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Microstructural and Chemical Investigations of Presolar Silicates from Diverse Stellar Environments

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Abstract

We report the structural and chemical investigation of nine presolar silicate grains from the CH3/CB3 chondrite Isheyevo and CR2 chondrite Northwest Africa (NWA) 801. Five of these grains belong to group 1, likely condensed in low- to intermediate-mass asymptotic giant branch (AGB) stars, super-AGB stars, or core-collapse supernovae, while the remaining four grains belong to group 4 and have a supernova origin. The advanced transmission electron microscopy and associated electron spectroscopy analyses show a diverse range of chemical and structural compositions for presolar silicates. Two GEMS (glass with embedded metal and sulfide)-like silicates, each from different groups, condensed under nonequilibrium conditions in stellar outflows. Two nonstoichiometric silicates from group 1 have dissimilar formation and alteration histories. An amorphous silicate from group 1 with olivine-like [(Mg,Fe)2SiO4] composition likely formed as a crystalline olivine that subsequently amorphized in the interstellar medium. An oldhamite (CaS) grain within a stoichiometric enstatite (MgSiO3) from group 1 probably formed by heterogeneous condensation in circumstellar outflows. Of the two crystalline grains from group 4, one is an antigorite [(Mg,Fe)2Si2O5(OH)4], while the other is a nontronite [Na2Fe3(Si,Al)5O10(OH)2·nH2O], both formed as a crystalline forsterite and later altered to have hydrated silicate composition. A group-4 silicate has a chemical composition similar to a low Ca-pyroxene [(Ca,Mg)(Si,Al)2O6]. Our data imply that presolar grains from different groups can have a similar range of grain-formation conditions.

Unified Astronomy Thesaurus concepts: Circumstellar grains (239); Asymptotic giant branch stars (2100); Type II supernovae (1731); Core-collapse supernovae (304); Meteorites (1038); Silicate grains (1456); Interstellar dust (836)

1. Introduction

Presolar silicate grains condensed in diverse stellar sources are found in primitive extraterrestrial materials like chondrite meteorites and interplanetary dust particles (hereafter IDPs; Zinner 2014; Floss & Haenecour 2016). They can be identified by their highly anomalous isotopic compositions in one or more elements. While the multi-isotopic compositions of presolar silicates help to constrain the type of stellar source from which they formed, the chemical and structural analysis of these grains provide a wealth of information about the physiochemical environments at the time of their formation and deeper insights on the grain alteration history in the interstellar medium (hereafter ISM), protoplanetary nebula, or on the meteorite parent bodies. Multi-isotopic analysis, followed by mineralogical characterization of stardust silicates, has helped to increase our understanding of various stellar grain condensation environments and alteration during their passage through the ISM to a level that cannot be achieved by spectroscopic observations and modeling.

Spectroscopic observations provide evidence for the presence of silicates in circumstellar environments. Spectroscopic features of both amorphous and crystalline silicates are observed in circumstellar envelopes around young stars (for example, Waelkens et al. 1996), oxygen-rich post-AGB stars (Waelkens et al. 1996; Waters et al. 1996, Molster et al. 1999), and circumstellar disks around young stars (Malfait et al. 1998, 1999). Moreover, the presence of silicates is also reported in type-II supernova remnants (Rho et al. 2008, 2009, 2018). The mineralogy and structure of presolar silicates have been studied in primitive meteorites, IDPs, and cometary materials (Messenger et al. 2003, 2005; Floss et al. 2006; Nguyen et al. 2007; Vollmer et al. 2007, 2009; Busemann et al. 2009; Floss & Stadermann 2009; Keller & Messenger 2011; Nguyen et al. 2016; Haenecour et al. 2018) and these studies have revealed huge diversity in the structural and mineralogical compositions that could not have been determined from astronomical observations. This detailed mineralogical and structural information for presolar silicates is extremely useful in constraining condensation conditions of their parent stellar sources, understanding parent-body alteration processes, and providing inputs to the astronomical models.
The astronomical data of silicates are in the form of emission and absorption lines that are compared with laboratory spectra of silicate minerals to infer their presence in stellar environments. For instance, both amorphous and crystalline silicates show mid-infrared spectral features around 10 and 20 μm resulting from Si–O stretching and O–Si–O bending modes arising from silicate tetrahedra. Crystalline features, due to the ordered arrangement of silicate tetrahedra and the metal-oxygen vibration bands in mid-infrared wavelengths, show sharp peaks, whereas broad, smooth features indicate the presence of amorphous silicates (Jäger et al. 1998, Molster & Kemper 2005). The relative contents of Mg and Fe are possible to constrain by comparing astronomical data of dust emission with the laboratory spectra of crystalline silicates. Further, increasing Fe content in silicates decreases the sharp features of the peaks and also shifts the peaks to longer wavelengths. The vast majority of silicates (>90%) found around evolved stars are amorphous and have olivine-like [(Mg, Fe)SiO₃] compositions (Tielens et al. 1998; Kemper et al. 2001; Molster & Kemper 2005), where Fe content is present up to ~50% (Kemper et al. 2001). Conversely, crystalline silicates in circumstellar environments are found to be Mg-rich, with pyroxene [(Mg, Fe)SiO₃] compositions dominating the crystalline fraction (Molster et al. 2002). In some exceptional cases, crystalline dust can be as high as 97% around O-rich stars (Jiang et al. 2013).

Supernovae have long been assumed to efficiently produce dust in galaxies. Nevertheless, supernova dust emission is challenging to observe because of the large distances, scarcity of SNe events, and the ISM background. However, studies show the presence of Mg-rich amorphous silicate dust (Arendt et al. 2014). Several other astronomical observations have also confirmed the production of various types of dust including silicates in the remnants of type-II supernova ejecta. A large amount of cold silicate dust was detected by the Herschel Space Observatory (Matsuura et al. 2011) and later by the Atacama Large Millimeter/Submillimeter Array (ALMA; Indebetouw et al. 2014) around SN1987A. Silicate dust is also observed in supernova remnants of Cassiopeia A (Cas A; Barlow et al. 2010) and in the Crab Nebula (Gomez et al. 2012) but the exact composition of this silicate dust is not known. Silicate dust was also found in Cas A remnants using the Spitzer Space Telescope and the dust spectral fittings revealed the presence of Mg-protosilicates, MgSiO₃ and Mg₂SiO₄ (Rho et al. 2008, 2009). Supernova dust-formation models (for example, Sarangi & Chercneff 2013) have predicted the growth of silicate clusters ~500 days after the type-II SN explosion, noting that the high-mass progenitors to SNe mainly produce silicate and alumina dust. Another type-II SNe dust-formation model by Todini & Ferrara (2001) predicted condensation of MgSiO₃ and Mg₂SiO₄ dust species that also have been observed by astronomical surveys (Rho et al. 2008, 2009).

The silicate dust in the ISM is largely amorphous and Mg-rich, with the stoichiometry between olivine-like and pyroxene-like (Kemper et al. 2004; Min et al. 2007). Several mechanisms like dust amorphization due to ion bombardments (Demyk et al. 2001), dust destruction due to cosmic radiation (Jäger et al. 2003; Bringa et al. 2007), and grain–grain collision and supernova shocks (Jones & Nuth 2011) have been proposed to explain the very low fraction of crystalline silicates in the ISM.

