DUST CONDENSATION IN CIRCUMSTELLAR ENVIRONMENTS: INSIGHT FROM CHEMICAL AND MICROSTRUCTURAL ANALYSES OF PRESOLAR GRAINS

by

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Department of Planetary Science
This dissertation represents the culmination of years of hard work that I would not have been able to complete without the support of those around me. I would first like to thank the LPL grads for supporting me through the struggles of a PhD program. Grad school is a truly difficult journey filled with many highs and lows, but in the end, we all made it through together and are moving on to amazing things.

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We respectfully acknowledge the University of Arizona is on the land and territories of Indigenous peoples. Today, Arizona is home to 22 federally recognized tribes, with Tucson being home to the O’odham and the Yaqui. Committed to diversity and inclusion, the University strives to build sustainable relationships with sovereign Native Nations and Indigenous communities through education offerings, partnerships, and community service.
DEDICATION

To my parents,

Mark and Kim Seifert,

for their never-ending support.
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<tr>
<td>CSE</td>
<td>Circumstellar envelope</td>
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<tr>
<td>ISM</td>
<td>Interstellar medium</td>
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<tr>
<td>AGB</td>
<td>Asymptotic giant branch</td>
</tr>
<tr>
<td>RGB</td>
<td>Red giant branch</td>
</tr>
<tr>
<td>SN/e</td>
<td>Supernova/e</td>
</tr>
<tr>
<td>GCE</td>
<td>Galactic chemical evolution</td>
</tr>
<tr>
<td>NanoSIMS</td>
<td>Nanoscale secondary-ion mass spectrometry</td>
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<tr>
<td>FIB-SEM</td>
<td>Focused-ion beam scanning-electron microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>BF</td>
<td>Bright-field</td>
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<tr>
<td>HAADF</td>
<td>High-angle annular dark-field</td>
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<tr>
<td>EDS</td>
<td>Energy-dispersive x-ray spectroscopy</td>
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<tr>
<td>EELS</td>
<td>Electron-energy loss spectroscopy</td>
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ABSTRACT

Presolar grains are among the original building blocks of our solar system from which the sun and planets formed. These grains formed in the circumstellar envelopes of evolved stars and in the ejecta of stellar explosions such as supernovae. Analysis of them provides ground-truth to astronomical observations and insights into their stellar origins. Silicates are a major dust component in the gaseous envelopes surrounding O-rich stars and the interstellar medium (ISM), and the analysis of them can provide a wealth of information about the thermodynamic landscape of circumstellar environments and supernovae. Further, such materials offer insight into transport through the interstellar medium, preservation in solar system materials, and any secondary alteration they may have experienced since their formation. This dissertation is broadly focused on studying silicate presolar grains preserved in primitive meteorites to investigate their structures and chemistries, understand how they are affected by secondary alteration, and how they are preserved in different chondrite groups. This work is supported by isotopic measurements using nanoscale secondary-ion mass spectrometry (NanoSIMS), but is focused on structural and chemical characterization using advanced electron microscopy techniques including focused-ion beam scanning-electron microscopy (FIB-SEM) and transmission electron microscopy (TEM).

Chapter 1 of this dissertation provides an introduction to molecular clouds, star formation, stellar nucleosynthesis, the injection of matter into the ISM, formation of the solar protoplanetary disk, incorporation of gas and dust from the ISM, and preservation of presolar grains in planetary materials such as meteorites. Chapter 2 describes the analytical methods used to complete this work including NanoSIMS, Auger spectroscopy, FIB-SEM, and TEM. Three subsequent research chapters aim to fill knowledge gaps in presolar-silicate research to date. First, very few presolar
silicate grains with origins in supernovae have been analyzed for their detailed structure and chemistry. Chapter 3 is focused on understanding the types of silicates that form in supernova environments, the thermodynamics of their formation, and comparing such data to presolar grains from other stellar origins. Second, presolar silicates are easily destroyed by secondary alteration in the solar nebula and on the parent asteroid and are therefore useful tracers of processing such as aqueous alteration and thermal metamorphism. Chapter 4 describes the alteration histories of presolar silicates in carbonaceous chondrites, particularly how they are preserved in solar system materials, the mechanisms by which they alter, and the extent to which they are affected by alteration processes. Finally, very little detailed structural and chemical characterization has been completed on presolar grains preserved in ordinary chondrites. The ordinary and carbonaceous chondrites are believed to have formed in separate reservoirs in the solar protoplanetary disk and therefore, analyzing presolar grains from both reservoirs could give insight into how the protoplanetary disk was seeded. Chapter 5 is focused on the analysis of presolar silicates in ordinary chondrites and comparing such data to presolar grain populations in carbonaceous chondrites and interplanetary dust particles to better understand if there are differences in presolar grains that were preserved in different chondrite reservoirs. Chapters 3 and 4 were published in Meteoritics & Planetary Science and Chapter 5 was submitted to Meteoritics & Planetary Science.
CHAPTER 1. INTRODUCTION

