Article

Si-disordering in $MgAl_2O_4$-spinel at high *P-T* conditions, with implication to Si-Mg disorder in Mg_2SiO_4-ringwoodite

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Abstract: A series of Si-bearing $MgAl_2O_4$-spinels were synthesized at 1500-1650 °C and 3-6 GPa. These spinels had SiO_2 contents up to ~1.03 wt%, and showed a substitution mechanism of $Si^{4+} + Mg^{2+} = 2Al^{3+}$. Unpolarized Raman spectra were collected from polished single grains, and displayed a set of well-defined Raman peaks at ~610, 823, 856 and 968 cm^{-1} which had not been observed before. Aided with the Raman features of natural Si-free $MgAl_2O_4$-spinel, synthetic Si-free $MgAl_2O_4$-spinel, natural low quartz, synthetic coesite, synthetic stishovite and synthetic forsterite, we infer that these Raman peaks should belong to the SiO_4 groups. The relations between the Raman intensities and SiO_2 contents of the Si-bearing $MgAl_2O_4$-spinels suggest that at some *P-T* conditions some Si must adopt the M-site. Unlike the SiO_4 groups with very intense Raman signals, the SiO_6 groups are largely Raman-inactive. We have further found that the Si cations primarily appear on the T-site at *P-T* conditions ≤ ~3-4 GPa and 1500 °C, but attain a random distribution between the T-site and M-site at *P-T* conditions ≥ ~5-6 GPa and 1630-1650 °C. This Si-disordering process observed for the Si-bearing $MgAl_2O_4$-spinels hints that similar Si-disordering might happen to the $(Mg,Fe)_2SiO_4$-spinels (ringwoodite), the major phase in the lower part of the mantle transition zone of the Earth and the index mineral for the very strong shock stage experienced by extraterrestrial materials. The likely consequences have been explored.

Keywords: 4-coordinated Si; 6-coordinated Si; $MgAl_2O_4$-spinel; Mg_2SiO_4-ringwoodite; Raman spectroscopy; Si-disordering

1. Introduction

Spinel (Sp; AB_2O_4) *sensu lato* plays a crucial role in Earth sciences. The so-called 2-3 Sp, A = 2+ cations and B = 3+ cations, is ubiquitous in most terrestrial rocks [1,2]. With significant compositional complexity and wide *P-T* stability field, it participates many phase equilibria, which can be calibrated as geothermometers, geobarometers and oxybarometers [3-5], and therefore has many geological implications. Taking the chromian Sp as an example, it has been widely used as a "petrological litmus paper" to classify upper mantle peridotites, explore melt compositional characteristics of the upper mantle, probe crystallization processes of basaltic magmas, and estimate *P-T* conditions of diamond formation [6-9]. Additionally, the 2-3 Sp is widely observed on some extraterrestrial planets, asteroids and meteorites [10-14]. Furthermore, it is even found as one of the major phases in some lunar rocks or lunar meteorites [15,16], implying some special features of the magma's evolution history of the Moon.

Less frequently observed, the so-called 4-2 Sp (A = 4+ cations and B = 2+ cations) is also geologically important, with the $(Mg,Fe)_2SiO_4$-Sp (or ringwoodite; Rw) being the most distinct example. It has been accepted that Rw with an $Mg^{\#}$ of ~89 ($Mg^{\#}$ = 100Mg/(Mg+Fe); molar ratio) is the most abundant phase in the lower part of the mantle transition zone (LP-MTZ; ~520-660 km). The physical-chemical properties of the Rw thus have significant implications in building the mineralogical models of the Earth's deep interior, constraining the origins of the 520-km and 660-km seismic discontinuities, and exploring the rheological behavior and convection process of the MTZ [17-21]. Recent discovery of a terrestrial Rw crystal included in a diamond confirms the superior role that Rw plays [22]. In comparison, extraterrestrial Rw has been commonly documented in L ordinary chondrites ([23]; and references therein), and less frequently recorded in H ordinary chondrites [24,25], LL ordinary chondrites [14,26], CV carbonaceous chondrite [27], and CB carbonaceous chondrite [28]. Furthermore, it has been observed in some lunar meteorites [29,30] and many Martian meteorites (for Rw in the shergottite, see Boonsue & Spray [31], Baziotis et al. [32], Greshake et al. [33], Walton [34], Walton et al. [35], Ma et al. [36,37], and Miyahara et al. [38]; for Rw in the chassigny, see Fritz & Greshake [12]). Rw has been proposed as the index mineral for the very strong shock stage experienced by the meteorites (S6; [39]), and its discoveries have set important constraints on the shock *P-T* conditions, shock durations, and sizes of the impactors, which may be combined with the radiometric ages of the shock events to provide valuable knowledge for the theoretical evolution models of the early solar system [23,40,41].

One distinct feature of the structure of Sp is its order-disorder phenomenon. Sp has the space group $Fd\bar{3}m$, and has two symmetrically different metal sites (tetrahedral and octahedral sites, with 1/8 of the former and 1/2 of the latter occupied by cations; T-site and M-site hereafter), so that its structural formula is usually written as $^{[4]}A^{[6]}B_2O_4$. The cations on these two sites readily switch positions, and Sp becomes disordered, leading to a more general formula $^{[4]}(A_{1-x}B_x)^{[6]}(A_xB_{2-x})O_4$, where x is the inversion parameter ($x = 0$ → normal Sp; $x = 1$ → inverse Sp; $x = 0.667$ → completely-disordered Sp). This order-disorder process is complicated, and influences many elastic, thermodynamic and thermochemical properties [19,42-46].

The order-disorder status of the 2-3 $MgAl_2O_4$-Sp, the archetype of all spinels, can be significantly affected by T, P, composition, and even grain size. The $MgAl_2O_4$-Sp is generally a normal Sp at ambient condition, but becomes partially or even fully disordered as T and P increase [42,43,45,47-57]. Its inversion parameter x increases as its grain size decreases [58]. Additionally, there have been some preliminary discussions on the effect of composition [42,53]. In contrast, the order-disorder issue of the 4-2 Mg_2SiO_4-Sp (Rw) is still hotly debated, and convincing evidence to the presence of 6-coordinated Si remains at large. From knowledge on ionic radius systematics and thermodynamic considerations [19,59,60], a small amount of structural disorder was suggested, with x reaching ~0.02-0.04 for the P-T conditions of the LP-MTZ. However, high-resolution ^{29}Si MAS NMR data indicated no 6-coordinated Si [61], a result potentially affected by a fast structural reequilibrating during sample-quenching process. Nevertheless, the Rw grains in the highly-shocked L6-type ordinary chondrites NWA 1662 and NWA 463, with distinct and different colors, showed clues of structural inversion [62], which was partially preserved presumably due to much larger cooling rates. Considering the large influence of the x parameter on the elastic constants, elastic anisotropy, and seismic velocities [19,46,63], the Mg-Si order-disorder process deserves more investigation, which is the focus of this study.

In Sp, the size of a cation has a profound influence in determining its site preference, with larger ions to prefer the T-site of the 2-3 Sp, but to prefer the M-site of the 4-2 Sp [59]. With a relatively small size difference between the Mg and Al cations in the $MgAl_2O_4$-Sp, the cation disorder achieved at high P-T conditions can be partially preserved [42,45,48,50,51,53]. In contrast, the relatively large size difference between the Mg and Si cations in the Rw may strengthen this size-dependent site preference, and accelerate the cation-redistribution process during cooling, so that the cation disorder attained at high P-T conditions may be easily lost, leading to null signals for cation disorder, as experimentally observed [61,64]. To circumvent this obstacle, we have taken an indirect approach by doping the $MgAl_2O_4$-Sp with some Si, and examined if Si can be disordered. It has been expected that silicon can readily enter the $MgAl_2O_4$-Sp, for the SiO_2 in natural 2-3 Sp reaches up to ~5.3 wt% (Fig. 1). In this study, we first synthetized the Si-bearing $MgAl_2O_4$-Sp at high P. We then analyzed the experimental products by Raman spectroscopy, a powerful method to study cation-disordering [49,57]. To facilitate

data interpretation, natural Si-free $MgAl_2O_4$-Sp (N-Sp), natural low quartz (N-Qz), and synthetic Si-free $MgAl_2O_4$-Sp, coesite (Coe), stishovite (St) and forsterite (Fo) were similarly analyzed. Here we report the first experimental evidence for the 6-coordinated Si in the Sp structure.