Presolar silicate grains studied in laboratories are found in primitive meteorite matrices and in IDPs, identified by their highly anomalous O-isotopic compositions. Silicates are found to be more abundant than other presolar phases like SiC, oxide, and graphite. Coordinated analyses of these silicates by scanning transmission electron microscopy ((S)TEM) have revealed an extensive range of chemical compositions, structures, and crystallographic information and showed grains with core–shell structures that could not be anticipated from condensation theory or spectroscopic investigations (for example Stroud et al. 2009, 2013; Nguyen et al. 2016). Several of the presolar silicates identified in meteorites and IDPs have been studied by the TEM (Messenger et al. 2003, 2005; Floss et al. 2006; Nguyen et al. 2007; Vollmer et al. 2007, 2009; Busemann et al. 2009; Floss & Stadermann 2009; Keller & Messenger 2011; Bose et al. 2012; Nguyen et al. 2016; Haencour et al. 2018). The small grain size (250 nm on average) and the need for targeted sample preparation make (S)TEM measurements significantly challenging. Presolar silicates need to be extracted from the meteorite matrix following their identification by O-isotopic scans in the NanoSIMS, which, in most cases, is achieved by the focused ion-beam (FIB) lift-out technique. Structural and chemical composition of these lifted grains are then analyzed using transmission electron microscopy. During the last decade, transmission electron microscopy has undergone a profound technological revolution resulting from the development of aberration correctors, monochromators, spectrometers, sample-holders, and imaging detectors. This new “advanced microscopy” provides access to structural, chemical, and physical information with a spatial resolution better than 1 Å and a spectral resolution better than 100 meV, and is a powerful tool for investigating the structure and chemistry of presolar grains. TEM investigations have revealed that presolar silicates are more diverse, both chemically and mineralogically, than other presolar phases studied so far (Nguyen et al. 2016). The majority of the presolar silicates studied in the laboratory are amorphous and have a wide spectrum of nonstoichiometric compositions (Stroud et al. 2008, 2009; Vollmer et al. 2009; Stroud et al. 2014; Nguyen et al. 2016); also, amorphous silicates are found to have a higher Fe concentration than crystalline silicates, concordant with astronomical findings. However, these studies could not confirm whether the source of Fe in presolar silicates is primary or secondary. Equilibrium dust-condensation theory predicts the formation of forsterite and enstatite, while nonequilibrium dust-condensation model calculations indicate condensation of Fe-bearing silicates in stellar outflows (Gail & Sedlmayr 1999; Ferrarotti & Gail 2001). Bose et al. (2010) observed that the majority of silicates in the Acker 094 meteorite were Fe-rich, most likely originating in nonequilibrium processes in stellar environments. Similarly, Bose et al. (2012) also found many Fe-rich presolar silicates in ALHA77307. The authors inferred that the kinetic stellar environment was likely responsible for the Fe content observed in the grains. Several studies have also shown Fe-isotopic anomalies in presolar silicates (Mostefaoui & Hoppe 2004; Floss et al. 2008; Vollmer & Hoppe 2010; Ong et al. 2012), confirming the primary origin for the Fe in the grains studied. Alternatively, Fe can be incorporated in presolar silicates as a result of secondary alteration on the meteorite parent bodies (Floss & Stadermann 2012; Nguyen & Messenger 2014). Crystalline silicates like olivine and enstatite, a CAI-like presolar grain with concentric core–rim structure, and Mg-rich grains with core–shell structure have also been identified using...
(S)TEM analysis combined with energy-dispersive X-ray spectroscopy (Vollmer et al. 2009; Stroud et al. 2013, 2014; Nguyen et al. 2016). Presolar silicates have exhibited a more diverse range of chemical and microstructural compositions than inferred by grain condensation models or astronomical observations. Studies have also reported a few (S)TEM results that show presolar grains with unique characteristics. For instance, Stroud et al. (2013) reported a presolar grain with a core–rim structure, where the CAI-like grain is surrounded by a Mg-silicate rim. The survival of presolar silicates and GEMS grains in the LAP 02342 meteorite was inferred to be related to organic coatings (Stroud et al. 2016). The huge diversity in chemical and mineralogical compositions of presolar silicates revealed by TEM and STEM studies suggests the possibility of finding systematic differences among different stellar environments.

In this contribution, we explore the chemical and microstructural composition of nine presolar silicates from the putative AGB stars and SNe. These grains were identified in two metal-rich carbonaceous chondrites, namely Ishiyeva and NWA 801, using the oxygen isotope imaging in the NanoSIMS ion microprobe (Sanghani et al. 2021). The primary aim of this research is to provide insights into the AGB and SNe grain condensation environments using the structural and chemical compositions of presolar silicates. Microscopic investigations of presolar silicates may also shed light on the heterogeneous formation of silicate dust in stellar winds, which is also one of the issues that we would like to address in this study. Moreover, studying the composition of the matrix surrounding presolar grains could help to identify specific signatures of terrestrial or parent-body alteration and also to identify preferentially preserved or lost grain types, as suggested by Stroud et al. (2014). Understanding the grain-formation history in stellar environments and collecting information complementary to astrophysical grain condensation models are also objectives of this study via mineralogical and chemical examination of individual presolar silicates.

2. Samples and Experimental Methods

Nine presolar silicates were chosen for (S)TEM investigations from the 33 presolar oxygen anomalous grains identified by Sanghani et al. (2021). The details on the discovery of these grains and oxygen isotopic compositions of the grains studied here can be found in Sanghani et al. (2021). The grain data are plotted in the oxygen isotopic diagram in Figure 1, which shows that the grains belong to two different groups. Five of nine grains have $^{17}$O enrichment and near solar $^{18}$O composition, suggesting the formation of these grains occurred in stellar winds of low- to intermediate-mass AGB stars (Nittler et al. 1997), “super-AGB” stars (Nittler 2019; Verdier-Paolletti et al. 2019), intermediate-mass AGB stars with super-solar metallicity (Leitner et al. 2019), or a core-collapse supernova (Leitner & Hoppe 2019). In contrast, the four grains that have higher-than-solar $^{18}$O and near solar to moderate excess in $^{17}$O compositions belong to group-4 grains. Isotopic compositions of these $^{18}$O-rich grains are best explained by partial zone-mixing in type-II SNe explosions. The Sections 2.1 and 2.2 below will provide details on the preparation of thin lamellae and (S)TEM measurements.

2.1. Preparation of Thin Lamellae for (S)TEM Using the Focused Ion-beam (FIB) Technique

Since the presolar grains selected for (S)TEM analysis are embedded within the meteorite matrix, in other words, surrounded by isotopically “normal” solar system silicates, they need to be lifted out from the matrix and thinned to electron transparency for further (S)TEM investigations. Ion milling is a versatile technique for (S)TEM sample preparation, where we have control over many experimental parameters like voltage of the ions used for thinning, angle of incidence, and thickness of the deposited protection layer (Williams & Barry 2009), and the FIB is an instrument that works on the principle of ion milling. All the presolar grains for (S)TEM investigations were first analyzed in the SEM and the regions containing presolar grains were studied in detail. The secondary ion images of the grains were carefully aligned with the high-resolution secondary electron (SE) images of the same location. For this purpose, different magnifications were used to precisely locate the grains within the thin sections of the meteorite during the FIB lift-out. The presolar grain sizes ranged from $\sim 60 \times 40$ nm to $\sim 660 \times 650$ nm, determined from the SE images. Electron-transparent lamellae for (S)TEM analysis were prepared using the TESCAN LYRA3 FIB-SEM at Curtin University. The instrument is equipped with a field-emission electron source, a monoisotopic $^{69}$Ga$^+$ ion source, a SmarAct micromanipulator and a Pt gas injector system. A custom sample preparation procedure was developed to ensure the exact grain of interest was located in the $<100$ nm cross section of the TEM lamella. We utilized electron-beam deposition (EBD) of Pt to avoid surface damage caused by ion-beam deposition (IBD) and to act as a fiducial marker for targeting the grains. The width of the linear EBD line was 150 nm. It was positioned at the widest part of the grain to maximize the amount of material in the cross section. EBD has a higher C content than IBD ($\sim$60% compared to $\sim$40%) and thus it can be differentiated in SEM imaging as it appears darker. A step-by-step guide to the preparation of the lamellae is shown in Figure 2. During the first step, a Pt-cap was deposited directly onto the grain using EBD to precisely indicate the grain position in the cross section. Additionally, two EBD triangles were deposited on opposite sides of the Pt-strip that were used to indicate the distance from the grain during thinning. An IBD Pt layer (typical size $\sim 500 \times 200$ nm) was then deposited over the Pt-cap and the triangles to further prevent the ion-beam damage during the sectioning and thinning of the lamellae. A third fiducial mark consisting of a set of crosses was milled into the IBD Pt layer to aid with the targeting of the grain. From there, the lift-out was performed using conventional FIB-SEM techniques (30 kV, $>1$ nA) and the lamellae were mounted onto Cu TEM grids. The lamellae were thinned in three different steps using a Ga$^+$ ion beam with gradually decreasing voltages. At first, an initial coarse thinning was done using a 30 kV Ga$^+$ ion beam with a 300 pA current to thin down the lamellae to $\sim 200$ nm. The edges of electron-beam deposited triangle were monitored on both surfaces of lamellae throughout this step, and thinning was stopped at the point where the triangle was almost removed. Similarly, in the second step, the lamellae were thinned down to $\sim 100$ nm using a 15 kV Ga$^+$ ion beam with 90 pA current until the point when the edge of the linear Pt-strap was clearly visible. Finally, a 5 kV, 20 pA Ga$^+$ ion beam was utilized to minimize beam damage and thin the lamellae and to achieve a
final thickness <100 nm. The final thickness of lamellae was verified by doing the SEM imaging when they were in the vertical position. This method of step-by-step thinning using markers ensures that the lamellae are optimally thinned for (S)TEM investigations.