1.1 Stellar Nucleosynthesis and Dust Production

Following the Big Bang, the universe was composed of mainly H and He with trace amounts of Li, Be, and B. The remaining elements were produced through stellar nucleosynthesis. The lifecycle of all stars begins with the formation of cold, dense cores within molecular clouds of gas and dust. A dense region of the cloud may become gravitationally unstable and collapse under self-gravity, causing a dense core to form with increases in temperature and gas pressure. Due to conservation of angular momentum, a rotating core collapses to form a disk. Depending on the mass of the system, binary or multiple systems or a single star with planets, like the solar system can form (Stahler, 2014). Mass accretes onto the object at the center of the disk, the protostar, which generates gravitational energy that heats the core and provides luminosity. As accretion slows, the protostar progresses to a pre-main sequence star (Stahler, 2014). Temperatures in the core continue to increase until they are sufficiently high to start core H fusion (Wiescher et al., 2010). Gravity is balanced by the radiation pressure associated with the start of H fusion and the star is now on the main sequence (Fig. 1.1).

The majority of a star’s lifetime is spent in a state of hydrostatic equilibrium, where the stellar radiation pressure supports the star under its self-gravity, preventing gravitational collapse. To maintain hydrostatic equilibrium, stars must consume nuclear fuel to replenish the energy lost by radiation. Stars evolve through a series of burning stages where the products of one stage are used as fuel for subsequent stages. Though these stages are referred to as burning stages, they are driven by nuclear fusion, rather than combustion. Following each ‘burning stage’, the star contracts
Figure 1.1: Hertzsprung-Russell (H-R) diagram showing the evolutionary stages of a star (Image from European Southern Observatory). Spectral class (O, B, A, F, G, K, and M) is indicated along with surface temperature and luminosity. Luminosity is normalized to 1 solar unit, i.e., our Sun, which is a low-mass G-class star.
before reigniting the next burning stage in a shell surrounding the core. As the star evolves, each new burning stage occurs on shorter timescales and at higher temperatures. This section is focused on highlighting the lifecycle and nucleosynthetic processes in low to intermediate mass (<8 solar masses (M☉)) stars and massive stars (>8 M☉).

The nuclear reactions by which H is fused into He in stellar cores of main sequence stars is dependent on stellar mass. During H core fusion in low mass stars (<1.5 M☉), the proton-proton (PP) chains take place, where four H nuclei are converted to He (Bethe, 1939). For higher mass stars (>1.5 M☉) that have higher core temperatures, the CNO cycle dominates (Bethe, 1939; Burbidge et al., 1957). During the CNO cycle, H fusion is catalyzed by the capture of protons by C, N, and O isotopes, the main product of which is ⁴He. The CNO cycle also produces ¹⁴N, ²⁶Al, and ¹⁷O is an additional product of the NO cycle. Following core H fusion, the star moves off the main sequence, where evolution is again based on mass.

1.1.1 Low to Intermediate Mass Stars (<8 M☉)

All stars with masses <8 M☉ undergo H and He burning stages. Following H fusion in the stellar core, the core begins to contract because the radiative pressure can no longer support the gravity of the star. As the core contracts, temperatures increase and as a result, the H shell surrounding the core begins to heat up. When temperatures in the shell are sufficiently hot, H shell burning begins. The resulting energy production during H shell burning is greater than that produced on the main sequence and results in an expansion of the star. The star is now on the red giant branch (RGB, Fig. 1.1). As a result of the expansion of the star, the outermost layers are less dense and are therefore easily expelled, resulting in high mass-loss rates. Energy is transported
through the star by a convective mixing process called the first dredge-up, which brings the products of stellar nucleosynthesis to the stellar surface (Fig. 1.2).

Following H shell burning, the core contracts and heats until it is sufficiently hot to start the He burning in the core (100 million K). The main products of He burning are $^{12}\text{C}$, produced via the “triple alpha” process $^{8}\text{Be}(\alpha, \gamma)^{12}\text{C}$, and $^{16}\text{O}$ produced by $^{12}\text{C}(\alpha, \gamma)^{16}\text{O}$ (Salpeter, 1952)). $^{18}\text{O}$, $^{22}\text{Ne}$, $^{25}\text{Mg}$, and s-process isotopes are also produced during He burning. Once He core burning is complete, the stellar core now contains C and O and begins to contract. Low to intermediate mass stars do not reach temperatures sufficient enough to begin C burning, however He burning does reigne in a shell surrounding the core during the ascent of the asymptotic giant branch (AGB, Fig. 1.1). He shell burning causes the star to expand and cool. Convective mixing in the form of the second dredge up (Fig. 1.2) again mixes nucleosynthetic products with the stellar envelope (Lattanzio and Boothroyd, 1997). H shell burning is reignited as a result of the contraction of outer stellar layers and associated heating of the H shell. The resulting He production from H-shell burning causes the He shell to heat up and results in a He flash (Fig. 1.2), which drives convection and mixes material from the shell with the stellar envelope in the third dredge-up (Lattanzio and Boothroyd, 1997). During the third dredge-up, s-process elements, C-rich material, and He are transported to the stellar surface. The s-process refers to the capture of neutrons on slow timescales relative to β-decay and is responsible for half the isotopes heavier than Fe (H. Y. McSween and Huss, 2010). During the thermally pulsing AGB (TP-AGB) phase, burning alternates between the H and He shells. Some stars experience an extra mixing process called hot bottom burning that brings material from the H burning shell to the stellar surface (Lattanzio and Boothroyd, 1997). He burning is the end-stage for stars of low-intermediate masses
Figure 1.2: Schematic showing the evolutionary stages of low to intermediate mass stars. From McSween and Huss (2010).
<8 \text{ M}_\odot. \text{ At this stage, the density of these stars is high enough that electron degeneracy provides sufficient pressure to support the star against gravitational collapse, allowing it to be stable without further nuclear reactions in its core. The star concludes its lifecycle as C/O white dwarf and finally a black dwarf (Fig. 1.2).}