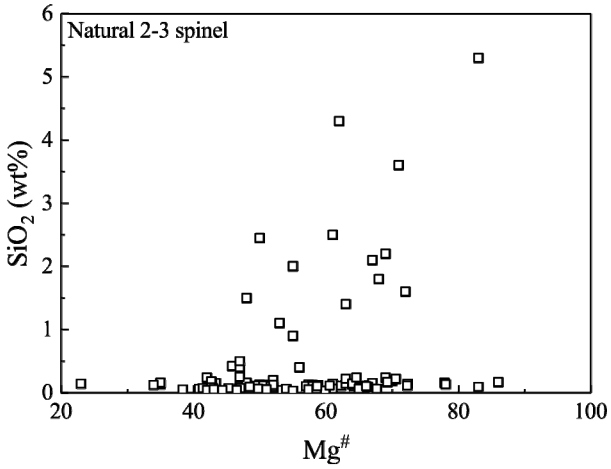

Figure 1. SiO_2 (wt%) vs $Mg^{\#}$ of some natural 2-3 spinels. $Mg^{\#}$, 100Mg/(Mg+Fe) in molar ratio. Data sources are Sigurdsson et al. [65], Sobolev & Nikogosian [66], Kamenetsky et al. [67], Franz & Wirth [68], and Chistyakova et al. [69].

2. Experimental and analytical methods

High-*P* experiments were conducted on a cubic press at the High-Pressure Laboratory of Peking University [70] and a multi-anvil press at the Geophysical Laboratory, Carnegie Institution of Washington [71]. With the experimental charges encapsulated in sealed Pt tubes, a series of Si-bearing $MgAl_2O_4$-Sp were synthesized in the system CaO-MgO-Al_2O_3-SiO_2-K_2O-CO_2 at 3-6 GPa and 1500-1650 ^oC by employing conventional electrical resistance heating technique (Table 1). In addition, we used the high-*P* experimental techniques to separately synthesize Si-free $MgAl_2O_4$-Sp, Coe and St (Table 1). The *P* and *T* uncertainties in our high-*P* experiments should be better than ~0.5 GPa and 50 ^oC [70-72].

Table 1. Experimental conditions, phase assemblages, and compositions of spinels and quartz (wt%)

Exp. #	P^a	T^a	t^a	Phase assemblage	MgO	Al_2O_3	SiO_2	Total
LMD565	3	1500	36	Sp(8)[b]+Melt	28.66(25)[c]	70.23(53)	0.39(5)	99.29(72)
LMD564	4	1500	36	Sp(8)+Melt	29.26(15)	70.29(18)	0.65(7)	100.22(33)
LMD563	4	1550	24	Sp(7)+Melt	28.44(22)	70.92(33)	0.30(7)	99.68(35)
LMD558	4	1550	36	Sp(5)+Fo+Melt	29.01(30)	69.98(60)	0.76(3)	99.75(86)
LMD578	5	1630	12	Sp(13)+Grt+Melt	28.94(18)	70.22(25)	0.76(7)	99.92(36)
LMD568	6	1650	12	Sp(13)+Grt+Melt	29.13(26)	69.27(59)	1.03(7)	99.45(78)
LMD487[d]	5	1600	12	Sp	--	--	--	--

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LMD659[e]	5	1500	12	Coe+Melt	--	--	--	--	
PL1316[e]	14	1400	8	St	--	--	--	--	

Natural spinel	N-Sp(10)	28.05(18)	70.81(22)	0.01(1)	100.03(39)
Natural quartz	N-Qz(10)	0.00(1)	0.13(9)	100.95(51)	101.17(57)

[a]*P*, pressure in GPa; *T*, temperature in °C; *t*, time in hour.

[b]Number in the parenthesis after the name of the phase is the number of successful EMP analyses performed on that phase. Sp, spinel; Melt, silicate melt; Fo, forsterite; Grt, garnet; Coe, coesite; St, stishovite; Qz, quartz.

[c]Number in the parenthesis is the analytical uncertainty reported as one standard deviation. 28.66(25) read as 28.66 ± 0.25.

[d]Starting material is a mixture of dried high purity MgO and Al_2O_3 powders, weighted out according to the stoichiometry of the $MgAl_2O_4$ spinel.

[e]Starting material is a dried high purity SiO_2 powder, with some water added later.

The compositions of the crystalline phases from the high-*P* experiments were obtained by using a JXA-8100 electron microprobe (EMP) in wavelength dispersive mode (WDS). For all the EMP analyses, the beam current was 10 nA, the accelerating voltage 15 kV, the beam spot size 1 μm, and the counting time 40 s. Calibration was based on optimization to some standards provided by the SPI Corporation (USA), with diopside for Mg and Ca calibrations, jadeite for Si, Al and Na calibrations, chromium oxide for Cr calibration, hematite for Fe, sanidine for K, rutile for Ti, rhodonite for Mn, and nickel silicide for Ni. Data correction was performed with the PRZ method. The results are shown in Table 1 (the CaO and K_2O contents below the detection limits).

Two natural gem-quality mineral samples were employed in this study as well: one was a red, Si-free Sp crystal (N-Sp) with an octahedral shape from Mogok (Burma), and the other was a clear low Qz crystal (N-Qz) from Donghai (China). Both were similarly analyzed for compositions with the EMP in the WDS mode. Besides the components shown in Table 1, extra components in the N-Sp included 0.06(3)% TiO_2, 0.95(6)% Cr_2O_3 and 0.10(1)% FeO, leading to the chemical formula $(Mg_{0.993}Fe_{0.002}Ti_{0.001})(Al_{1.983}Cr_{0.018})O_4$ (all iron assumed as Fe^{2+}). Extra components in the N-Qz were below the detection limits.

Unpolarized Raman spectra were collected from 100 to 1350 cm^{-1} with a Renishaw inVia Reflex system in a back-scattering geometry at ambient *P*-*T* conditions. A 532 nm laser with an emission power of ~50 mW and a 50× long-distance objective were used in all analyses. Other analytical conditions were ~1 μm light spot, 1 cm^{-1} spectral resolution, and 20 successive scans for every analysis (10 s for each scan). For every high-*P* product, multiple analyses were conducted on well-polished and arbitrarily-selected Sp, Coe, St and Fo grains with unknown orientations. In comparison, the Raman spectrum of the N-Sp was

collected from the (111) plane whereas that of the N-Qz was from the (001) plane. The Raman data were processed by using the PeakFit V4.12 software (SPSS Inc.).

In addition, we analyzed one fragment of the N-Sp for its order-disorder state by single-crystal XRD method. Data were collected using an Agilent Technologies Rigaku micro-focused diffractometer (Mo Kα radiation; λ = 0.71073 nm), and processed using the SHELXT software included in the SHELXTL package. From the single-crystal XRD data we directly obtained an x value of 0.129, probably with relatively large uncertainty due to the similar scattering factors of Mg and Al. Following the method of Carbonin et al. [73], with the bond distances from Lavina et al. [74] and with x = 0.129 as one of the input variables, further, we calculated a new x value, which was in turn used as an input in the next round of crystal structural analysis. The final cycles of the least-squares refinement, including atomic coordinates and anisotropic thermal parameters for the atoms [I > 2sigma(I)], converged at R_1 = 0.0164, wR_2 = 0.0730 and S = 1.065, and yielded x = 0.162 (see Supplementary Material for the details). Using the empirical equation proposed by Andreozzi & Princivalle [55],

$$x = 21.396 - 80.714u \quad (1),$$

where u is the oxygen positional parameter in the Sp structure (u = 0.26329(24) for our N-Sp), alternatively, we constrained the x value as 0.145. x = 0.145 is preferred in this study.