2.2. Structural and Chemical Analyses by (S)TEM

Microstructural and chemical analysis of presolar grains was performed by combining high-resolution scanning TEM (HR-STEM) imaging, spatially resolved electron energy-loss spectroscopy (SR-EELS), and spatially resolved energy-dispersive X-ray spectroscopy (EDS). These analyses were performed with an FEI Titan Cubed Themis microscope (University of Cádiz), which was operated at 200 kV. It is equipped with a double Cs aberration-corrector, a monochromator, an X-FEG gun, an ultra-high-resolution energy filter (Gatan Quantum ERS), which allows working in dual-EELS mode, and a super-X EDS detector, which consists of four windowless SDD detectors that can be read out independently. HR-STEM imaging was performed using a high-angle annular dark-field (HAADF) detector. EDS quantification was achieved using the Brown–Powell model for the ionization cross sections (Powell 1976a, 1976b). Quantification for the major elements was corrected by using a standard reference sample of known composition and density (Icelandic Basalt, BIR-1 see Flanagan 1984; Gladney & Roelandts 1988). Absorption correction was taken into account by determining the thickness of the probed area using low-loss EELS. For this purpose, the t/λ ratio (where t is the thickness of the analyzed crystal and λ is the inelastic mean-free path) was derived from the corresponding low-loss EELS data and λ was calculated using the modified Iakoubovskii formula (Egerton 2011; Lajaunie et al. 2013). The SR-EELS spectra were acquired in dual-EELS mode allowing the precise calibration of the spectra and correction of energetic instabilities by recording simultaneously low-loss and core-loss spectra. EELS acquisition was performed in spectrum imaging mode and data sets were processed using Digital Micrograph and Hyperspy programs. In particular, principal component analysis routines were used for denoising and multiple scattering was removed using the Fourier-ratio deconvolution method. For this purpose, low-loss data acquired simultaneously as core-loss spectra were used as input. For elemental quantification, SR-EELS spectra were acquired with an energy dispersion of 0.5 eV pixel$^{-1}$, an acquisition time of about 0.05 s pixel$^{-1}$, and an energy resolution of 2 eV. Convergence and collection angles were 21 and 25 mrad, respectively. EELS spectrum images for fine structures analysis (around Fe-L$_{2,3}$ and Si-L$_{2,3}$ edges

![Figure 1. Oxygen isotopic compositions of the nine grains in this study. Group classification is from Nittler et al. (1997) and the dashed line represents the solar values. B & S 1999: the first dredge-up model by Boothroyd & Sackmann (1999) (plot data from Sanghani et al. 2021).](image1)

![Figure 2. FIB section preparation of presolar silicates. (a) SE image of a presolar grain NWA 801_14 (yellow boundaries) and the approximate location of the FIB section. (b) Electron beam deposited Pt cap for grain protection and two triangular markers. (c) Ion-beam deposited Pt-strap over the Pt-cap and cross marks. (d) Ion milling to remove material from the surroundings. (e) Edge of the triangular marker as an indicator to monitor the thinning of the section. (f) HAADF image of the grain and the Pt-cap. (g) Chemical map showing the Fe-rich grain and C-rich Pt-cap.](image2)
mostly) were acquired with a dispersion of 0.05 eV pixel$^{-1}$, an acquisition time of 0.05 s pixel$^{-1}$ and with the monochromator excited allowing an energy resolution of about 0.4 eV. For the determination of Fe valence states, energy dispersion and drift were carefully calibrated using the Fe L$_3$-edge maximum of predominantly Fe$^{2+}$ and Fe$^{3+}$ samples at 707.8 eV and 709.5 eV, respectively, in agreement with previously reported values (Van Aken et al. 1998a). Chemical mapping of the Fe$^{3+}/\Sigma$ Fe ratios was then performed by using a homemade Python routine based on the method proposed by Van Aken et al. (1998a) and Van Aken & Liebscher (2002). For this purpose, a double artan function was built by setting two fixed inflexion points at 708.65 and 721.65 eV and with a width of 0.4 eV. The double artan function was fitted to the experimental spectrum in the energy range 726.4–730.4 eV and was then subtracted from the EELS data set. The modified white-line ratio $I_{\text{L3}}/I_{\text{L2}}$ was then obtained by solving the calibration equation proposed by Van Aken & Liebscher (2002): \[
I_{\text{L3}}/I_{\text{L2}} = \frac{1}{ax^2 + bx + c} - 1
\]

Where $I_{\text{L3}}/I_{\text{L2}}$ is the modified white-line ratio, x is the ratio Fe$^{3+}/\Sigma$ Fe, a is equal to 0.193, b to $-0.465$, and c to 0.366. The errors on the fitting procedure are around 5% while the errors on the precision were estimated to be around 3%–4% (Van Aken & Liebscher 2002). Overall, the standard errors on the determination of the Fe oxidation state are estimated to be below 10%. Information on the crystallinity of the grains was acquired using HR-TEM images and selected area electron diffraction (SAED). For this purpose, SAED and fast Fourier transform (FFT) patterns were automatically indexed using the JEMS software (Stadelmann 2014).

3. Results

3.1. Microstructural and Chemical Compositions of Group 1 Grains

Grain NWA 801_15: According to the SE image shown in the Appendix (Figure A1), the grain looks circular. It has a diameter of ~140 nm and is extended 50 nm below the surface (Figure 3). The composition of the grain determined by EDS analysis is given in Table 1 and it suggests that this grain is an Fe-bearing silicate with nonstoichiometric composition close to olivine. The grain has a broad Fe-rich (Fe/Si = 3.6 ± 1.3) rim at the bottom and is surface-rich in silicon (Figure 3(b)). The Mg/Si and Fe/Si ratios at the surface are 1.1 ± 0.4 and 0.8 ± 0.3, respectively. The HR-TEM image of the grain is shown in Figure 4. The presolar grain is clearly polycrystalline and is constituted by smaller grains with diameters in the range of 5–20 nm. Automatic indexation of the FFT pattern performed on a single grain shows that it can be ascribed to the olivine $Pnmm$ crystal structure (Litvin et al. 1993) as already reported for other meteorites, which is consistent with the chemical composition given by the EDS analysis. However, the low $^{28}$Si/$^{16}$O ratio [(4.8 ± 0.2) × 10$^{-3}$] obtained from the NanoSIMS analysis suggested the grain to be an oxide (Sanghani et al. 2021). This shows that the use of complementary techniques such as (S)TEM analyses are necessary to get a complete picture on the composition and origin of presolar grains. Figure 5(a) shows the EELS spectra acquired on the grain NWA 801_15 at the vicinity of the Fe-L$_{23}$ edges, and Figure 5(b) shows the corresponding Fe$^{3+}/\Sigma$ Fe chemical map. It clearly shows variations of the EELS fine structure, highlighting the chemical inhomogeneity of the grain. In particular, the right part of the surface of the grain is mostly Fe$^{2+}$ (average value of Fe$^{3+}/\Sigma$ Fe is ~0.2), although strong variations can be observed from one pixel to the other. The left part of the surface has an Fe$^{3+}/\Sigma$ Fe ratio of about 0.6. The right and lower parts of the Fe-rich rim surrounding the grain have an average Fe$^{3+}/\Sigma$ Fe ratio equal to 0.8 and 0.4,
Table 1
Elemental Compositions (at. %) of Presolar Silicates from Isheyevo and NWA 801

<table>
<thead>
<tr>
<th>Grain Name</th>
<th>O</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Fe</th>
<th>S</th>
<th>Mg#a</th>
<th>(Fe+Mg+Ca)/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>NWA801_15</td>
<td>50.4 ± 5.0</td>
<td>17.0 ± 3.8</td>
<td>1.1 ± 0.3</td>
<td>16.1 ± 3.5</td>
<td>0.7 ± 0.1</td>
<td>12.8 ± 2.1</td>
<td>...</td>
<td>56.9 ± 9.5</td>
<td>1.9 ± 0.8</td>
</tr>
<tr>
<td>NWA801_18</td>
<td>53.1 ± 5.1</td>
<td>17.3 ± 3.8</td>
<td>1.4 ± 0.3</td>
<td>15.1 ± 3.2</td>
<td>0.8 ± 0.1</td>
<td>11.1 ± 1.8</td>
<td>0.3 ± 0.1</td>
<td>68.0 ± 9.1</td>
<td>1.7 ± 0.9</td>
</tr>
<tr>
<td>NWA801_21</td>
<td>56.9 ± 5.4</td>
<td>8.2 ± 1.8</td>
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<td>16.8 ± 3.6</td>
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<td>15.4 ± 2.5</td>
<td>...</td>
<td>21.2 ± 8.7</td>
<td>0.7 ± 0.3</td>
</tr>
<tr>
<td>Isheyevo_9b</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<td>5.2 ± 1.0</td>
<td>30.4 ± 3.2</td>
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</tr>
<tr>
<td>Isheyevo_9c</td>
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<td>12.7 ± 2.7</td>
<td>0.3 ± 0.1</td>
<td>13.5 ± 2.8</td>
<td>1.4 ± 0.2</td>
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<td>1.1 ± 0.5</td>
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<td>NWA801_23</td>
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<td>12.2 ± 4.7</td>
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<td>11.0 ± 2.3</td>
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<td>0.1 ± 0.1</td>
<td>67.0 ± 13.7</td>
<td>2.2 ± 0.7</td>
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SN Grains

<table>
<thead>
<tr>
<th>Grain Name</th>
<th>O</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Fe</th>
<th>S</th>
<th>Mg#a</th>
<th>(Fe+Mg+Ca)/Si</th>
</tr>
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<tbody>
<tr>
<td>NWA801_14</td>
<td>63.2 ± 6.4</td>
<td>2.7 ± 0.6</td>
<td>1.6 ± 0.4</td>
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<td>10.4 ± 3.7</td>
<td>2.7 ± 1.1</td>
</tr>
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<td>NWA801_17</td>
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<td>1.0 ± 0.2</td>
<td>15.6 ± 3.4</td>
<td>0.4 ± 0.1</td>
<td>5.2 ± 0.9</td>
<td>...</td>
<td>68.7 ± 8.7</td>
<td>1.1 ± 0.5</td>
</tr>
<tr>
<td>NWA801_20</td>
<td>53.1 ± 5.0</td>
<td>13.2 ± 2.9</td>
<td>1.5 ± 0.3</td>
<td>19.4 ± 4.2</td>
<td>2.6 ± 0.4</td>
<td>9.1 ± 1.5</td>
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<td>59.1 ± 3.2</td>
<td>1.3 ± 0.6</td>
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<td>Isheyevo_4</td>
<td>57.3 ± 6.8</td>
<td>25.8 ± 6.0</td>
<td>0.4 ± 0.1</td>
<td>15.2 ± 3.4</td>
<td>0.1 ± 0.1</td>
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<td>...</td>
<td>95.7 ± 0.6</td>
<td>1.8 ± 0.8</td>
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</table>

Notes.

a Mg# is defined as [(Mg/(Mg+Fe))]100.
b Isheyevo_9 grain with an oldhamite-like composition.
c Isheyevo_9 grain with an enstatite composition.