1.1.2 Massive Stars (>8 \text{ M}_\odot)

Stars with masses greater than 8 \text{ M}_\odot can fuse heavier nuclei together and continue on to subsequent burning stages including C, Ne, O, and Si burning. After the main sequence, high-mass stars either evolve into red or blue supergiants, which have mass ranges of about 10 to 40 \text{ M}_\odot and 20 to 40 \text{ M}_\odot, respectively (Fig. 1.3). Following He shell burning, the C burning stage produces $^{24}\text{Mg}$, $^{20}\text{Ne}$, and $^{23}\text{Na}$. C burning is the final burning stage in stars with masses ranging from 8 to 10 \text{ M}_\odot. In even higher mass stars, following C burning, the Ne burning stage begins and mainly produces $^{16}\text{O}$ and $^{24}\text{Mg}$. As the star continues to heat up, O burning begins and produces $^{28}\text{Si}$, $^{32}\text{S}$, and $^{31}\text{P}$. The final stage in high-mass stars is Si burning that produces the Fe-group elements including $^{56}\text{Fe}$, $^{54}\text{Fe}$, $^{56}\text{Ni}$, and $^{56}\text{Co}$ (Woosley and Janka, 2005). Following the Si burning stage, the star has an onion-shell structure with an Fe-Ni core, surrounded by Si, O, Ne, C, He, and H shells (Fig. 1.3). As no further fuel remains, the star becomes unstable as a result of electron captures and the disintegration of Fe nuclei to He nuclei (Woosley and Janka, 2005). The stellar core collapses and rebounds, sending a shock wave propagating through the stellar structure and ejecting the outer layers of the star in a massive explosion called a Type-II core-collapse supernova.
Figure 1.3: Schematic showing the evolutionary stages of massive stars. From McSween and Huss (2010).
Following the SN explosion, the mass of the star determines what remains, where stars <20 M☉ form a neutron star, while higher mass stars (>20 M☉) result in a black hole.

1.1.3 Dust Injection into the ISM

During the latter stages of their evolution, RGB and AGB stars eject their matter into the interstellar medium (ISM). The material that is ejected includes atoms, ions, and molecules that originate in the inner circumstellar envelope (CSE, Fig. 1.4). Solid dust grains condense at larger radial distances where temperatures are cooler in the intermediate CSE (Fig. 1.4) and also in the ejecta of SNe, inheriting the star’s nucleosynthetic makeup and thermodynamic properties of their host CSE or ejecta. Strong stellar winds drive circumstellar dust grains away from the star and into the ISM (Fig. 1.4).

The type of dust that is formed is dependent on the C/O ratio. In C-rich stars with C/O>1, C-rich and reduced phases are expected to form, including SiC, graphite, amorphous C, MgS, and Fe grains (Lodders and Fegley, 1999). Alternatively, in O-rich stars with C/O<1, dust is dominated by silicate and oxide phases including olivine (Mg2SiO4), pyroxene (MgSiO3), corundum (Al₂O₃) and spinel (MgAl₂O₄) (Lodders and Fegley, 1999; Speck et al., 2000). Some of the dust that was produced in stars and the ejecta of SNe made its way to the local part of the galaxy where the solar system was forming 4.567 billion years ago and a fraction of that dust is preserved inside of primitive meteorites. These ‘presolar’ grains are among the building blocks of the solar system and have origins in ancient stars that no longer exist.
Figure 1.4: Schematic of AGB star showing locations of dynamical atmosphere, dust condensation zone and injection of material into the ISM, adapted from Decin et al. (2010).
1.2 Presolar Grains

1.2.1 Incorporation of Presolar Dust into the Early Solar System

The formation of the protosun and the solar nebula is believed to have resulted from the gravitational collapse of a dense molecular cloud core. The ‘presolar’ molecular cloud contained primarily molecular hydrogen, helium, and molecules like CO gas, with small amounts of gaseous molecules and atoms of elements heavier than helium (Boss and Goswami, 2006). In addition, a portion of the presolar dust grains that formed in the gaseous envelopes surrounding ancient stars and in the ejecta of stellar explosions such as novae and supernovae were incorporated into the ‘presolar’ molecular cloud. Following the collapse of the presolar molecular cloud forming the protosun, a protoplanetary disk was formed. Some of these grains survived the formation of the solar system and were preserved inside of asteroids and comets (Fig. 1.5).