3. Results and discussions

3.1 Synthetic $MgAl_2O_4$-Sp and its SiO_2

In total, nine high-P experiments with long durations were conducted (Table 1): six of them for synthesizing Si-bearing $MgAl_2O_4$-Sp, one for Si-free $MgAl_2O_4$-Sp, one for Coe, and one for St. In the synthesizing experiments for the Si-bearing $MgAl_2O_4$-Sp, a CO_2-rich melt phase with intense quench-modification texture was always observed. Some other crystalline phases like Fo and garnet (Grt) were occasionally detected. The crystalline phases in all these experiments had large grain sizes up to ~600 μm, showed sharp grain boundaries and attained homogeneous chemical compositions. Typical electron back-scatter images from some of these experiments are shown in Fig. 2. In the experiments for the Si-free $MgAl_2O_4$-Sp, Coe and St, a melt phase was clearly observed in LMD659 only (Table 1). The grain boundaries of the Si-free $MgAl_2O_4$-Sp, Coe and St were well defined, their grain sizes large (up to ~100 μm in diameter), and their compositions expected to be homogeneous.

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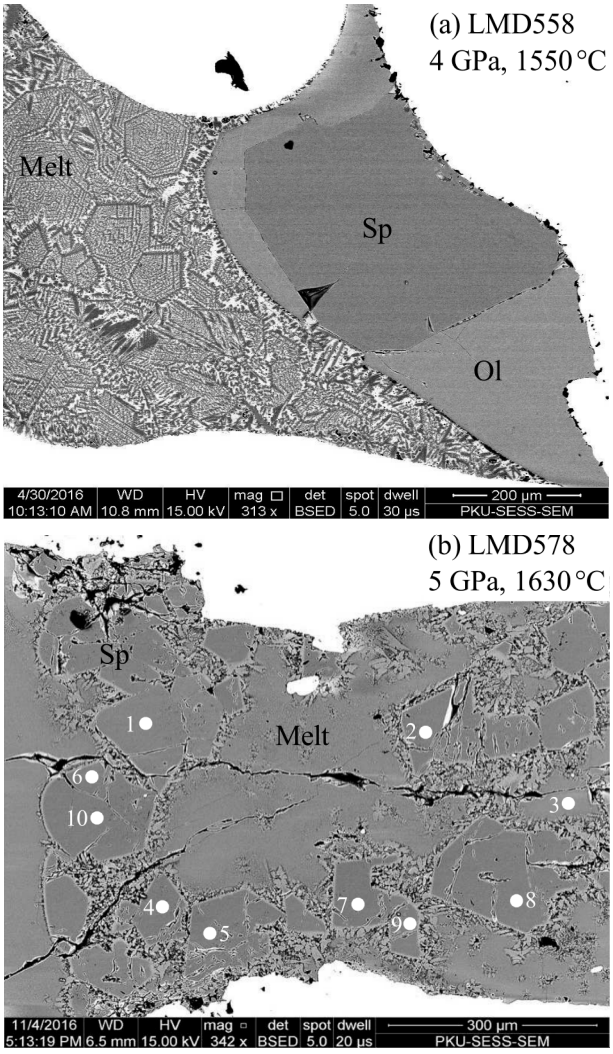

Figure 2. Typical electron back-scatter images: (a) LMD558 at 4 GPa and 1550 °C; (b) LMD578 at 5 GPa and 1630 °C. On the exposed sample surface of LMD558, we observed just one large Sp grain, surrounded by olivine compositionally approximating Fo ($Mg_{2.034(30)}Ca_{0.004(0)}Si_{0.973(15)}Al_{0.011(1)}O_4$; five EMP analyses). In contrast, many Sp grains were found on the exposed sample surface of LMD578, coexisting with Grt grains (not shown in (b); $Mg_{2.765(66)}Ca_{0.294(67)}Al_{1.968(18)}Si_{2.995(11)}O_{12}$, based on 10 EMP analyses). The white spots numbered from 1 to 10 in (b) represent the positions, where the Raman spectra shown in Fig. 7b were taken.

With up to ~1 wt% SiO_2 (Table 1), the compositions of the Si-bearing $MgAl_2O_4$-Sp are shown in Fig. 3. A primary observation here is that one Si^{4+} and one Mg^{2+} substitute for two Al^{3+},

$$Si^{4+} + Mg^{2+} = 2Al^{3+} \quad (2).$$

In detail, the (Si_{pfu}) values seem slightly lower than the (Mg_{pfu}-1) values, which perhaps relates to the compositional characteristics of the coexisting phase(s). Nevertheless, the effects of *P*, *T* and coexisting phases on this cation substitution reaction are not clear, but presently under a thorough experimental investigation.

The cation radii of Mg (r_{Mg}), Al (r_{Al}) and Si (r_{Si}) are very different, r_{Mg} = 0.585 Å > r_{Al} = 0.39 Å > r_{Si} = 0.275 Å on the T-site and r_{Mg} = 0.715 Å > r_{Al} = 0.53 Å > r_{Si} = 0.40 Å on the M-site at ambient conditions [59]. Since larger ions prefer the T-site of the 2-3 Sp, the Si-free $MgAl_2O_4$-Sp should generally adopt a normal Sp structure, as verified by some studies on natural Sp with compositions close to the $MgAl_2O_4$ formula (x = ~0.02-0.04 in Schmocker & Waldner [47]; x = 0.05 in Maekawa et al. [51]). By the same token, Si in the $MgAl_2O_4$-Sp should occupy the M-site. However, existing single-crystal XRD studies on natural 2-3 Sp locate Si on the T-site [73,75-77]. The coupled substitution of Si and Mg for 2Al as observed in our high-P synthetic $MgAl_2O_4$-Sp and the site-occupation knowledge to be revealed by our Raman spectroscopic data should shed light on the Si distribution.

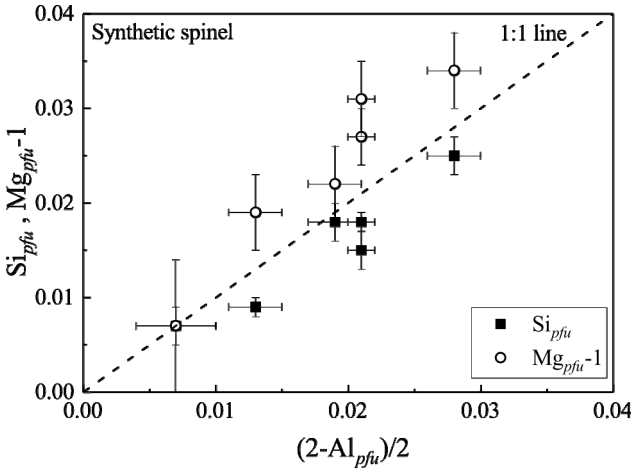

Figure 3. Si_{pfu} and Mg_{pfu-1} vs $(2\text{-}Al_{pfu})/2$ of synthetic spinels from our high-P experiments. *pfu* stands for per formula unit.

3.2 Raman features of nearly normal $MgAl_2O_4$-Sp

There are two chemical formula units per primitive unit cell of normal $MgAl_2O_4$-Sp (14 atoms), which leads to three acoustic modes and 39 optic modes according to group theory. Five Raman-active fundamental vibrations, A_{1g} + E_g + $3T_{2g}$, are predicted [78]. Theoretical calculations yield the A_{1g} at ~762 cm^{-1}, E_g at ~408 cm^{-1}, and T_{2g} at ~667 cm^{-1} ($T_{2g(2)}$), ~557 cm^{-1} ($T_{2g(3)}$) and ~317 cm^{-1} ($T_{2g(1)}$; [79-85]). The intensity of these Raman modes decreases in the order of $E_g > T_{2g(2)} > A_{1g} > T_{2g(1)} > T_{2g(3)}$ [83]. Except the weakest $T_{2g(3)}$ peak, all other four peaks were routinely observed on natural $MgAl_2O_4$-Sp with very low and insignificant amounts of impurities like SiO_2, TiO_2, Cr_2O_3, FeO and/or ZnO [49,57,78,86,87].