Figure 4. HR-TEM image of the grain NWA 801_15; the red square highlights the area used to calculate the FFT pattern shown in the inset. Automatic indexation was obtained with the olivine Phnom crystal structure observed along the [125] zone axis (Litvin et al. 1993).

respectively. However, the silicon L2,3 edge fine structures (Figure A2 in the Appendix) are similar to previously reported silicate fine structures (Garvie et al. 1994), which confirms the silicate nature of the grain.

Grain NWA 801_18: This grain appears with a bright contrast in the SE image and has a platy-smooth surface morphology (Figure 6(a)). It has a circular shape with a diameter of 280 nm and extends ~150 nm below the surface (Figures 6(b) and (d), respectively). The average composition of the grain determined by EDS analysis is given in Table 1. Compared to the surrounding matrix, this grain is Mg-rich (Mg/Si = 1.2 ± 0.4) and Fe-poor (Fe/Si = 0.7 ± 0.3), the corresponding values being around 0.3 ± 0.2 and 1.5 ± 0.4 for the matrix, respectively. STEM-EDS measurements show that the major elements are homogeneously distributed within the grain. In addition, small metal and metal sulfide inclusions with a diameter of about 30-50 nm are observed within the grain and in the surrounding matrix. The SR-EELS measurements in the vicinity of Fe-L2,3 edges indicate a mix of Fe2+ and Fe3+ oxidation states (Figure A3, Appendix) with an Fe3+/Σ Fe ratio measured on the whole grain equal to 0.4. Comparatively higher thickness of the lamella hindered HR-TEM and Si-L23 analyses.

Grain NWA 801_21: The grain has an irregular shape and a size of ~160 × 150 nm (from SE image). The grain is extended to only ~25 nm below surface, as shown in the STEM-EDS map (Figure 7). The chemical composition is heterogeneous within the grain. The grain surface up to 10 nm depth is rich in silicon (Mg/Si = 0.2 ± 0.1 and Fe/Si = 0.5 ± 0.2 in at. %), while below surface between 10 and 25 nm, the grain is rich in Mg and Fe (Mg/Si = 1.1 ± 0.4 and Fe/Si = 1.3 ± 0.5 in at.%). The increase in the Fe content (Fe/Si = 0.6 to 2.4 at. %) is seen while moving inward from the grain surface, accompanied by an increase of the Fe3+/Σ Fe ratio (from 0.1 to 1.0). The Fe3+/Σ Fe ratio of the presolar grain close to the surface is about 0.1. Moreover, the Si- L2,3 edges of the grain have fine structures that are characteristic of silicates (Figure A4, Appendix).

Grain Isheyevo_9: This is the biggest of all the putative AGB grains in this study. As seen from the SE image in plane-view orientation (Figure A5, Appendix), this grain has an ovoid shape, with a platy-smooth surface and a size of 370 × 350 nm. The STEM HAADF image of the sample prepared in cross section geometry (Figure 8(a)) shows that the grain is extended up to 290 nm below the surface. As seen from the EDS analyses (Figures 8(b)–(f)), the grain corresponds to a local increase in Mg and a local decrease in Fe with respect to the surrounding matrix. The grain surface of up to ~40 nm is composed of Ca and S (Ca/S = 1.5 ± 0.5 at. %). The chemical composition of the grain below the Ca-rich surface grain is similar to homogeneous stoichiometric enstatite with Mg/Si = 0.9 ± 0.4 at. % and very low Fe composition (Fe/Si below 0.1). In addition, the automatic indexation of the
FFTs performed on single nanoparticles also confirmed the extent of enstatite and olivine phases. The Si-edge data from the STEM-EELS analysis confirms the presence of silicate tetrahedra from the enstatite grain. Below the surface of the grain and on the left side, diffusion streaks rich in Ca can be observed up to the lower boundary of the grain (on about 250 nm, see Figure 8(b)). Figure A6 in the Appendix shows typical EELS spectra acquired on several areas of the grain and Figure 9 shows the corresponding elemental maps extracted from the EELS data set. Feature corresponding to the F-K edges can be highlighted in some part of the grain whereas the Fe-L23 signal is really weak with regard to the surrounding matrix (Appendix Figures A6 and 9(a) and (d)). The right part of the presolar grain shows an increase in Fe at. % whereas the left part, which showed Ca diffusion streaks, presents an increase in O (Figures 9(b) and (d)). In addition, the O-K edge fine structures show some variations within the grain. In particular, an intense oxygen pre-peak can also be highlighted in the lower part of the presolar grains, which will be discussed later (Appendix Figures A6 and 9(c)). In addition, an Fe-rich rim of varying thickness (<10 nm) is also seen around the enstatite grain with an Fe\(^{3+}/\Sigma\) Fe ratio of about 0.6-0.7. The presence of several spherical nodules (30-45 nm in size) of Fe and Ni sulfide can also be highlighted in the matrix around the grain in the EDS and EELS chemical maps (yellow and white arrows in Figures 8 and 9, respectively). Interestingly, they present a core/shell structure that can clearly be highlighted in the EELS chemical maps (white arrows in Figure 9). The shell has a thickness of about 10 nm and corresponds to an increase of (i) the oxygen content, (ii) intensity of the O-K pre-peak, and (iii) of the Fe\(^{3+}/\Sigma\) Fe ratio (0.3 and 0.6 for the core and shell parts, respectively). HR-TEM micrographs taken on the Ca-rich area of the grain highlights the presence of small nanoparticles with a diameter of about 10–20 nm (Figures A7 and A8 in the Appendix).

Grain NWA 801_23: This grain has an irregular-shaped grain and a size of about 300 × 270 nm as seen in the SE image in plane-view orientation. STEM imaging and EDS analysis reveal that the grain is extending between 20 and 80 nm down the surface (Figure 10). The atomic ratios of Mg/Si and Fe/Si are equal to 1.1 ± 0.5 and 1.0 ± 0.4, respectively, and close to a near stoichiometric olivine ((Mg+Fe)/Si = 2.1 ± 0.8). However, the right part of the grain has Mg-rich composition (Mg/Si = 1.5 ± 0.3 and Mg/Fe = 0.7 ± 0.3 in at.%). STEM-EDS maps show that the grain is surrounded by an Fe-rich rim predominating below the Mg-rich part of the grain. STEM-EELS analysis shows that the Fe\(^{3+}/\Sigma\) Fe ratio of the grain is about 0.5, whereas the ratios for the lower and left rims are 0.8 and 0.7, respectively.

3.2. Microstructural and Chemical Compositions of Supernova Grains

Grain NWA 801_14: The grain appears irregular in the plane view and has a size of about 420 × 420 nm as seen in the SE micrograph (Figure 12(a)). It is extending up to 240 nm below the surface (Figure 12(b)). The presolar grain corresponds to highly Fe-rich (Fe/Si = 2.4 ± 0.8 at. %) and Mg-poor (Mg/Si = 0.3 ± 0.1 at. %) areas with respect to the surrounding matrix (Figure 12(c)), the corresponding values for the matrix being equal to 0.9 ± 0.4 and 0.5 ± 0.2, respectively. A Mg- and Si-rich rim, prominent on the left side of the grain, is seen in the STEM-EDS chemical maps. Nodules rich in Ni and S are also spotted in the right part of the spectrum image (Figure A9, Appendix). STEM-EELS analysis shows that the grain is mostly Fe\(^{3+}\) (Fe\(^{3+}/\Sigma\) Fe ratio ~0.9, whereas the ratios for the surrounding grains on the left and right side have a Fe\(^{3+}/\Sigma\) Fe ratio of about 0.6. It should be noted that some areas with zero values of the Fe\(^{3+}/\Sigma\) Fe ratio can be highlighted in the lower part of the spectrum image and correspond to thick areas which hindered the proper multiple scattering removal. The grain is crystalline and interpretation of selected area electron diffraction patterns, and of the FFT patterns obtained from the HR-TEM micrographs suggest the presence of a nontronite [Na\(_x\)Fe\(_y\)(Si,Al)\(_{10}\)(OH)\(_{2}\)\(_2\)nH\(_2\)O] crystal structure (Figures A10 and A11, Appendix). This is also in good agreement with the Fe\(^{3+}/\Sigma\) Fe ratio determined by EELS.