Such dust grains are called ‘presolar’ because they formed before the solar system in the gaseous envelopes or ejecta of stars that no longer exist. The grains occur in a fine-grained matrix within primitive meteorites, surrounded by silicates, oxides, and other material with chemical and isotopic compositions generally matching the solar system, i.e., solar abundances. Thus, presolar grains are identified in the laboratory by their anomalous isotopic compositions, which reflect the stellar nucleosynthetic processes they inherited when they condensed in their progenitor star’s CSE, some of which differ from the solar system by orders of magnitude. A variety of planetary materials contain presolar grains such as meteorites, micrometeorites, interplanetary dust particles, and samples returned from the Stardust and Hayabusa2 missions (Barosch et al., 2022b; Busemann et al., 2009; Floss et al., 2013; McKeegan et al., 2006). Evidence for presolar grains in meteoritic
**Figure 1.5:** Cartoon illustrating the seeding of presolar grains in the early solar system, preservation in asteroids and comets, and transport to Earth via planetary materials that can be studied in the laboratory (image credit: NASA, Haenecour et al. 2020; Messenger et al. 2006).
samples were first reported in 1964 when John Reynolds and Grenville Turner identified isotopic anomalies in the noble gas Xe in the Renazzo chondrite (Reynolds & Turner, 1964). Such Xe anomalies were identified in several carbonaceous chondrites and subsequent work focused on identifying the carrier phase of the Xe isotope anomaly. In 1987, Roy Lewis and Edward Anders successfully identified the carrier of the anomalous Xe as nanodiamond (Lewis et al., 1987; Zinner, 2014). Since then, several other presolar grain types were identified. These include: carbides (SiC, graphite, nanodiamond); oxides (corundum, hibonite, spinel, chromite, and magnetite); silicates (olivine, pyroxene, phases intermediate between the two, SiO₂, and many nonstoichiometric silicates); nitride (Si₃N₄); and sub-grains inside other presolar grains (TiC, MoC, ZrC, RuC, FeC, Fe–Ni).

1.2.2 Preservation in Meteorites

Presolar grains occur in part-per-thousand to part-per-billion levels in primitive meteorite samples and are surrounded by isotopically ‘solar’ matrix materials that likely formed in the solar nebula. In other words, the chemical and physical processes that formed our solar system were efficient at destroying the presolar material inherited from the parent molecular cloud. To date, the highest abundances of presolar grains are found in the carbonaceous chondrites Dominion Range 08006 (CO3.0) and Asuka 12169 (CM) at 257 ppm and 236 ppm, respectively (Haenecour et al., 2018; Nittler et al., 2018, 2021).

Due to the low abundances of presolar grains in meteorites, locating them has been likened to finding needles in a haystack (Zinner, 2014). Thus, multiple methods have evolved for isolating
presolar grains from meteorites. Acid-dissolution and density separation of meteoritic samples allowed for the isolation of many grains at once and was essential to identifying and studying the origins of different grain types, providing ground-truth information on the inner workings of stars. However, most dissolution techniques are designed to destroy silicate materials that compose the bulk of chondritic matrix, leaving behind acid-resistant grains like SiC and oxides. Such approaches increase the odds of finding presolar materials. The drawback of dissolution is that it destroys petrographic context of the grain within the surrounding matrix. Such context is useful for understanding grain histories, i.e., how they were preserved and whether they experienced nebular or parent-body processing, and so in situ techniques are essential. In situ techniques including focused ion beam-scanning electron microscopy (FIB-SEM) have since been developed and applied to presolar grains, as will be discussed in detail in Chapter 2 (Floss et al., 2006; Haenecour et al., 2018, 2019, 2020; Nguyen et al., 2007, 2010, 2016; Seifert et al., 2022; Vollmer et al., 2007, 2009; Zega et al., 2007, 2011, 2014, 2015, 2020;). The implementation of FIB as a viable mineralogical tool bridged the gap between in situ measurements of isotopic composition via nanoscale secondary-ion mass spectrometry (NanoSIMS) and structural and crystal-chemical analysis by transmission electron microscopy (TEM), enabling coordinated analysis on the same grain.

1.2.3 Presolar Silicates

The main focus of this dissertation is the analysis of presolar silicate grains. Astronomical observations indicate that silicates are the most abundant type of dust in the CSEs of O-rich stars and the ISM (Kemper et al., 2004; Speck et al., 2000; Tielens et al., 1998). An abundance of
amorphous silicate material is also observed in supernova remnants (e.g., Arendt et al. 1999; Rho et al. 2008, 2009). The coordinated analyses of presolar silicate grains in the laboratory provides ground truth to astronomical observations and can help to constrain astronomical models of circumstellar and interstellar mineralogy.