Our N-Sp displays four sharp peaks at ~312, 407, 664 and 766 cm^{-1}, compatible with the Raman features established for normal $MgAl_2O_4$-Sp (Fig. 4). Furthermore, two weak and broad peaks are observed at ~222 and 715 cm^{-1}, which are attributable to the slightly-disordered structural feature (x = 0.145). The small peak at ~715 cm^{-1} was also evident in the Raman spectra of the natural $MgAl_2O_4$-Sp studied by Chopelas & Hofmeister [78] and by Cynn et al. [86]. Both samples attained some

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structural disorder: using Equation (1), the x value of the former sample is calculated as ~0.144 (u = 0.2633); the x value of the latter sample was claimed as ~0.02, which might have been slightly underestimated (more discussion later). On the other hand, it was not observed for the natural $MgAl_2O_4$-Sp studied by Cynn et al. [49], Van Minh & Yang [87] or Slotznick & Shim [57], implying x values at least smaller than ~0.145. No Raman spectra previously collected on unannealed natural $MgAl_2O_4$-Sp showed the weak peak at ~222 cm^{-1}. The sample studied by Chopelas & Hofmeister [78] had an x value much comparable to our N-Sp, so that a weak peak at ~222 cm^{-1} should be expected. Chopelas & Hofmeister [78], however, did not report any Raman data below ~250 cm^{-1}.

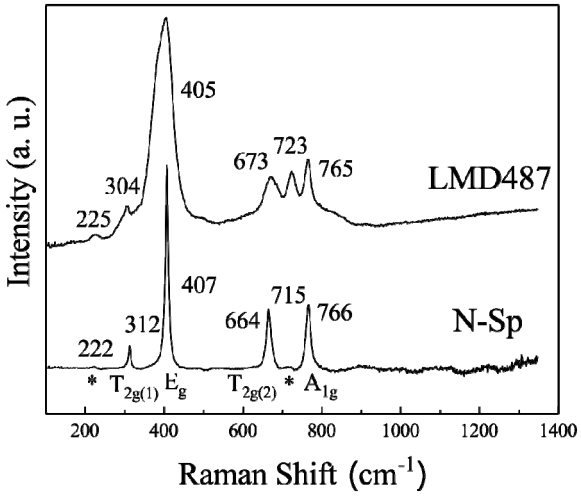

Figure 4. Raman features of Si-free N-Sp, and synthetic Si-free $MgAl_2O_4$-Sp from LMD487.

In-situ high-T Raman spectroscopic investigations on natural $MgAl_2O_4$-Sp were conducted by Cynn et al. [49,86], Van Minh & Yang [87], and Slotznick & Shim [57]. The weak peak at ~715 cm^{-1} evidently emerged or intensified at high T, and persisted to ambient T after cooling, so that it could be confidently attributed to the high-T structural disorder process. Theoretical investigations have confirmed this attribution [81,83]. In comparison, the even weaker Raman peak at ~222 cm^{-1} was detected at high T by Slotznick & Shim [57] only, and similarly attributed to the high-T structural disorder process. Additionally, it was observed by Cynn et al. [86] on the natural $MgAl_2O_4$-Sp after rather than before their high-T Raman spectroscopic experiments.

The two Raman peaks at ~222 and 715 cm^{-1} directly observed on our N-Sp (x = ~0.145) may provide a convenient and inexpensive method to quantify the disorder extent of natural 2-3 Sp. Recording rich genetic conditions such as chemical environment, geological setting, and cooling history [77,88], natural 2-3 Sp commonly have x values ranging from 0 to ~0.23 ([89]; and references therein). The x parameters are usually constrained by applying single-crystal XRD method, powder neutron diffraction or nuclear magnetic resonance spectroscopy, which is often instrumentally unavailable, technically challenging, requires large quantity of

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homogeneous sample, and/or costs too much in terms of funds and time. Raman spectroscopy is however right to the opposite. The Raman feature at ~715 cm^{-1} has high intensity, and is well separated from the A_{1g} band at ~766 cm^{-1}, so that it can be readily used to estimate the disorder extent (Fig. 4). With fixed analytical conditions in the Raman spectroscopic experiments, the intensity ratio of these two peaks should reflect the inversion extent according to the following equation [86]:

$$x = 1/[1 + c(I_{715}/I_{766})] \quad (3),$$

where c is an unknown coefficient presumably dependent to the analytical setups, and I represents either the peak height or integrated area. With the peak height data (or integrated area data) of our N-Sp, I_{715} = 1672(437) and I_{766} = 30257(548) cps (or I_{715} = 22995(5993) and I_{766} = 664010(7038) cps cm^{-1}), c is estimated as 0.33(9) (or 0.20(6)). Applying this value to the Raman data of the unannealed natural $MgAl_2O_4$-Sp of Cynn et al. [86] leads to an x value of ~0.06 (or 0.09). Cynn et al. [86] obtained x = 0.02 by assuming c = 1. We prefer the larger x value, simply because a disorder extent of 0.02 in the $MgAl_2O_4$-Sp structure may not be high enough to bring forth the Raman peak at ~715 cm^{-1}.

3.3 Mg-Al order-disorder state of synthetic $MgAl_2O_4$-Sp

The Mg-Al order-disorder states of our synthetic $MgAl_2O_4$-Sp can be estimated using the results from the in-situ observations at high P-T conditions made by Méducin et al. [45], as shown in Fig. 5.

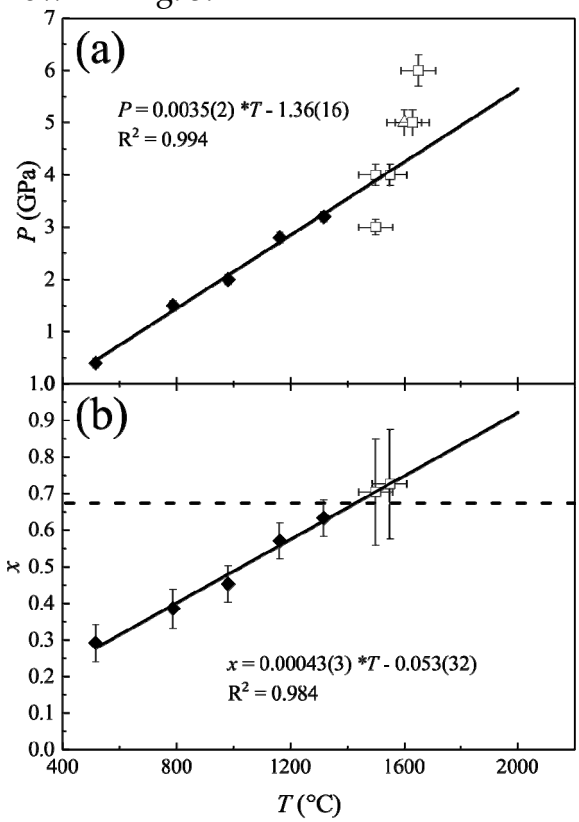

Figure 5. (a) Comparison of P-T conditions of our high-P Sp-synthesizing experiments and those of the heating-up experiments closely approaching Mg-Al

redistribution equilibrium at $T \geq 500$ °C from Méducin et al. [45]. The P and T values of the five experiments from Méducin et al. [45] were highly correlated, as shown by the solid line $P = 0.0035(2)*T - 1.36(16)$. (b) x-T relation of those five experiments from Méducin et al. [45], as shown by the solid line $x = 0.00043(3)*T - 0.053(32)$. Filled diamonds are for the five experiments from Méducin et al. [45], whereas empty triangle is for our experiment synthesizing Si-free $MgAl_2O_4$-Sp and empty squares are for our experiments synthesizing Si-bearing $MgAl_2O_4$-Sp. The broken line in (b) is shown for a hypothetic fully-disordered $MgAl_2O_4$-Sp with $x = 0.667$.

There has been excellent agreement on the T effect on the Mg-Al disorder process of the $MgAl_2O_4$-Sp at ambient P: x increases as T increases [42,47,48,50,51,53-57]. As to the P effect at ambient T, discrepancy exists presumably because the order-disorder reaction could not be readily activated and adequately approach its equilibrium during the course of a conventional high-P study [52,90,91]. Thanks to Méducin et al. [45] who conducted an investigation at simultaneously high-P and high-T conditions (up to 3.2 GPa and 1318 °C), the P effect at relatively high T has been well established: x increases as P increases. It is thus clear that our synthetic $MgAl_2O_4$-Sp formed at high P-T conditions should attain large degrees of cation disorder, which should be well preserved due to the quick quench process in the cubic press experiments (T decreased to < 600 °C in ~20 seconds).