Grain NWA 801_17: The grain is irregular in shape and the size of the grain in plane-view is 180 × 170 nm. The grain extends below the surface up to 80 nm. Compared with the surrounding matrix, the presolar grain is Mg- and Si-rich and Fe-poor [Mg/Si (at. %) = 0.7 ± 0.3 and Fe/Si (at. %) = 0.3 ± 0.1]. The values for the matrix on the left side of the presolar grain are equal to 0.1 ± 0.1 and 1.5 ± 0.5 for Mg/Si and Fe/Si ratios, respectively. The chemical composition of the
Table 2
STEM-EDS and STEM-EELS Data of Presolar Silicates from Isheyevo and NWA 801

<table>
<thead>
<tr>
<th>Grain</th>
<th>Non-stoichiometric Silicate</th>
<th>Mg-rich GEMS-like</th>
<th>Fe-rich nonstoichiometric Silicate</th>
<th>Oldhamite/Enstatite</th>
<th>Olivine-like Silicate</th>
<th>Structure</th>
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<tbody>
<tr>
<td>NWA 801_15</td>
<td>Non-stoichiometric Silicate</td>
<td>Grain Mix of Fe$^{2+}$ and Fe$^{3+}$</td>
<td>Grain Fe$^{2+}$</td>
<td>Grain surface 0.1</td>
<td>Grain Fe$^{3+}$</td>
<td>Polycrystalline (&lt;20 nm individual subgrains)</td>
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<td>Putative AGB Grains</td>
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<tr>
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<td>Grain</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Grain</td>
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<td>S-rich grain</td>
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<td>Fe/Si 2.4 ± 0.9</td>
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<td>Mg-rich grain Fe$^{3+}$</td>
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<tr>
<td>Fe/Si 2.4 ± 0.9</td>
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<tr>
<td>Grain</td>
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<td>Grain surface 0.1</td>
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<tr>
<td>Mg/Si 0.9 ± 0.3</td>
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<tr>
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<td>Grain</td>
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<td>Enstatite</td>
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<td>Grain</td>
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<td>Mg/Si 0.9 ± 0.3</td>
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<td>Fe$^{3+}/Σ$ Fe</td>
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<td>Mg/Si 0.3 ± 0.1</td>
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Table 2 (Continued)

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<th>STEM-EDS Quantification (at.%)</th>
<th>STEM-EELS Structure</th>
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<td>GEMS-like</td>
<td>Ca–Fe Silicate, Grain Fe²⁺, Surrounding Fe³⁺ (Variable)</td>
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<td>Mg/Si 0.7 ± 0.3, Fe/Si 0.3 ± 0.1</td>
<td>Matrix</td>
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<tr>
<td>NWA 801_20</td>
<td>Low Ca-pyroxene</td>
<td>Surface Fe²⁺, Grain Fe³⁺ (with some Fe²⁺), Surrounding Fe³⁺</td>
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<tr>
<td>Grain</td>
<td>Mg/Si 0.7 ± 0.3, Fe/Si 0.5 ± 0.2, Ca/Si 0.1 ± 0.1</td>
<td>Fe-rich Grain</td>
</tr>
<tr>
<td>Isheyevo_4</td>
<td>Antigorite Silicate</td>
<td>Fe³⁺</td>
</tr>
<tr>
<td>Grain</td>
<td>Mg/Si 1.7 ± 0.8, Fe/Si 0.1 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

grain is heterogeneous as seen in EDS and EELS maps. In particular, the core part of the grain is rich in fluorine and shows some deficiency in Fe on the left side (Figures 13(e) and (f)). The EELS Fe-L2,3 signal is homogeneous on the whole grain and corresponds to a Fe^{2+} signature (Figure 13(g) and Appendix Figure A12).

**Grain NWA 801_20:** This irregular-shaped grain is very small in size. The plane view of the grain is 60 × 40 nm and extends 70 nm down the surface. The presolar grain corresponds to a Ca-rich area sandwiched between Mg-rich and Fe-rich grains (Figure 14(c)). The Ca/Si ratio is equal to 0.1 ± 0.1 for the presolar grain. The grain composition is similar to a low...
Ca-pyroxene with \((\text{Mg}+\text{Fe}+\text{Ca})/\text{Si} = 1.3 \pm 0.6\) in at.%. It should also be noted that the surface of the presolar grain is richer in fluorine than the surrounding grains (Figure A13, Appendix). The average \(\text{Fe}^{3+}/\Sigma\text{Fe}\) ratio of the presolar grain is about 0.6. However, the local chemical order is inhomogeneous and strong variations of the Fe–L2,3 fine structures are observed from one pixel to another. The Fe-rich neighbor grain is mostly \(\text{Fe}^{3+}\); however, variations of the \(\text{Fe}^{3+}/\Sigma\text{Fe}\) ratio can be highlighted at the surface (\(\text{Fe}^{3+}/\Sigma\text{Fe} \sim 0.3–0.4\)).

**Grain Isheyevo_4:** This presolar grain is irregularly shaped and extends up to 155 nm below the surface. Compared with the surrounding matrix, the grain is Mg-rich and Fe-poor (\(\text{Fe}/\text{Si} = 0.1 \pm 0.1\) in at. %). The \(\text{Mg}/\text{O}, \text{Si}/\text{O},\) and \(\text{Mg}/\text{Si}\) ratios for Isheyevo_4 are equal to 0.45 \(\pm 0.20, 0.27 \pm 0.10,\) and \(1.7 \pm 0.8\). The surrounding environment of the grain has an \(\text{Fe}^{3+}/\Sigma\text{Fe}\) ratio of about 0.8. The Fe concentration of the grain is too low to allow a spatially resolved determination of the iron oxidation state. However, it can be noted that the average Fe–L2,3 response of the grain is similar to that of the surrounding environment (Figure A14, Appendix). Analyses of the EELS O–K edge fine structure show that the oxygen atoms of the Mg-rich grain present a different local chemical environment than for the surrounding grains and highlight the presence of hydrated minerals (Figure A15, Appendix). In addition, silicon L2,3 edge fine structures are also similar to the fine structure of silicates (Garvie et al. 1994; Figure A16, Appendix). HR-TEM micrographs highlight the crystalline nature of the presolar grain (Figure A17, Appendix). Automatic indexation of the FFT pattern using the JEMS software can be successfully obtained with both the crystalline structures of talc (Gruner 1934) and antigorite (Uehara 1998), which are hydrated silicate minerals. However, the EDS composition of Isheyevo_4 is closer to an antigorite \([\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]\) composition than to the talc composition with the \(\text{Mg}/\text{O}, \text{Si}/\text{O},\) and \(\text{Mg}/\text{Si}\) ratios for the antigorite being equal to 0.33, 0.22, and 1.50, respectively.

### 4. Discussion

#### 4.1. Silicates from AGB Stars

Spectroscopic observations have shown that silicate dust grains condense in oxygen-rich (O/C > 1) circumstellar dust shells around AGB stars (for example, Groenewegen et al. 1995) with high mass-loss rates. The relative abundance of Mg and Si in stellar envelopes is a determining factor for the composition of silicate dust that forms in the dust shells (Ferrarotti & Gail 2001). Equilibrium condensation calculations predict the formation of Mg-rich silicates (forsterite, \(\text{Mg}_2\text{SiO}_4\) and enstatite, \(\text{MgSiO}_3\)) around stars when \(1 \lesssim \text{Mg}/\text{Si} \lesssim 2\), and around 90% of the observed stars have such conditions (Ferrarotti & Gail 2001). However, for the remaining stars, the relative abundance of Mg and Si is
different ($\text{Mg}/\text{Si} \lesssim 1$), and a mixture of enstatite and quartz is formed (Ferrarotti & Gail 2001). However, it should be noted that the formation of Fe-bearing silicates is possible when the stellar outflows are not in chemical equilibrium.

Dust is generally known to condense on a tiny seed nucleus that acts as a nucleation site for later growth (Ferrarotti & Gail 2001). Laboratory studies of presolar silicates show a few grains with core–shell (rim) structure or grains made of two or more subgrains, the so-called complex/composite grains (Vollmer et al. 2009; Bose et al. 2012; Floss & Stadermann 2012; Nguyen et al. 2014; Sanghani et al. 2021). According to equilibrium condensation theory, oxide grains such as TiO$_2$ and Al$_2$O$_3$ could work as a nucleation site for silicate grain growth in circumstellar environments (Nguyen et al. 2014). The difference in elemental phase for the core and the shell could possibly be generated if the composition of the gas changes during grain condensation, as discussed by Vollmer et al. (2009). Also, Bose et al. (2012) suggested that subgrains within a composite grain with similar isotopic compositions but different chemical composition might imply the decoupling of isotopic and elemental compositions of grain-formation environments.

After their formation in stellar outflows, the structure (and composition) of silicate dust may possibly change in circumstellar and interstellar environments and also during the accretion of the protoplanetary disk around young protostars. Calculations by Sogawa & Kozasa (1999) showed that heterogeneous grains with corundum (Al$_2$O$_3$) cores and silicate mantles can be completely crystallized by thermal processing, whereas homogeneous silicate grains remain amorphous. Experimental studies on silicates suggested that Mg-rich amorphous silicate grains turn crystalline around temperatures 1000–1100 K within a month (at most), while Fe-rich silicates require higher temperatures ($>1300$ K) to anneal (Nuth et al. 2002). Experiments by Nagahara et al. (2009) showed that amorphous Mg-rich nonstoichiometric silicates condensed at $\sim 500^\circ$C by rapid cooling, and their chemical composition is determined by gas kinematics and local gas composition from which they are condensed. The authors further suggested that stoichiometric amorphous silicates are formed from crystalline silicate that is damaged because of radiation exposure due to cosmic rays. Silicate dust grains are also destroyed in the ISM on timescales of $\sim 10^8$ yr (Jones et al. 1994, 1996). The major dust destruction processes in the ISM include sputtering (due to gas–grain collisions) and vaporization (due to gas–gas

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**Figure 9.** Chemical maps derived from the EELS analysis for the grain Isheyevo_9 and corresponding to (a) Fe, (b) O, (c) the O–K pre-peak, (d) F and (e) the Fe$^{3+}/\Sigma$Fe ratio. The white scale bar represents 0.08 $\mu$m. The white arrows highlight the presence of GEMS-like materials.
amorphization are ion implantation (Demyk et al. 2001) and long-term cosmic-ray exposures (Jäger et al. 2003; Brinja et al. 2007).