Presolar silicates are the most abundant presolar grain type following nanodiamond (Floss and Haenecour, 2016c) and are compositionally and structurally diverse (Floss and Stadermann, 2009a; Floss et al., 2006; Haenecour et al., 2018, 2020; Keller and Messenger, 2011; Messenger et al., 2003, 2005; Nguyen et al., 2007, 2010, 2016; Nittler et al., 2018, 2021; Sanghani et al., 2022; Seifert et al., 2022; Singerling et al., 2022; Stroud et al., 2009, 2014; Vollmer et al., 2007, 2009, 2013). Silicates are unique in that they are one of the most susceptible presolar grain types to secondary alteration processes in the ISM, solar nebula, and on the parent body asteroid (Bose et al., 2014; Haenecour et al., 2018, 2020; Nguyen et al., 2010, 2016; Zega et al., 2020). Therefore, these grains can be useful tracers of the earliest stages of such processes. Presolar silicate grains are very small (submicrometer) and therefore require high spatial resolution analytical techniques including NanoSIMS and TEM for identification and to analyze their structure and chemistry. To date, more than 1,500 presolar silicates were identified in primitive planetary materials by their anomalous isotopic composition. However, only a small fraction of such grains were analyzed for their detailed structure and chemistry using TEM, making further studies necessary to understand their origins and histories. Nevertheless, those TEM studies that were completed on presolar silicate grains show diverse stellar origins including AGB stars, RGB stars, and supernovae (Messenger et al. 2003, 2005; Floss et al. 2006; Nguyen et al. 2007, 2010, 2016; Vollmer et al. 2007, 2009, 2013; Floss & Stadermann 2009; Keller & Messenger 2011; Stroud et al. 2009, 2013,
Presolar grains preserve information on their host stars and can therefore provide information on processes such as stellar nucleosynthesis, SN mixing, and galactic chemical evolution (GCE), which describes how the chemical composition of the galaxy varies with time. In particular, the isotopic composition of presolar grains is necessary for both their identification and understanding their stellar origins. Isotopic measurements are largely carried out using NanoSIMS, which will be discussed in detail in Chapter 2.

The isotopic compositions of presolar grains are reproducible with nucleosynthetic models of stellar evolution (e.g., Boothroyd et al. 1994; Nittler et al. 1997, 2008; Boothroyd & Sackmann, 2014; Nittler et al. 2018, 2020; Zega et al. 2020; Haenecour et al. 2020; Seifert et al. 2022, 2023; Sanghani et al. 2022; Singerling et al. 2022). These studies have provided useful insight into their formation, transport, and alteration histories and revealed diverse structures, including single crystals, polycrystalline assemblages, amorphous grains, and aggregates. Presolar silicates are also compositionally diverse, including olivine, pyroxene, compositions intermediate between the two, and many nonstoichiometric silicates (Messenger et al. 2003, 2005; Floss et al. 2006; Nguyen et al. 2007, 2010, 2016; Vollmer et al. 2007, 2009, 2013; Floss & Stadermann 2009; Keller & Messenger 2011; Stroud et al. 2009, 2013, 2014; Nittler et al. 2018, 2020; Zega et al. 2020; Haenecour et al. 2020; Seifert et al. 2022, 2023; Sanghani et al. 2022; Singerling et al. 2022). Presolar grains are among the building blocks of the solar system and the diversity in the chemical compositions and structures of presolar silicate grains highlights their complex histories and necessitates further work to understand their origins and preservation in solar system materials.

1.2.4 Nucleosynthetic Origins of O-rich Presolar Grains

Presolar grains preserve information on their host stars and can therefore provide information on processes such as stellar nucleosynthesis, SN mixing, and galactic chemical evolution (GCE), which describes how the chemical composition of the galaxy varies with time. In particular, the isotopic composition of presolar grains is necessary for both their identification and understanding their stellar origins. Isotopic measurements are largely carried out using NanoSIMS, which will be discussed in detail in Chapter 2.
Comparison of grain data with nucleosynthetic models of stellar evolution can be useful in determining the type, mass, and fraction of elements heavier than H and He (metallicity) of the progenitor star from which the grains originated as well as mixing processes that occurred within them. The $^{17}\text{O}/^{16}\text{O}$ ratio generally depends on stellar mass, while the $^{18}\text{O}/^{16}\text{O}$ ratio relates to metallicity (Boothroyd et al. 1994; Boothroyd & Sackmann, 1999). Therefore, the O-isotopic ratios observed in O-rich presolar grains can be compared to model predictions in order estimate the mass and metallicity of the progenitor star, relative to solar composition. The O-rich presolar grains, including oxides and silicates plot into four distinct groups in three O-isotope space (Fig. 1.6), indicating stellar origins including RGB and AGB stars and SNe (Nittler et al. 1997, 2008). Group 1 presolar grains are believed to have formed in CSEs of O-rich RGB or AGB stars (Boothroyd and Sackmann, 1999; Nittler et al., 1997; Nollett et al., 2003). These grains have excesses in $^{17}\text{O}$ relative to the oxygen isotopic composition of the solar system (‘solar composition’). Their isotopic compositions can be explained by H burning in the core of the progenitor star, followed by dredge up processes that occur at the end of the main-sequence in which the convective envelope around the star transports the ashes of the first stage of nucleosynthesis to the CSE. Solid dust grains condense in this envelope, inheriting its nucleosynthetic makeup and recording its thermodynamic properties. Group 2 grains have long been attributed to origins in low-mass ($< 2\ M_\odot$) AGB stars (Boothroyd 1994; Boothroyd & Sackmann 1999; Nollett et al. 2003), but revised nucleosynthetic models suggest possible origins in intermediate mass (4 to 8 $M_\odot$) AGB stars (Lugaro et al., 2017). Group 2 grains have excesses in $^{17}\text{O}$ and large depletions in $^{18}\text{O}$ relative to solar system values. Their isotopic compositions
cannot be reproduced with dredge-up processes alone, and therefore require an extra mixing process called “cool bottom processing” during the AGB phase that destroys $^{18}$O. Such processing mixes material from the stellar envelope with material close to the H burning shell. Given that $^{18}$O is destroyed during cool bottom processing, the measured $^{18}$O composition in O-rich presolar grains cannot be used to infer the metallicity of the progenitor star. Group 3 grains have depletions in both $^{17}$O and $^{18}$O and likely originate in low mass, thermally pulsing AGB stars (TP-AGB) that experienced a third dredge-up (Nittler et al. 1997; Nollett et al. 2003). Alternatively, some Group 3 grains could have origins in the ejecta of supernovae (Nittler et al. 2008). Some Group 3 grains are consistent with the GCE trend, which suggests that the $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O ratios of the galaxy increase linearly as a function of time and metallicity (Nittler et al. 1997, 2008). Those grains that plot on the GCE trend below “solar” indicate a progenitor star of lower than solar metallicity and likely formed early in galactic history. Group 4 grains likely originate in the ejecta of type II core-collapse SNe (Choi et al., 1998; Nittler, 2008). These grains have enrichments in $^{18}$O and some have enrichment in $^{17}$O relative to solar system values. The enrichments in $^{18}$O result from partial He burning in the He/C zone of massive stars. Some Group 4 grains plot above “solar” composition and are also suggested to follow the GCE trend and indicate a progenitor star with a metallicity greater than solar.