Claimed by Méducin et al. [45], the heating-up experiments at $T \geq 500$ °C closely reached their cation order-disorder equilibrium, with the P almost linearly correlating with the T (Fig. 5a). Since both P and T promote Mg-Al disorder at simultaneously high-P and high-T conditions, the effects of P and T can be lumped together and adequately accounted for by using just one independent variable. Here we have chosen T (Fig. 5b). Coincidently, our synthesizing experiments at 4 GPa and 1500 to 1550 °C (Table 1) plot rather near the P-T locus defined by those heating-up experiments at $T \geq 500$ °C (Fig. 5a), suggesting that, with a short-distance extrapolation, the x values of the $MgAl_2O_4$-Sp from our experiments at 4 GPa can be accurately estimated. Using the equation shown in Fig. 5b, the derived x values are from 0.70(15) to 0.73(15), so that the true x values should be close to 0.667 (random Mg-Al distribution). In addition, the x values of our synthetic $MgAl_2O_4$-Sp at 5 and 6 GPa should also be ~0.667 due to the even higher experimental P and T (Fig. 5a). Furthermore, the x values obtained for the P-T conditions of 2.8 GPa and 1163 °C, and 3.2 GPa and 1318 °C by Méducin et al. (2004) were 0.571(49) and 0.633(50), respectively, implying that the x of our $MgAl_2O_4$-Sp at a similar P of 3 GPa but a much higher T of 1500 °C (LMD565; Table 1) should be close to 0.667 as well.

Assuming no effect of the additional Si with abundances ≤ ~0.025 pfu (Fig. 3), we conclude that our synthetic $MgAl_2O_4$-Sp should achieve a nearly random Mg-Al distribution.

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3.4 Raman features of fully-disordered $MgAl_2O_4$-Sp

The Raman spectrum of our synthetic Si-free $MgAl_2O_4$-Sp (LMD487) is compared to that of our N-Sp in Fig. 4. It similarly shows six peaks at slightly different energies, with all peaks being significantly broadened though. Compatible with the observations made by Cynn et al. [49,86] and Slotznick & Shim [57], the A_{1g}, E_g and $T_{2g(1)}$ modes shift slightly to lower wavenumbers whereas the $T_{2g(2)}$ mode shifts slightly to higher wavenumbers, as x increases from ~0.145 to 0.667. In addition, the E_g band becomes not only very broad, but highly asymmetric as well, indicating a possible hiding Raman peak. According to Caracas & Banigan [84], a very intense Raman feature should occur at the lower wavenumber side of the E_g peak when the $MgAl_2O_4$-Sp disorders. Moreover, the two weak, broad, and Mg-Al disorder-related peaks at ~715 and 222 cm^{-1} become much more distinct in the Raman spectrum of the synthetic Si-free $MgAl_2O_4$-Sp. All these are diagnostic features for a high degree of Mg-Al disorder.

With Equation (3) and adopting x = 0.667, the peak height data (or integrated area data) of our synthetic Si-free $MgAl_2O_4$-Sp, I_{723} = 7148(215) and I_{765} = 10986(228) cps (or I_{723} = 181810(5451) and I_{765} = 240020(6329) cps cm^{-1}), lead to a c value as 0.32(2) (or 0.38(2)), which is again much smaller than the assumed value of 1 in Cynn et al. [86]. Combining this result with that determined by the Raman data of our N-Sp, 0.33(9) or 0.20(6), the c coefficient appears generally constant for a large range of x, supporting the constant c assumption made by Cynn et al. [86]. To confirm this, more investigation on the $MgAl_2O_4$-Sp with different disorder extents using jointed experimental methods to simultaneously obtain Raman spectroscopic data, chemical compositional data and crystal structural data like what we have done in this study is highly desirable.

3.5 Raman features of Si-bearing fully-disordered $MgAl_2O_4$-Sp

The octahedra in the Sp structure share six edges with six neighboring octahedra, resulting in an extensively edge-linked structure in three dimensions [92]. In comparison, the tetrahedra are fully isolated to each other, with their four oxygen atoms linking to four neighboring octahedra. If Si occupied the M-site of the $MgAl_2O_4$-Sp, its Raman signals would be much analogous to those of St, which similarly places Si in edge-shared octahedra [93]. If Si occupied the T-site, alternatively, its Raman signals would resemble those of Fo because Si in Fo also adopts isolated T-site and forms separate SiO_4 group, with the oxygen atoms shared by neighboring octahedral [94]. On the other hand, Si atoms in low Qz [95] and Coe [96] are 4-coordinated, but the SiO_4 tetrahedra are fully polymerized into a three-dimensional framework, so that the Raman features of low Qz and Coe should be very different to those of potential SiO_4 groups in the Sp structure.

Apart from those six bands previously described, the Si-bearing $MgAl_2O_4$-Sp shows a new set of well-defined Raman bands at ~610, 823, 856 and 968 cm^{-1} (Fig. 6). These peaks are distinctly different to the Raman features of St, Coe and N-Qz, but highly resemble those of Fo. Furthermore, a less well-defined peak with low

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intensity occasionally appears at ~920 cm^{-1}, and perfectly matches the relatively weak 920 cm^{-1} Raman peak of Fo (Fig. 6). Accordingly, we tend to attribute these five peaks to potential separate SiO_4 groups in our Si-bearing, fully Mg-Al disordered $MgAl_2O_4$-Sp, and assign the peaks at ~968, 920 and 856 cm^{-1} to the asymmetric stretching of the SiO_4 groups, the peak at ~823 cm^{-1} to the symmetric stretching, and the peak at ~610 cm^{-1} to the bending. It follows that at least some Si atoms adopt the T-site.

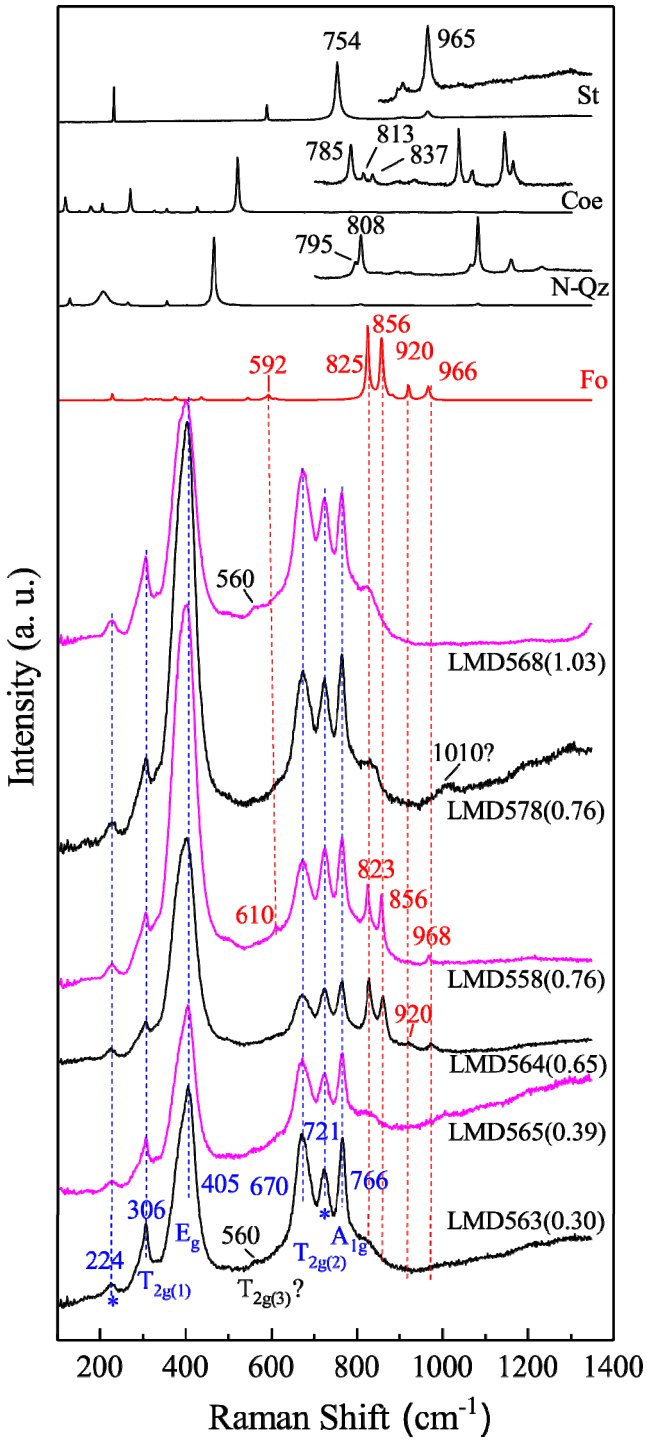

Figure 6. Raman features of synthetic Si-bearing $MgAl_2O_4$-Sp from our high-*P* experiments. As comparisons, Raman spectra of N-Qz, synthetic Coe, St and Fo

(LMD558; Table 1) are shown as well. For the purpose of illustration, some portions of the Raman spectra of St, Coe and N-Qz have been expanded and shown as insets whereas the entire Raman spectrum of Fo has been compressed by a factor of 60. LMD563(0.30), Exp. # followed by the SiO_2 content of the Sp. To illustrate clearly, only one Raman spectrum is shown for each synthetic phase, although multiple Raman spectra have been collected.