Of the five putative AGB (group 1) grains in this study, NWA 801_15 is a Mg-rich nonstoichiometric ferromagnesian silicate. The olivine-like chemical composition of the grain is suggestive of formation under variable conditions in stellar environments. The microstructure and chemical composition of NWA 801_15 is comparable to the grains investigated by Stroud et al. (2008, 2009) and indicative of formation under complex nonequilibrium conditions in stellar outflows. In addition, Vollmer et al. (2009) also reported RGB/AGB silicates forming in nonequilibrium conditions at \(\sim 1000^\circ\text{C}\). The grain NWA 801_15 likely condensed as an amorphous olivine in nonequilibrium conditions close to \(1000^\circ\text{C}\) in stellar outflows. The polycrystalline structure of NWA 801_15 points toward thermal annealing experienced by the grain. While low-temperature crystallization in circumstellar disks (Molster et al. 1999) could not be completely ruled out, the amorphous olivine precursor of grain NWA 801_15 possibly turned polycrystalline due to nebular shock waves triggered by gravitationally instabilities in the PPD at 5–10 au from the proto-Sun (Harker & Desch 2002). Alternatively, the grain could also be thermally annealed within 1 au from the proto-Sun where temperatures \(\geq 1000\) K were achieved (Bell et al. 1997). However, this scenario requires radial transport of material from the inner part to the outer part of the disk, which seems less likely in the case of the grain NWA 801_15. Furthermore, the rim and surrounding matrix has a higher Fe/Si ratio and high \(\text{Fe}^{3+}/\Sigma\text{Fe}\), indicative of the higher order of aqueous alteration experienced by the rim and the surrounding matrix grains (Keller & Messenger 2012, Hopp & Vollmer 2018).

Another Mg-rich amorphous silicate grain, namely NWA 801_18, also has homogeneous chemical composition. The average Mg/Si and Fe/Si ratios are comparable to the GEMS grains in the IDPs and GEMS-like grains in carbonaceous chondrites (Messenger et al. 2003; Nguyen et al. 2007; Keller & Messenger 2008; Vollmer et al. 2009; Keller & Messenger 2011; Nguyen et al. 2016). In addition, the metal and sulfide grains found within NWA 801_18 further confirms the grain to be a GEMS-like one. The majority of GEMS grains display solar isotopic compositions, while a minor population of GEMS grains demonstrate isotopic anomalies exhibiting their circumstellar origin (Messenger et al. 2003). The grain NWA 801_18 is fairly similar in chemical composition and appearance to the GEMS-like grains reported by Vollmer et al. (2009), and likely condensed under strong nonequilibrium conditions with comparably low Fe content (\(\sim 11\) at%). Also, the grain NWA 801_18 might not be significantly affected by ion irradiation and sputtering processes as proposed by Keller & Messenger (2008). The presence of trivalent Fe along with \(\text{Fe}^{2+}\) within the grain likely reflects a parent-body oxidation reaction (Keller & Messenger 2012).

The grain NWA 801_23 has an amorphous structure, with a homogeneous composition of the grain resembling near stoichiometric olivine. Silicates with high Mg content condense under equilibrium conditions in stellar outflows at temperatures \(\sim 1000\) K (Gail 2003; Min et al. 2007). However, this equilibrium may not be maintained when the temperature drops as a result of the outward motion of gas and dust due to radiation pressure and Fe starts incorporating into the condensing silicate grains (Gail & Sedlmayr 1999; Gail 2003). Once formed in the stellar outflows, crystalline silicates can be amorphized in the ISM and later thermal annealing of amorphous silicates in the solar nebula could explain the higher fraction of crystalline silicates found in meteorites.
Nguyen et al. (2016). Also, Vollmer et al. (2009) proposed ISM amorphization to explain the mineralogy of a silicate with a core–rim structure. Using the results of ion irradiation experiments, Demyk et al. (2001) inferred that Mg-rich olivines and other crystalline silicates can be amorphized by irradiation of He\(^{+}\) ions (>4 keV) with >400 km s\(^{-1}\) velocity in a supernova shock wave. It is likely that the grain NWA 801_23 condensed as a crystalline olivine or stoichiometric silicate in a stellar environment which was not highly variable. Specifically, the grain condensation temperature would not have changed abruptly. The grain was subsequently amorphized by ion irradiation in the ISM, retaining its chemical composition (Keller et al. 2005). The grain probably escaped high-temperature (>1000°C) thermal metamorphism in the solar nebula or during the secondary processing that would have led to its crystallization. Presuming the grain formed as an olivine, Fe\(^{3+}\) in the grain suggests that it may have experienced oxidation during parent-body processing.

The Grain NWA 801_21 is a nonstoichiometric silicate with comparably high Fe content (∼15 at%), compatible with many of the presolar silicates with relatively high Fe contents (for example, Bose et al. 2010). The origin of Fe in presolar silicates is poorly constrained and studies have suggested that either a primary condensation or a secondary alteration is responsible for Fe enrichment (Floss et al. 2008; Vollmer et al. 2009; Bose et al. 2010; Nguyen et al. 2016; Leitner et al. 2020). The Fe-rich silicates condense in nonequilibrium grain-formation conditions in circumstellar outflows (Vollmer et al. 2009; Bose et al. 2010). The radiation pressure from the star drives gas and dust in an outward direction, rapidly decreasing the temperature. In this condition, equilibrium might not be maintained, and a significant amount of Fe can be incorporated.

Figure 12. (a) SE image of the grain with FIB section mark of the grain NWA 801_14. (b) STEM HAADF image of the same grain; the green line highlights the boundary of the grain. (c) EDS elemental maps of the grain corresponding to the Mg, Si, and Fe elements. (d) Fe\(^{3+}/\Sigma\) Fe chemical map determined from the EELS data set.
in the silicate grains that are condensing (Gail & Sedlmayr 1999; Ferrarotti & Gail 2001). Several of the laboratory experiments also support this scenario (Rietmeijer et al. 1999; Nuth et al. 2000). The experiments by Rietmeijer et al. (1999) further indicated that the silicates with Fe–Si compositions (ferrosilica) and Mg–Si compositions (magnesiosilica) form directly from the vapor, whereas grains with Mg and Fe compositions are not among the primary condensates. It is likely that the grain NWA 801_21 with intermediate Mg–Fe composition is not a primary condensate. Secondary processes responsible for Fe-enrichment include Fe ion implantation and parent-body processes like aqueous alteration and thermal metamorphism. The Fe ion implantation preferentially removes Mg and Si as compared to Fe from the silicate grain (Jones 2000). It is possible that the Fe ion implantation into the grain NWA 801_21 is responsible for the Fe-rich composition (Mg# = 35) of the grain. However, the Fe content at the surface of the grain is lower compared to the region below the surface, suggesting that Fe implantation in the grain might not have occurred. Enrichment of Fe can in the grain can also happen if the Fe is injected into the grain via fluid–mineral interaction (Le Guillou et al. 2015) or diffusion (Vollmer et al. 2009 and references therein) due to aqueous alteration or thermal metamorphism. Floss & Stadermann (2009) have thoroughly discussed Fe enrichments in silicate grains. The formation of Fe-bearing silicates in solar nebula is unlikely because of the very slow diffusion rates (Palme & Fegley 1990). Moreover, Abreu & Brearley (2008) explain that because of the gradual removal of Fe from the fine-grained material, aqueous alteration is likely not responsible for Fe enrichment in silicate grains. Terrestrial hot-desert weathering could also enhance Fe abundance in presolar silicates. Bland et al. (1998) suggested that terrestrial weathering could be responsible for Fe enrichment in presolar silicates from Acfer 094. Sanghani et al. (2021) found cracks and alteration veins likely due to terrestrial weathering in the fine-grained rims around chondrules (FGRs) in NWA 801 containing presolar grains. In addition, Sanghani et al. (2021) inferred that preferential destruction of silicates due to terrestrial weathering could also be the reason for the low silicate-to-oxide ratio observed for the FGRs in NWA 801. Hence it is more likely that the comparably high Fe content observed for the grain NWA 801_21 is due to terrestrial weathering experienced by the NWA 801 meteorite.

