \times 1 \times 2$ supercell. Therefore, the exchange enthalpy for Mg-Zn in $(\text{Mg}_{0.5}\text{Zn}_{0.5})_2\text{SiO}_4$ can be estimated to be 27.8 kJ/mol per unit cell. It is interesting to note that there are quite contrasting changes in lattice parameters for the two substitution models. For example, the *c*-axis length change is much smaller for the Zn1 model than the Zn2 model, whereas the opposite is true for the *b*-axis. These features can be compared with the observed lattice parameter changes with composition in this solid solution series (Syono et al., 1971). The lattice parameters show little changes in the *c*-axis, but large changes in the *b*-axis in the Zn-poor portion. Comparing with Table 2, these observed features could be favorably interpreted as preferred occupancy of Zn in M1 sites in the Zn-poor portion of the series. For further discussions over a wider compositional range, calculations of more Zn-rich compositions with various configurations would be necessary.

The calculated ^{29}Si chemical shifts for the Zn1 and Zn2 models are listed in Table 2. There is significant difference in chemical shift between edge-sharing and corner-sharing configurations of a Si tetrahedron and a Zn octahedron. The relative chemical shift change for the former (1.62, 2.99 ppm) is an order of magnitude larger than the latter (0.17, 0.34 ppm). Large changes in ^{29}Si chemical shifts for Si-Al substitution in edge-shared octahedral neighbors than corner-shared neighbors were also noted in our previous study of phase ‘egg’ (AlSiO_3OH) (Xue et al., 2006). Additionally, the chemical shift for Si tetrahedron with one Zn neighbor in edge-shared

M1 octahedron (2.99 ppm) is well separated with that in edge-shared M2 octahedron (1.62 ppm). This suggests that Si tetrahedra sharing an edge with M1 or M2 octahedral site can be distinguished by ^{29}Si chemical shift.

The chemical shifts for the new peaks of the $(\text{Mg,Zn})_2\text{SiO}_4$ olivine samples listed in Table 1 can be compared with the calculated values in Table 2 for their assignments. The peaks at -59.5, -60.7 and -61.6 ppm in the ^{29}Si MAS NMR spectra may be assigned, respectively, to Si tetrahedra with one Zn in a neighboring edge-shared M1 octahedron, one Zn in a neighboring edge-shared M2 octahedron, and one Zn in a neighboring corner-shared M1 or M2 octahedron. The main peak at -61.8 ppm is assigned to Si tetrahedra with no Zn octahedral neighbor. Although quantitative comparison shows that the calculated relative shifts are overestimated by 30–50%, there is no ambiguity in the present peak assignment. The ^{29}Si MAS NMR spectra can be reasonably fitted with four (five for the more Zn-rich sample) Lorentzian peaks (not shown). The obtained chemical shifts, FWHM and relative intensities are listed in Table 1. Note that because of poor S/N, the relative intensities for the natural isotopic abundance samples contain large uncertainties. Nevertheless, it is clear even by visual inspection of the NMR spectra in Figure 1 that the intensity ratios between the peaks at -59.5 ppm and -60.7 ppm are all greater than 2. The latter value is the expected ratio when Zn is randomly distributed in M1 and M2 sites, because each Si tetrahedron shares edges with two M1 octahedra and one M2 octahedron. Therefore, Zn apparently prefers M1 site to M2 site. In this preliminary study, no further quantification is conducted. Preference of Zn for M1 sites is consistent with the enthalpy and lattice parameters obtained from first-principles calculations. Even greater preference for M1 sites should be expected for more slowly cooled samples.

The present study is limited to Zn-poor compositions. With increasing amount of substituted Zn, Si sites with more than one edge-shared Zn second-nearest-neighbors are expected. Peaks due to such Si sites should be further shifted from the main peak of forsterite. Accordingly, at higher Zn contents three additional groups of peaks are

expected to appear at increasingly larger peak shifts from the main peak: Si tetrahedra with one edge-shared Zn neighbor in M1 octahedron and one edge-shared Zn neighbor in M2 octahedron, Si tetrahedra with two edge-shared Zn neighbors in M1 octahedra, and Si tetrahedra with two edge-shared Zn neighbors in M1 octahedra and one edge-shared Zn neighbor in M2 octahedron. The presence of additional Zn neighbors in corner-shared M1 or M2 octahedra will contribute to shoulders to these peaks. In fact, for the $(\text{Mg}_{0.90}\text{Zn}_{0.10})_2\text{SiO}_4$ sample, the peak near -59.5 ppm is asymmetric and may be simulated with two components near -59.5 and -59.3 ppm attributable to Si with zero and one Zn neighbor in a corner-shared M1 or M2 octahedron, respectively, in addition to one Zn neighbor in an edge-shared M1 octahedron. Therefore, it is likely that cation distributions can still be estimated for Zn-rich compositions by quantifying the observed peak intensities.

The present study demonstrated the usefulness of ^{29}Si MAS NMR to clarify cation distributions in the olivine structure. This approach can be extended to other silicate structures with more than one M sites, such as modified spinel (wadsleyite) and pyroxenes. As shown above, the existence of edge sharing between Si tetrahedra and M octahedra is essential to obtain well resolved ^{29}Si NMR peak(s) from the main peak. Therefore, a quick evaluation can be made by inspecting the crystal structures for edge-sharing neighbors. There is no edge sharing between Si tetrahedra and M octahedral sites in wadsleyite, and thus it is likely difficult to distinguish cation distributions by ^{29}Si MAS NMR alone. Similar situation is found for clinopyroxene with $C2/c$ space group. For orthopyroxene and clinopyroxene with $P2_1/c$, one of the two Si tetrahedral sites shares edge with one M2 octahedron. This site might give a separate ^{29}Si NMR peak accompanying cation substitution in the M2 sites, if the additional peak does not overlap with that of the other Si site. Although only peaks due to cation substitution in the M2 site could possibly be distinguished, the abundance of the substituted cation in the M1 sites might still be constrained from the relative intensity of the peak due to cation substitution in the edge-shared M2 octahedral site, the total intensities of other peaks and the bulk composition. Therefore, the approach demonstrated in the present study could be applicable to other selected silicate phases.

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