Furthermore, two weak and diffusive Raman peaks have been occasionally observed at ~560 and 1010 cm^{-1} for our Si-bearing $MgAl_2O_4$-Sp (Fig. 6), with the former attributable to the usually-undetected fifth fundamental Raman band of the $MgAl_2O_4$-Sp ($T_{2g(3)}$) and the latter likely featured as a combination band/overtone.

The intensities of the Raman peaks attributable to the SiO_4 groups show interesting behavior. Considering the very low SiO_2 contents in the $MgAl_2O_4$-Sp from LMD563 and LMD565 (0.30(7) wt% and 0.39(5) wt%, respectively; Table 1), the low intensities of the new Raman peaks at ~610, 823, 856 and 968 cm^{-1} can be readily explained by the small amounts of the SiO_4 group (Fig. 6). As the SiO_2 contents increase, one would anticipate these peaks to grow if some of the added Si entered the T-site. Surprisingly, the Raman spectra of our $MgAl_2O_4$-Sp with higher SiO_2 contents, from 0.65(7) to 1.03(7) wt%, show distinctly divergent behaviors (Fig. 6), with the new Raman peaks at ~610, 823, 856 and 968 cm^{-1} intensifying for the $MgAl_2O_4$-Sp synthesized at relatively low *P-T* conditions (4 GPa and 1500 °C for LMD564, and 4 GPa and 1550 °C for LMD558; Table 1) but increasing little for the $MgAl_2O_4$-Sp synthesized at relatively high *P-T* conditions (5 GPa and 1630 °C for LMD578, and 6 GPa and 1650 °C for LMD568). Evidently, some of the Si atoms added into the $MgAl_2O_4$-Sp did take the T-site at relatively low *P-T* conditions, but most them did not at relatively high *P-T* conditions. It follows that some Si atoms in the $MgAl_2O_4$-Sp from LMD578 and LMD568 must have adopted the M-site and formed SiO_6 groups (Fig. 6).

The SiO_6 groups seem Raman-inactive. With similar amounts of SiO_2, the $MgAl_2O_4$-Sp from LMD558 shows much stronger Raman peaks for its SiO_4 groups than that from LMD578 (Fig. 7), suggesting that the former generally contains more SiO_4 groups, but the latter contains more SiO_6 groups. In both cases, no new Raman peaks can be confidently identified, implying that the SiO_6 groups in the $MgAl_2O_4$-Sp are by and large Raman-inactive. Different crystallographic orientations unlikely affect this conclusion. As shown in Fig. 7a, the two sets of unpolarized Raman spectra for the $MgAl_2O_4$-Sp in LMD558 (Set A and Set B), taken from the only crystal shown in Fig. 2a but with crystallographic orientations normal to each other, do display some variations in the intensities of the Raman peaks for the SiO_4 groups, but overall exhibit very similar patterns. Furthermore, the 10 unpolarized Raman spectra taken from 10 randomly-selected $MgAl_2O_4$-Sp grains in LMD578 do not show much variation in their overall appearance as well (Fig. 7b).

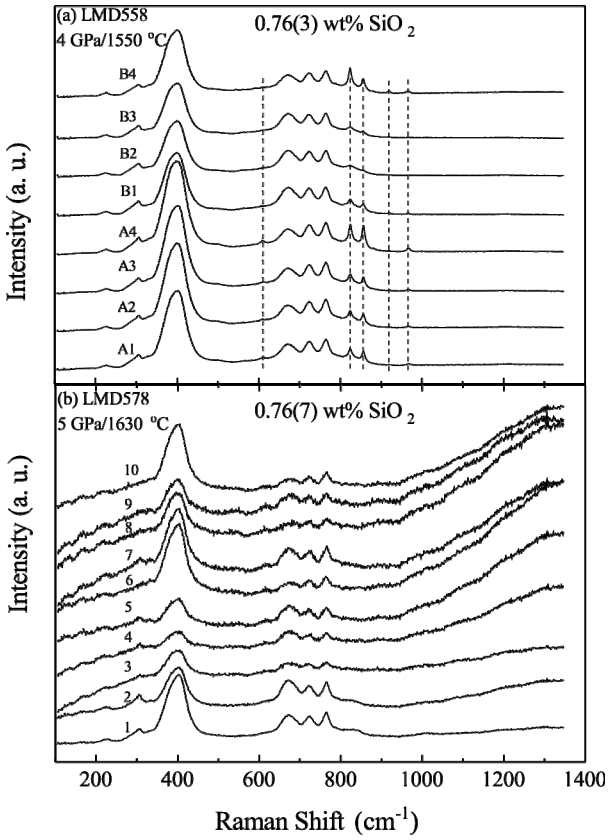

Figure 7. Raman spectra of $MgAl_2O_4$-Sp with almost identical amounts of SiO_2 from LMD558 (a) and LMD578 (b). The two sets of Raman spectra (A1, A2, A3 and A4 as Set A, and B1, B2, B3 and B4 as Set B) shown in (a) were collected from the only Sp grain shown in Fig. 2a, but with their orientations normal to each other. After obtaining the Raman spectra of Set A, we reprocessed the sample to make a new exposure normal to the previous one and then collected the Raman spectra of Set B. Ten Raman spectra shown in (b) were acquired from ten different Sp grains (see Fig. 2b for the positions). Due to data compression, the weak Raman peaks for the SiO_4 groups of the $MgAl_2O_4$-Sp from LMD578, visible in Fig. 6, are now barely discernable in (b).

3.6 Si-disordering in fully-disordered $MgAl_2O_4$-Sp

In the $MgAl_2O_4$-Sp with SiO_2 contents as low as ~0.65-0.76 wt%, the Raman peaks for the minor SiO_4 groups can be as intense as those for the major $(Mg,Al)O_4$ groups (Fig. 6 and Fig. 7a), so that the relationships among the Raman intensity, SiO_2 content, Si disorder state and *P-T* condition are worth of further exploration.