In addition to the O-isotopic composition of O-rich presolar grains, Mg, Al, and Si isotopes have also been used to gain further insight into stellar origins (Hoppe et al., 2021; Leitner and Hoppe, 2019; Verdier-Paoletti et al., 2019). Grains containing $^{26}$Al require dredge-up during the TP-AGB stage, therefore suggesting that grains that lack $^{26}$Al were formed before this phase (Nittler et al. 1997. Recent Mg and Si isotopic measurements on presolar silicates have indicated
the potential need to further subdivide the Group 1 O-rich presolar grains (Hoppe et al., 2021; Leitner and Hoppe, 2019; Verdier-Paoletti et al., 2019). Grains with enrichments in $^{25}$Mg could have origins in intermediate-mass AGB stars or in SNe. Alternatively, $^{26}$Mg-rich and $^{25}$Mg-poor isotopic compositions are suggested to have origins in supergiants or SNe. Such results suggest that a larger fraction of presolar silicate grains could have origins in SNe than previously thought. Further isotopic analyses of presolar grains will continue to provide insight into stellar origins and drive future nucleosynthetic models.

1.3 Thermodynamic Landscape of Circumstellar Environments

Presolar grains preserve information on their thermodynamic origins. The structure and chemistry of such grains can be compared to thermodynamic model predictions with the goal of constraining the pressure (P) and temperature (T) of condensation for each grain. Such fundamental thermodynamic parameters are important for understanding the thermodynamic landscape of circumstellar envelopes and the ejecta of supernovae. Detailed analysis of such grains provides information on long-range atomic order and phase identification, in addition to local disorder that might hold additional clues to whether condensation conforms to equilibrium predictions. Generally, equilibrium models predict ordered, single, stoichiometric crystals, while disordered, defected, and non-stoichiometric crystals are consistent with kinetic origins.

Models for both equilibrium and kinetic condensation processes were reported and are applicable to circumstellar environments (Ebel et al., 2000; Ferrarotti and Gail, 2001; Gail and Sedlmayr, 1999; Lodders, 2003; Lodders and Fegley, 1995). Equilibrium models of dust condensation predict the temperatures at which minerals will condense from a gas, generally
defined as solar composition, at a set of constant pressures. Alternatively, kinetic models of dust condensation take into consideration nucleation and grain growth and predict additional information such as the composition of grains, their sizes, and the timescale of their formation. In the case of supernovae, models of dust condensation in their ejecta are available in the literature (Cherchneff and Dwek, 2010; Fedkin et al., 2010; Nozawa et al., 2003; Todini and Ferrara, 2001) and can provide useful information on the types of materials formed in these environments. Thermodynamic models relevant for both CSEs and the ejecta of supernovae provide first-order constraints on dust condensation in stellar environments. Several assumptions are made in equilibrium thermodynamic calculations, including that stellar outflows are assumed to be spherically symmetric, expand adiabatically, gas behaves as a closed system, and temperatures decrease monotonically with distance from the star. These assumptions may not be reasonable for all stellar systems and therefore additional development of such thermodynamic models is necessary, but outside the scope of this dissertation.
CHAPTER 2. METHODS

2.1 Introduction

The experimental work in this dissertation requires a coordinated approach that includes multiple analytical techniques for the identification, sample preparation, and analysis of the presolar grains. Advancements in electron microscopy techniques including FIB-SEM have enabled the in situ extraction of presolar grains. Subsequent TEM analyses allow for a detailed understanding of the structure and chemistry of such grains. Chapters 3, 4, and 5 of this dissertation contain shortened methods sections and the results of NanoSIMS and TEM measurements. The NanoSIMS measurements were completed by collaborators and so the focus of this chapter will be on sample preparation using FIB-SEM and TEM techniques including imaging, energy-dispersive x-ray spectroscopy (EDS), selected-area electron diffraction (SAED) and high-resolution imaging. Related theory and experimental procedures will be discussed, however, the interested reader is directed to several textbooks on TEM, e.g., Williams and Carter (2009), Carter and Williams (2010), and Brydson (2011) for a more detailed discussion.