The Isheyevo_9 grain is a unique compound grain consisting of an oldhamite-like (CaS) grain within an enstatite grain. From the possible scenarios for oldhamite formation, nebular condensation (Lodders & Fegley 1993) and igneous crystallization (Hsu 1998) could be ruled out as the formation of a very high-temperature phase within a presolar enstatite in the solar nebula is unlikely. A recent study by Haberle & Garvie (2017) suggested the in situ formation of oldhamite in the

Figure 13. SE and STEM images of the grain NWA 801_17. (a) SE image of the grain; the location of the FIB section is marked with dashed line. (b) STEM HAADF image of the grain with the outer boundary marked with a green line. (c) Elemental map of the grain by EDS. (d) Dark-field image of the grain (e) and (f) EELS map of Fe and F for the grain. (g) EELS Fe L2,3 edges of the grain.
Sutter’s Mill carbonaceous chondrite as a result of thermal metamorphism of calcite. This study showed that oxide sulfidation of CaO occurs above 700°C to form CaS. However, the thermal metamorphic temperature of Isheyevo A clasts did not reach such high temperatures (Bonal et al. 2010) and therefore in situ formation is probably not a viable scenario for oldhamite formation within the grain Isheyevo 9. Oldhamite has also been suggested to form as circumstellar dust around stars with high C/O ratios (Gilman 1969). Further, Hynes et al. (2011) found oldhamite subgrains with close-to-stoichiometric compositions within presolar SiC grains (AB type) and one possible stellar source of such grains is a J-type star.

Figure 14. SE and STEM images of the grain NWA 801_20. (a) SE image and approximate FIB section location. (b) STEM HAADF image of the grain (highlighted by a red circle). (c) Mg, Si, Ca, and Fe EDS elemental maps. (d) Fe$^{+3}$/ΣFe map. The red circle highlights the presolar grain and the pink circle highlights variations in the values of Fe + 3/ΣFe.
J-type stars are unique C-rich stars with O-rich atmospheres. Spectroscopic observations by Lloyd Evans (1990) have confirmed the presence of silicate dust shells around J-type C stars, hence indicating that the formation of O-rich dust around a carbon star is possible. The oldhamite in Isheyevo_9 likely formed first in the dust-forming outer envelopes of the parent star (possibly a J-type) and acted as a seed nucleus, and later, the enstatite was formed. In fact, the oxygen isotopic ratios of a J-type carbon star (T LYr) matches considerably well with the observed isotopic ratios of Isheyevo_9 (Harris et al. 1987). The $^{17}$O/$^{16}$O ratio and $^{18}$O/$^{16}$O ratio observed for Isheyevo_9 are quite close to the upper limits of the respective ratios for the J-type carbon star T LYr. Hence, it is likely that the parent star of the grain Isheyevo_9 is a J-type carbon star with a mass and metallicity close to the star T LYr. Further, STEM EDS data show that oldhamite has a near stoichiometric composition and nanocrystalline structure. In contrast, the enstatite grain has a close-to-stoichiometric chemical composition with a predominant amorphous structure. Studies have found silicate grains with a nanocrystalline core and an amorphous mantle (Vollmer et al. 2009; Nguyen et al. 2014). Vollmer et al. (2009) proposed that such grains could have formed by amorphization of the originally crystalline grain in the ISM. Alternatively, amorphous enstatite could also condense on the oldhamite grain. However, it is more likely that the enstatite condensed as a crystalline enstatite and subsequently amorphized in the ISM, given the stoichiometric composition of the enstatite.

Moreover, an oxygen pre-peak is also observed for Isheyevo_9. The interpretation of such an O–K pre-peak is subject to controversy in the literature. It was first suggested that it could be ascribed to the presence of water and OH groups (Wirth 1997). However, other authors suggested that it could be related to band-structure effects or even to the presence of O$_2$ created by electron irradiation processes (Garvie 2010; Van Aken et al. 1998a; Winkler et al. 2013). However, electron-beam damage in minerals is achieved more readily in the presence of OH groups and H$_2$O and thus this pre-peak could be a signature of altered hydrated minerals (Nasdala et al. 2009; Garvie 2010). This hypothesis is supported by the fact that only the left part of the grain shows the presence of the O–K pre-peak and that the pre-peak chemical maps cannot be ascribed to the thickness variation of the sample ($t/\lambda=0.8\pm0.1$ for the presolar grain; see Figure A18, Appendix) which would lead to preferential beam damage. Also, the left part of the Fe-rich rim surrounding the enstatite grain has higher values of Fe$^{3+}/\Sigma$ Fe, highlighting the aqueous alteration that occurred in part of the sample. In

Figure 15. SE and STEM images of the grain Isheyevo_4. (a) SE image of the grain with FIB section marked. (b) STEM HAADF image showing the grain (green boundary). (c) HR-TEM image of the grain; the white square highlights the area used to calculate the FFT pattern shown in the inset. (d) EDS elemental map of the grain; scale bar represents 50 nm. (e) EELS Fe map of the grain and surrounding.
addition, the Fe–Ni metal sulfide nodules observed within the matrix show core–shell structure due to the aqueous alteration. The exterior shell shows a higher oxygen content, higher Fe$^{3+}/\Sigma$ Fe values, and higher intensity of the O pre-peak. All these results highlight the process of aqueous alteration undergone by the presolar grain and the surrounding matrix. The F and O chemical maps are in spatial opposition: the right part of the grain is richer in F whereas the left part is richer in O. The left part of the grain is also more affected by aqueous alteration than the right part (Ca diffusion streaks, presence of the O–K pre-peak) suggesting that the presence of F is an original feature of the presolar grain and that the aqueous alteration led to a washing out of the fluorine from the structure and a substitution of fluorine by oxygen. The presence of F has been confirmed by EELS for several presolar grains: Isheyevo 9, NWA801_23, NWA801_17, and NWA801_20. The first two grains have been identified as belonging to low- to intermediate-mass AGB stars, “super-AGB” stars, intermediate-mass AGB stars with super-solar metallicity, or a core-collapse supernova. The last two grains have been identified as resulting from type-II SNe explosions. The cosmic origin of fluorine is still not well constrained and the main possible production sites of fluorine are still a matter of debate (Abia et al. 2015; Grisoni et al. 2020; Ryde 2020; Ryde et al. 2020). It was suggested that several processes are need to explain the presence of fluorine at different metallicities including AGB stars and nu-process in conventional Type-II supernovae explosions (Grisoni et al. 2020; Ryde 2020). Our current work supports multiple cosmic origins of fluorine.

### 4.2. Silicates from Supernovae

Four presolar silicates belonging to group 4 are supernova grains (Sanghani et al. 2021), investigated in this study for their microstructural and chemical compositions. The grains are described below, including a detailed discussion on the possible formation and alteration scenario of each grain.

The grain NWA 801_17 is a GEMS-like grain, and likely condensed in nonequilibrium conditions from stellar outflows (Vollmer et al. 2009). Comparably low Fe content (~5 at%) is suggestive of formation in an Fe-depleted stellar environment. Nanocrystalline Fe minerals observed within the grain are similar to the homogeneous glass 14_2_3a described by Vollmer et al. (2009). These Fe mineral grains probably formed as individual crystallites and seem to define zoning within the grain. STEM-EELS results of the Si edge are suggestive of a Ca–Fe silicate. The oxidation state of Fe within the grain is $\text{Fe}^{2+}$, typically observed for GEMS grains, indicating grain formation in a reducing environment.

The grain NWA 801_20 has a pyroxene-like composition with low Ca content. Presolar silicates with Ca content are also found in several other studies (Floss & Stadermann 2009; Vollmer et al. 2009; Bose et al. 2010; Zhao et al. 2013; Nguyen et al. 2016; Haenecour et al. 2018). Calcium-rich silicate phases are not observed spectroscopically in type-II supernova ejecta. However, equilibrium condensation calculations for a 21 $M_\odot$ supernova by Fedkin et al. (2010) showed that the majority of Ca-rich pyroxene condenses as a diopside (CaMgSi$_2$O$_6$) and is stable in the H zone below 1163 K. Leitner et al. (2020) reported a presolar silicate with an åkermanite–diopside composition. The authors proposed that the åkermanite core was first condensed in circumstellar outflows followed by the formation of a diopside around the åkermanite core. For the grain NWA 801_20, it is likely that the grain condensed as a diopside in a type-II supernova ejecta and later secondary processes altered the grain to have Ca-poor composition. A strongly varying Fe$^{3+}/\Sigma$ Fe ratio within the grain NWA 801_20 and neighboring Fe-rich grain surface probably reflect weathering experienced by NWA 801, which is also supported by the inference from Sanghani et al. (2021).

The EELS data for the grain Isheyevo_4 imply that the grain consists of silicate fine structures. In addition, the HR-TEM data confirm the grain to be crystalline in nature. Hence, the grain is a crystalline silicate from group 4. Furthermore, from the diffraction experiment, the automatic indexation of the FFT pattern could be obtained for both talc and antigorite minerals. However, the chemical composition acquired from the EDS spectra closely resembles an antigorite, which is a hydrated silicate mineral of the serpentinite group. Serpentine can form from hydration of forsterite in the presence of silica by several reactions (for example, Frost & Beard 2007; Coleman 1977). Crystalline aggregates from supernova with mineralogy similar to forsterite has been identified previously. Messenger et al. (2005) proposed a forsterite aggregate (Fo83) formed under equilibrium condensation conditions within cooling supernova ejecta. Supernova dust-condensation models do predict the formation of crystalline grains such as forsterites (Todini & Ferrara 2001); the models are also supported by spectroscopic observations of type-II supernova ejecta (Rho et al. 2008, 2009). Homogeneous chemical composition of Isheyevo_4 revealed by STEM-EDS together with EELS data suggest that the grain likely condensed as a crystalline forsterite from the cooling type-II SN ejecta. Moreover, very low Fe content of the grain and the presence of only trivalent Fe within the grain as well as in the surrounding matrix likely indicate the incorporation of Fe as a result of aqueous alteration on the Isheyevo parent body.