We can write the formula $^{[4]}(Mg_{0.333}Al_{0.667})^{[6]}(Al_{1.333}Mg_{0.667})O_4$ for a Si-free Mg-Al fully-disordered $MgAl_2O_4$-Sp (x = 0.667). Ignoring the effect of small amounts of Si, one obtains $^{[4]}(Mg_{0.333}Al_{0.667}Si_y)^{[6]}(Al_{1.333}Mg_{0.667}Si_z)O_4$ for the Si-containing Mg-Al fully-disordered $MgAl_2O_4$-Sp. The Si disorder state is then defined as $y = [Si_y]/([Si_y] + [Si_z]) = [Si_y]/[Si_{total}]$, with y = 1 indicating all Si on the T-site, y = 0 all Si on the M-site, and y = 0.333 a Si random distribution. Under certain analytical conditions

491 in the Raman spectroscopic experiments, the intensity of a Raman peak caused by
492 one type of structural unit i (SiO_4 here) is proportional to its abundance ([i]; [Si_y]
493 here), $I_i = c_i \times [i]$ ([86]; c_i is a constant), leading to
494 $$I_{SiO_4} = c_{SiO_4} \times [Si_y] = c_{SiO_4} \times y \times ([Si_y] + [Si_z]) \quad (4),$$

495 where $[Si_y] + [Si_z] = Si_{total} = 0.0237 \times SiO_2$ wt% for the cases with small amounts of
496 SiO_2. With the SiO_4 groups represented by the Raman peaks at ~823 and 856 cm^{-1}
497 and the $(Mg,Al)O_4$ groups by those at ~725 and 766 cm^{-1}, we obtain
498 $$\frac{I_{SiO_4}}{I_{(Mg,Al)O_4}} = \frac{I_{823} + I_{856}}{I_{725} + I_{766}} = \frac{c_{SiO_4} \times y \times 0.0237 \times SiO_2 wt\%}{I_{725} + I_{766}} \quad (5).$$

499 The term $\frac{c_{SiO_4} \times 0.0237}{I_{725} + I_{766}}$ is essentially a constant (C), so that Equation (5) can be
500 briefed as
501 $$\frac{I_{823} + I_{856}}{I_{725} + I_{766}} = C \times y \times SiO_2 wt\% \quad (6).$$

502 Evidently, the variable $\frac{I_{823} + I_{856}}{I_{725} + I_{766}}$ of the Mg-Al fully-disordered $MgAl_2O_4$-Sp with
503 certain y should be linearly correlated with the SiO_2, and the curve should pass
504 through the origin (the case of zero SiO_2).
505 Without knowing the y value, it is impossible to obtain the value of the
506 constant C, which in turn impairs the application of Equation (6). Nevertheless, for
507 the two extreme cases with all Si entering the T-site (y = 1) and Si attaining a full
508 disorder distribution (y = 0.333), the ratio of the two slopes (C and 0.333C,
509 respectively) should be 3, which in fact represents the maximum ratio of any two
510 slopes.
511 Our experimental data are summarized in Table 2, and shown in Fig. 8. Both
512 LMD563 and LMD558 ran at 4 GPa and 1550 °C, so that they formed a special
513 group (Group 2) acquiring similar Si order-disorder states (identical y values).
514 These two experimental data, plus the zero SiO_2 case, then define a curve for this
515 particular y, with its slope as S_2 = 0.703(248). The uncertainty of the slope is
516 somehow large, reflecting the limited accuracy of the data.

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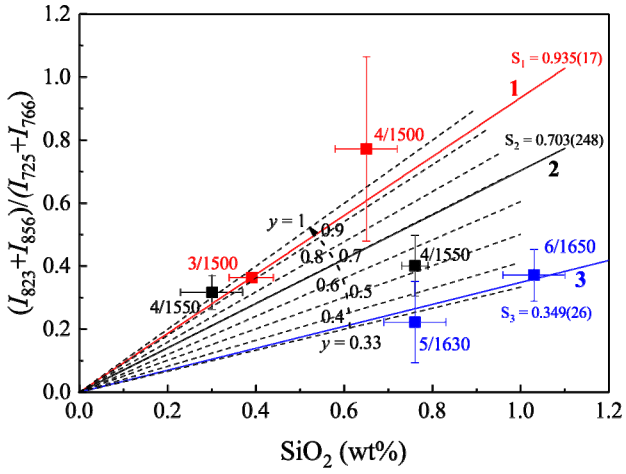

Figure 8. $\frac{I_{823}+I_{856}}{I_{725}+I_{766}}$ vs SiO_2 content of our synthetic Si-bearing $MgAl_2O_4$-Sp. Note that the analytical conditions in the Raman spectroscopic experiments were identical, and all the $MgAl_2O_4$-Sp generally had the maximum amount of Mg-Al disorder (x = 0.667). The experimental P-T conditions are indicated along the symbols; 4/1500, for example, should be read as 4 GPa and 1500 °C. The experiments have been divided into three groups, with Group 1 containing LMD565 and LMD564 (red squares), Group 2 containing LMD563 and LMD558 (black squares), and Group 3 containing LMD578 and LMD568 (blue squares). Aided with the origin (the zero SiO_2 case), the experiments in each group have been used to determine the relationship between the $\frac{I_{823}+I_{856}}{I_{725}+I_{766}}$ and SiO_2 content. Using C = 1.02(14), Equation (6) is shown as the pencil of broken lines radiating from the origin, with different y values ranging from 0.33 to 1.

Table 2. Ratio of integrated area of the Raman peaks at ~823 and 856 cm^{-1} for the SiO_4 group to those at ~725 and 766 cm^{-1} for the $(Mg,Al)O_4$ group

Exp. #	$P/T/SiO_2$[a]	#[b]	$(I_{823}+I_{856})/(I_{725}+I_{766})$
LMD565	3/1500/0.39(5)[c]	3	0.36(1)
LMD564	4/1500/0.65(7)	3	0.77(29)
LMD563	4/1550/0.30(7)	3	0.32(5)
LMD558	4/1550/0.76(3)	8	0.40(10)
LMD578[d]	5/1630/0.76(7)	4	0.22(13)
LMD568	6/1650/1.03(7)	3	0.37(8)

[a] P, GPa; T, °C; SiO_2, SiO_2 content (wt%) in our synthetic Sp.

[b] Number of Raman spectra collected.

[c] Number in the parenthesis representing one standard

deviation; 0.39(5) read as 0.39 ± 0.05.

[d]Ten Raman spectra were collected (Fig. 7a), but only four of them were used here. Since the Raman spectra were numerically dominated by those without visible peaks for the SiO_4 groups, we selected four Raman spectra, with the SiO_4 Raman peaks ranging from the lowest to the highest, to derive our result in order to avoid possible data bias. Of course, this procedure might have led to new data bias.

The curve constrained by the experiments of Group 2 divides the rest four experiments into two groups, with one group including LMD565 and LMD564 conducted at relatively low *P*-*T* conditions (Group 1 with larger y) whereas the other group including LMD578 and LMD568 conducted at relatively high *P*-*T* conditions (Group 3 with smaller y). Due to the good linear relations (Fig. 8), we have attempted weighted linear least-squares fit and obtained $S_1 = 0.935(17)$ for the experiments of Group 1 and $S_3 = 0.349(26)$ for the experiments of Group 3. The assumption behind this practice is that the y values of the $MgAl_2O_4$-Sp from the experiments in either Group 1 or Group 3 are constant. Whether this assumption is justified or not is unimportant, since one can always draw a line through the origin and one single experimental data, and subsequently define a slope for that particular case. The key observation here is that the ratio between S_1 and S_3 is 2.68(21), a value close to 3. This means that the curve defined by the experiments of Group 1 generally approximates the case of all Si residing on the T-site ($y = 1$), and the curve defined by the experiments of Group 3 closely approaches the case of a fully random Si distribution ($y = 0.333$). It thus follows that with small variations of *P* and *T*, from 3-4 GPa to 5-6 GPa, and from 1500 to 1630-1650 °C, Si in the Mg-Al fully-disordered $MgAl_2O_4$-Sp drastically changes from a fully-ordered distribution on the T-site to a completely random distribution.

With the y values for the Mg-Al fully-disordered $MgAl_2O_4$-Sp from LMD565, LMD564, LMD578 and LMD568, we have calculated the constant *C*, and obtained 0.93(15), 1.19(58), 0.88(59) and 1.08(31), respectively. Indeed, the constant *C* is constant, averagely 1.02(14), which then allows us to add into Fig. 8 a set of curves with fixed y values to show the relationship between the $\frac{I_{823}+I_{856}}{I_{725}+I_{766}}$ and SiO_2.

Some interesting points emerge from Fig. 8. Firstly, the Raman peaks of the minor SiO_4 group are very prominent, compared to those of the major $(Mg,Al)O_4$ group. For ~1.1 wt% SiO_2 fully-ordered on the T-site ($y = 1$), for example, the Raman peaks at ~823 and 856 cm^{-1} are generally as intense as the Raman peeks at ~725 and 766 cm^{-1}. Secondly, the behavior of the Raman peaks of the SiO_4 group strongly correlates with the SiO_2 content, relatively weak and changing little for the SiO_2-poor $MgAl_2O_4$-Sp but strong and varying significantly for the SiO_2-rich $MgAl_2O_4$-Sp. Thirdly, the Si-disordering process is independent to the SiO_2 content, but controlled by the formation *P* and *T* of the $MgAl_2O_4$-Sp. With the *P*-*T* conditions change from ~3-4 GPa and 1500 °C to ~5-6 GPa and 1630-1650 °C, the Si

cations radically change from fully ordering on the T-site (y = 1) to randomly distributing between the T-site and M-site (y = 0.333). For the $MgAl_2O_4$-Sp with similar SiO_2 contents, finally, the ones displaying relatively strong Raman peaks at ~823 and 856 cm^{-1} should have formed in a relatively low *P-T* environment, and vice versa.