2.2 NanoSIMS Isotopic Measurements and Auger Spectroscopy

All presolar grains studied over the course of this dissertation were identified using NanoSIMS raster ion imaging techniques due to their superior spatial resolution. NanoSIMS techniques applied to presolar grains generally involve rastering a Cs⁺ primary ion beam over a small area (10 × 10 μm²) of the meteorite thin section where secondary ions and secondary electrons are collected (Fig. 2.1). As the sample surface is bombarded by the Cs⁺ beam, cascade
Figure 2.1: Schematic illustrating SIMS. The primary ions impact the sample surface resulting in sputtering or ejection of atoms or small molecules, a fraction of which are ionized. These secondary ions are collected with a mass spectrometer and counted. From Lechene et al. (2006).
collisions are triggered, causing atoms and small molecules from the top (5-20 nm) of the sample to be sputtered away. A portion of these sputtered particles are ionized. Relevant here are the secondary ions of the oxygen isotopes $^{16}\text{O}^-$, $^{17}\text{O}^-$, and $^{18}\text{O}^-$ and the secondary ions of the carbon isotopes $^{12}\text{C}^-$ and $^{13}\text{C}^-$. These secondary ions are transmitted through a mass spectrometer where they are physically separated by their mass to charge ratio and collected by a series of detectors. Alternatively, secondary electrons (SE) are produced as a result of inelastic interactions between the beam and the sample and are used to produce SE images in the NanoSIMS. The O-isotopes are relevant for the identification of O-rich presolar grains such as silicates and oxides and the C-isotopes are used to identify C-rich presolar grains such as SiC. Such measurements can be completed in an automated mode, where the instrument stage moves to pre-defined analysis regions. Further details on the NanoSIMS analyses relevant to this dissertation can be found in Haenecour et al. (2018, 2020).

Several presolar silicate grains included in this dissertation were also analyzed using Auger spectroscopy by collaborators to gain information about their chemical compositions prior to TEM analysis. Auger spectroscopy is a surface analytical technique that collects Auger electrons of characteristic energies from a sample that is irradiated with an electron beam. When the electron beam interacts with the inner shell electrons of the atoms in a sample, an electron can be ejected, forming a vacancy that can be filled with an outer shell electron. The filling of this vacancy results in the emission of an Auger electron with a characteristic energy (Fig. 2.2). The release of Auger electrons from a sample is a competing process to characteristic x-ray generation (discussed in section 2.4.2), the difference of which is the sample region being probed. Auger electrons originate from the top few nanometers of the sample surface and the energies of these electrons contain
information about the sample composition. A primary electron beam is rastered over the grains of interest and multiple scans are combined together to form one Auger spectrum. From the Auger spectra, quantitative elemental compositions of the grains of interest can be determined using sensitivity factors derived from silicate standards. In addition to obtaining Auger spectra, Auger elemental maps can also be obtained to provide information on the distribution of elements in given grain. Further details on Auger spectroscopy methodology, processing, and quantification of Auger spectra can be found in Haenecour et al. (2018) and Stadermann et al. (2009).

**Figure 2.2:** Schematic of Auger electron and characteristic x-ray generation. The primary beam removes an inner shell electron, resulting in a vacancy that can be filled by an electron from the outer shell. The release of energy from such a transition results in either the formation of an Auger electron with a characteristic energy or a characteristic X-ray. From Stadermann et al. (2009).
2.3 FIB-SEM Sample Preparation

2.3.1 Introduction

Applying FIB-SEM techniques to the analysis of planetary materials allows for the site-specific extraction of samples that can be thinned to electron transparency (<100 nm) for TEM analysis. The FIB-SEM combines imaging capabilities of an SEM with etching capabilities of an ion beam (Ga⁺, Fig. 2.3). Thus, the surface geometry of a material can be modified and imaged simultaneously. The presolar grains studied here all occur in the fine-grained matrices of meteoritic samples. Therefore, to prepare FIB sections of them for TEM analysis, several steps are necessary to locate and mark the presolar grain of interest through the placement of fiducial markers before in situ extraction and thinning to electron transparency.

2.3.2 Grain Alignment and Fiducial Marker Placement

The first step in preparing FIB sections containing presolar grains is to relocate the grain of interest in the FIB-SEM. Using the SE images obtained from the NanoSIMS analysis, grains of interest are relocated in the FIB-SEM and higher-resolution (than NanoSIMS) SE images of the region are collected. Following the higher-resolution imaging, a detailed alignment procedure is used to correlate images acquired across different instruments including the NanoSIMS, the Auger nanoprobe (where applicable), and the FIB-SEM. It is very important that care is taken during the alignment procedure to ensure that the precise location of the presolar grains is correctly identified.