Lastly, chemical composition of the grain NWA 801_14 resembles a nontronite, which is a crystalline Fe-III smectite. In addition, indexation of FFT patterns and selected area electron diffraction patterns are consistent with the nontronite crystallographic structure as reported by Manceau et al. (1998). Nontronites are clay-like minerals formed as a result of terrestrial weathering of olivine (Sherman et al. 1962). More recently, Gaudin et al. (2018) experimentally demonstrated the formation of nontronite (smectite) as a result of the weathering of forsterite, the process that is invoked to explain the presence of smectite minerals on the Martian surface. Moreover, smectites are also found in meteorites, and probably formed by hydrous alteration of olivine or feldspar (Alexander et al. 1989). The grain NWA 801_14 likely formed as a forsterite (or a crystalline olivine) in type-II SN ejecta, and later weathered to form a clay-like structure and composition. The present lower $^{18}$O excess in the grain could possibly reflect the hydrous alteration experienced by the grain that may have diluted the isotopic anomaly of the grain.

### 5. Concluding Remarks

We have reported on the detailed microstructural and chemical composition of five putative AGB silicates and four SNe silicates. The main conclusions of our study can be summarized as follows:

1. The two presolar silicates from group 1 with putative AGB origin likely formed under different formation
conditions and probably also have dissimilar alteration histories. The grain NWA 801_15 formed as an amorphous olivine-like silicate in a nonequilibrium stellar environment with variable grain-formation conditions, whereas the grain NWA 801_23 probably condensed as a crystalline olivine in a stellar environment where the grain condensation conditions (such as temperatures) were not varying abruptly. Moreover, the grain NWA 801_15 turned polycrystalline in the solar nebula by the nebular shock waves, while the grain NWA 801_23 likely amorphized by ion irradiation in the ISM.

2. The significant Fe enrichment in the grain NWA 801_21 is probably due to the terrestrial weathering experienced by NWA 801.

3. Two GEMS-like grains belong to different groups condensed in nonequilibrium conditions. It is likely that both the grains condensed in nonequilibrium stellar environment depleted in Fe, owing to the comparably low Fe content of the grains (∼5–11 at%).

4. One of the two crystalline grains with chemical composition close to an antigorite likely formed as forsterite from cooling type-II SN ejecta and later aqueously altered. Very low Fe content in the grain is more likely the result of aqueous alteration on the Isheyevo parent body. Another crystalline grain is likely a weathered product of forsterite. A low $^{18}$O anomaly exhibited by the grain probably indicates the fluid exchange and dilution of an isotopic anomaly during weathering.

5. The silicate NWA 801_20 likely formed as a diopside and later, secondary processing could have altered the composition of the grain on the Ca-poor side.

6. A unique compound grain-oldhamite-bearing enstatite likely formed by heterogeneous grain condensation in stellar outflows, where oldhamite might have acted as a seed nucleus for enstatite formation. The Ca diffusion profile is indicative of the thermal metamorphism experienced by the grain. This is, to the best of our knowledge, the first discovery of an oldhamite grain acting as a seed nucleus for presolar silicate grain formation. This discovery highlights the complexity of the formation histories of presolar silicates.

7. The presence of fluorine in several of the presolar grains suggests a multiple cosmic origin of fluorine.

Our results show the broad range of microstructural and chemical compositions of presolar silicates from various stellar sources, namely the putative AGB stars and supernovae. In general, both the AGB stars and supernovae reveal equilibrium and nonequilibrium formation conditions. Monochromated SR-EELS analysis has been utilized to investigate Fe oxidation states and to highlight the effects of secondary alteration. The $\text{Fe}^{3+}/\Sigma \text{Fe}$ ratio is found to be very sensitive to aqueous alteration. A higher $\text{Fe}^{3+}/\Sigma \text{Fe}$ ratio for the rims surrounding the presolar grains/neighbor matrix grains with increasing Fe/Si (at. %) as compared to the grains generally indicates a higher order of aqueous alteration experienced by the rim/surrounding matrix in comparison to the grains. Presolar silicates show a very wide range of microstructural and chemical compositions that is in contrast to the majority of other presolar phases. The exceptionally detailed information obtained regarding the grain condensation and alteration using STEM-HAADF, EDS, and EELS is unparalleled. Lastly, our findings point out the importance of coordinated isotopic, microstructural, and chemical studies of presolar silicates as a tool to investigate the processes that may have played a role in shaping our solar system as we see it today.

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Appendix

![Image](image.png)

**Figure A1.** Secondary electron (SE) image of the grain NWA 801_15.
Figure A2. EELS spectrum acquired on grain NWA 801_15 at the vicinity of the Si-L\textsubscript{23} edges.

Figure A3. EELS spectrum acquired on grain NWA 801_18 at the vicinity of the Fe-L\textsubscript{23} edges.

Figure A4. EELS spectrum acquired on grain NWA 801_21 at the vicinity of the Si-L\textsubscript{23} edges.

Figure A5. Secondary electron (SE) image of the grain Isheyevo_9.
Figure A6. Monochromated EELS spectra acquired on the grain Isheyev9 showing the O–K, F–K and Fe–L23 edges. The inset shows the dark-field image acquired simultaneously as the EELS data set. The spectra labeled 1 and 2 have been acquired on the area highlighted by the red and blue squares, respectively. The black scale bar in the inset image is 0.1 μm.

Figure A7. HR-TEM image of the grain Isheyev9; the red square highlights the area used to calculate the FFT pattern shown in the inset. Automatic indexation was obtained with the oldhamite Fm3m crystal structure observed along the [001] zone axis (Wyckoff 1963. Interscience publishers, New York, NY. “Rocksalt structure.” Crystal structures, 1, 85–237).
Figure A8. HR-TEM image of the grain Isheyev_9, the red square highlights the area used to calculate the FFT pattern shown in the inset. Automatic indexation was obtained with the enstatite Pbca crystal structure observed along the $[3213]$ zone axis$(b) (Domeneghetti et al. 1995)$. Orthopyroxene from the Serra de Magé Meteorite: Structure refinement and estimation of C 2/c pyroxene contributions to apparent Pbca diffraction violations. *American Mineralogist*, 80(9–10), 923–929.

Figure A9. STEM HAADF, S, and Ni elemental maps of the grain NWA 801_14.
Automatic indexation was obtained with the nontronite C 1 \( 2/m \) crystal structure observed along the \([3 \ -2 \ 2]\) zone axis. (Manceau 1998). Polarized EXAFS, distance–valence least-squares modeling (DVLS) and quantitative texture analysis approaches to the structural refinement of the Garfield nontronite. *Physics and Chemistry of Minerals*, 25 (5), 347–365.

Figure A10. HR-TEM image of the grain NWA 801_14, the red square highlights the area used to calculate the FFT pattern shown in the inset. Automatic indexation was obtained with the nontronite C 1 \( 2/m \) crystal structure observed along the \([3 \ -2 \ 2]\) zone axis. (Manceau 1998). Polarized EXAFS, distance–valence least-squares modeling (DVLS) and quantitative texture analysis approaches to the structural refinement of the Garfield nontronite. *Physics and Chemistry of Minerals*, 25 (5), 347–365.

Figure A11. Selected area electron diffractogram obtained on the grain NWA 801_14. The diffractogram can be interpreted as the superposition of two nontronite crystals: one seen along the \([3 \ -2 \ 2]\) zone axis and the other seen along the \([\ -6 \ -5 \ 14]\) zone axis. The indexation here is given for the \([\ -6 \ -5 \ 14]\) zone axis. The scale bar corresponds to 8 nm\(^{-1}\).
Figure A12. Grain NWA 801_17. (left) Dark-field image acquired simultaneously with the EELS data set. (right) Corresponding Fe$^{3+}/\sum$ Fe chemical map.

Figure A13. Grain NWA 801_20. EELS elemental maps of F (top) and Fe (bottom). The red circles highlight the position of the presolar grain.
**Figure A14.** Grain *Isheyeva_4*. EELS spectra at the vicinity of the Fe–L23 edges. The spectra labeled 2, 3, 4 have been extracted from the corresponding areas shown in the inset.

**Figure A15.** Grain *Isheyeva_4*. EELS spectra at the vicinity of the O–K edges. The spectra labeled 1, 2, 3 have been extracted from the corresponding areas shown in the inset.
Figure A16. Grain Isheyevo_4. EELS spectra at the vicinity of the Si-L23 edges.

Figure A17. (left) HR-TEM image of the grain Isheyevo_4. (right) Corresponding FFT pattern. Automatic indexation was obtained with the antigorite crystal structure observed along the [1 1 7] zone axis.\textsuperscript{4} ref UEHARA, Seiichiro. TEM and XRD study of antigorite superstructures. \textit{The Canadian Mineralogist}, 1998, vol. 36, no 6, pp. 1595–1605.
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