4. Implications

Electrostatic lattice energy calculations and consideration of the structure of the Sp group of minerals suggest that the larger Mg cations prefer the T-site and the smaller Al cations prefer the M-site, resulting in a generally normal $MgAl_2O_4$-Sp at ambient *P* and *T* [59]. This principle seems inapplicable to the minor components. The present study indicates that at *P-T* conditions ≤ ~3-4 GPa and 1500 °C, covering the *P-T* range of the top upper mantle of the Earth [97], the even smaller Si cations incorporated by the $MgAl_2O_4$-Sp structure appear on the T-site, rather than on the anticipated M-site (y = 1; Fig. 8). This result is compatible with existing single-crystal XRD studies on terrestrial Sp, which locate Si on the T-site [73,75-77,98]. The current study further shows that presenting as SiO_4 groups in the Sp, a small amount of SiO_2 like ~1 wt% exhibits very intense Raman peaks at ~823 and 856 cm^{-1}, and can completely alter the stereotypical overall appearance of the Raman spectra established with some SiO_2-poor natural 2-3 Sp. Since Si readily enters the 2-3 Sp structure, this result should have important application in identifying the Sp phase, particularly for the circumstances where direct petrographic observation cannot be made. A Raman spectrometer will be launched shortly as part of the ExoMars analytical laboratory and deployed on the Martian surface to investigate the mineralogical and biological aspects of the Mars [99,100]. Considering the wide spreading of the 2-3 Sp on the Earth, the Moon, and the extraterrestrial planets, asteroids and meteorites, it will have high chance to encounter some Sp and collect in-situ Raman spectra. A correct interpretation of these Raman spectra must critically evaluate the effect of Si.

Si starts to enter the M-site of the $MgAl_2O_4$-Sp at *P-T* conditions ≥ ~3-4 GPa and 1500 °C, and become fully disordered at *P-T* conditions ≥ ~5-6 GPa and 1630-1650 °C (Fig. 8). However, the 6-coordinated Si may not be easily observed in natural $MgAl_2O_4$-Sp. High-*P* experimental studies have showed that Al-rich 2-3 Sp is not a stable phase for the upper mantle at *P* > ~3 GPa [101]. On the other hand, adding Cr may stabilize the 2-3 Sp to much higher *P* [4], and encapsulating the 2-3 Sp in diamonds may lead to the same result [102]. The Cr-rich 2-3 Sp inclusions in diamonds are thus the best targets to look for the 6-coordinated Si.

The almost random Si distribution observed for our Si-bearing $MgAl_2O_4$-Sp at *P-T* conditions ≥ ~5-6 GPa and 1630-1650 °C strongly hints that at some high *P-T* conditions the Si cations in the $(Mg,Fe)_2SiO_4$-Sp (Rw) might be disordered to large extents. Mg_2SiO_4-Rw has been conventionally regarded as a normal 4-2 spinel with nearly all Si taking the T-site. The single-crystal XRD data of Sasaki et al. [64] and high-resolution ^{29}Si NMR data of Stebbins et al. [61] did not show any convincing

627 evidence for 6-coordinated Si. In contrast, ~4% Si was inferred to appear on the
628 M-site, based on the systematic deviations of the Si-O bond length determined by
629 new single-crystal XRD data from an average value in silicates [60]. Consideration
630 of the bond length systematics and experimentally-measured cation distributions
631 led to a similar conclusion [59]. However, all these conclusions were drawn from
632 the experimental data collected on quenched samples or based on some crystal
633 structural features established for ambient *P*. In the former cases, the cation
634 disorder information of the Rw at high *P* might be completely lost. In analogy to the
635 well-known partial preservation of the high-*T* equilibrium state of the Al-Mg
636 disorder in the $MgAl_2O_4$-Sp after quenching [42,53], reordering the Si and Mg
637 cations in the Mg_2SiO_4-Sp presumably happens fast and proceeds towards its
638 completion as the high-*P* synthesizing experiment quenches. In the latter cases, the
639 bond length systematics and structural features established for ambient *P* might not
640 be applicable to the high-*P* structures. As pointed out by Méducin et al. [45], *P* has a
641 significant impact on the order-disorder process of the $MgAl_2O_4$-Sp, especially in
642 the *T* range of 477-1227 °C. Some high-*P* single-crystal XRD investigations have
643 been conducted up to ~28.9 GPa at ambient *T*, but could not shed light on the Si
644 disorder issue, partially due to the low experimental *T* potentially unable to trigger
645 the order-disorder reaction, and partially due to the low data resolution caused by
646 the similar X-ray scattering factors of Mg and Si [103,104].

647 The most likely evidences in the literature to the presence of 6-coordinated Si in
648 the Rw came from a high-*P* Raman spectroscopic investigation on synthetic
649 Mg_2SiO_4-Rw [105] and a spectroscopic study on some meteoritic Rw [62]. At *P* > ~30
650 GPa, a weak and diffusive Raman peak appeared and was interpreted as the
651 signature for the presence of Si-O-Si linkages and/or partial increase in the
652 coordination of Si [105]. We propose that this peak might belong to the MgO_4
653 groups in the Mg_2SiO_4-Rw, which would in turn indicate the presence of the SiO_6
654 groups resulted from the position exchange of the Si and Mg cations. According to
655 Chopelas et al. [106], the MgO_6 groups in the normal Mg_2SiO_4-Rw are Raman-silent,
656 and the SiO_4 groups are responsible for all the Raman peaks. Since the
657 order-disorder process in the Sp is non-convergent (i.e., the symmetry of the Sp is
658 maintained at any inversion), no new Raman peaks should be expected from the
659 SiO_6 groups in the disordered Mg_2SiO_4-Rw, exactly like what we have observed for
660 the Si-bearing $MgAl_2O_4$-Sp (Figs. 6, 7). On the line of the study about the meteoritic
661 Rw, Taran et al. [62] used a range of analytical methods including optical
662 absorption spectroscopy to investigate some synthetic $(Mg,Fe)_2SiO_4$-Rw, and two
663 compositionally homogenous but doubly-colored meteoritic Rw grains (Grain 1,
664 one part being colorless and the other part blue; Grain 2, one part being blue and
665 the other part dark blue) from two L6-type ordinary chondrites NWA 1662 and
666 NWA 463. They proposed that for the meteoritic Rw, the part with no color was
667 inverse Rw, other parts with various colors were Rw with different amounts of
668 cation inversion. In order to confirm their hypothesis, more investigation should be
669 conducted on the meteoritic Rw, which represent the best natural specimen to
670 study high-*P* structural features including the Mg-Si order-disorder state due to

much larger quench rates. Rw with various colors have been documented in many meteorites such as the L ordinary chondrites [107-111], LL ordinary chondrites [14,26], and Martian meteorites like the shergottites [32,34,37]. If the relationship among the color, composition, inverse magnitude, *P* and *T* can be adequately quantified, a fine scale for accurately estimating the shock *P-T* conditions may be derived, which may serve well the theoretical evolution models of the early solar system.

If the Rw in the LP-MTZ attained substantially higher degrees of inverse than those experimentally observed so far, the mineralogical model of the upper mantle and the nature of the 520-km and 620-km seismic discontinuities would need further careful examination. Some empirical and theoretical studies have demonstrated that the cation disorder process in the Rw leads to significantly larger thermal expansion coefficients, smaller bulk modulus, and smaller shear modulus [19,44,46,63]. As a result, a 12.5% Si-Mg disorder can decrease the seismic velocities by ~3-5% [19,46]. Direct experimental investigations on the cation inversion of the Rw at the *P-T* conditions of the LP-MTZ are therefore of high priority.

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