To aid in the alignment process, the ImageAlign software is used (Floss and Stadermann, 2009a, 2012; Floss et al., 2006). ImageAlign works by correlating the SE and ion images obtained
Figure 2.3: Schematic of dual-beam FIB-SEM with expanded view (left) highlighting electron and ion beam interactions with sample. From Volkert and Minor (2007).
from the NanoSIMS and Auger nanoprobe with the higher resolution SE images obtained using the FIB-SEM. The software matches morphologic features between two images and can align images that have a different orientation or magnification. Once the datasets are aligned, the software allows the user to trace the anomalous presolar grain in one image and the corresponding region is traced in the second image.

The work in this dissertation goes through this alignment procedure with several sets of data (Fig. 2.4). First, the NanoSIMS and Auger images are correlated and the anomalous presolar grain is traced on the Auger SE image. Next, the Auger SE image with the traced anomalous presolar grain and higher magnification Auger SE image are correlated. Finally, the higher magnification Auger SE image is correlated with the higher resolution FIB-SEM image to ensure the correct identification of the anomalous grain of interest. For those grains that do not have associated Auger datasets, the NanoSIMS and FIB-SEM images are directly aligned. As a final step, the alignments are confirmed by manually overlaying the NanoSIMS SE images, isotopic maps, and the SE images from the FIB.

In general, when possible, the longest dimension of the isotopic anomaly is transected in order to capture as much of the isotopically anomalous material as possible. However, there are certain cases where other FIB transects are necessary because of surface topography such as cracks in the meteorite thin section. Following the alignment procedure, special fiducial markers are placed in three different locations across the FIB transect. Fiducial markers are deposited (Fig. 2.4) using the Pt gas injection system (GIS) on the FIB and serve multiple purposes including (i) providing an protective layer over the presolar grain of interest, (ii) to mark the location of presolar
Figure 2.4: Overview of grain alignment and fiducial marker placement. a) NanoSIMS SE and $\delta^{17}O$ overlay. Arrow indicates anomalous presolar grain. Legend at left in units of per mil ($\‰$). b) Overlay of SE Auger image and NanoSIMS $\delta^{17}O$ map with arrow indicating presolar grain. c) SE image from FIB-SEM showing the FIB transect to section the longest dimension of the O-anomaly. d) SE FIB-SEM image showing placement of presolar grain and thinning fiducials.
grains in cross-section to easily locate the regions of interest in the TEM, and (iii) to assist in the thinning process as discussed below. The FIB-SEM used to complete the work in this dissertation contains both a C and a Pt GIS. Pt is used because it is a high atomic number (Z) element and appears bright in high-angle annular dark-field (HAADF) images in the TEM and is therefore useful for marking the location of the presolar grains in cross-section. The presolar grain fiducial marker is deposited first, the dimensions of which are roughly the same as the dimensions of the grain suggested by the NanoSIMS analysis. All fiducial markers are deposited using the electron beam at conditions of 5 kV, 0.8 nA. Thinning fiducial markers are deposited next on either side of the presolar grain fiducial marker to assist in the thinning process (Fig. 2.4). These markers are aligned with the center of the presolar grain marker and measure 100 nm in thickness. Therefore, during the thinning process, once the thinning fiducial markers are visible along with the presolar grain fiducial, the section is roughly 100 nm in thickness, which is required for TEM characterization.

Following the deposition of Pt fiducial markers, a C capping layer is deposited using the Ga⁺ ion beam on top of the Pt markers that extends the whole length of the FIB transect (Fig. 2.5). The C capping layer is used to protect the FIB section from ion implantation and radiation damage during the ion milling process. Generally, C capping layers used for the work in this dissertation range from 6 μm to 10 μm in length (x), 1 μm in width (y) and 3 μm in height (z) with ion beam conditions of 30 kv, 0.23 nA. There are also several matrix FIB sections described in this dissertation that do not contain presolar grains. For those sections, the placement of fiducial markers is not necessary and therefore the steps to deposit such markers can be skipped. Alternatively, before final deposition of the C capping layer in ion beam, a small amount (~500
Figure 2.5: Overview of milling and liftout process including C-capping layer deposition (a), trenching (b-c), side cut (d), undercut (e), liftout and weld to grid (f), thinning (g), and the final section once thinned to electron transparency (h).
nm) of C is deposited using the electron beam (5 kV, 0.8 nA) in the same dimensions as the ion beam capping layer. This small amount of C protects the region of the FIB transect before exposure to the ion beam.

2.3.3 FIB Section Lift Out and Thinning

Following the deposition of fiducial markers and protective capping layers, cross-sectioning can proceed, which involves the removal of material from either side of the capping layer during the coarse cutting process (Fig. 2.5). Coarse cutting is completed using the ion beam at 30 kV, 2.5 nA. Milling patterns are usually stair-step or ramp-shaped, which allows for detachment of the section but conserves substrate material, and can be scaled to the proper proportions (x, y, z) based on the size of the desired FIB section. Generally, the length (x) of the trench is about 1 μm wider than the capping layer, the depth of the trench is about 5 μm, and the width (y) of the trench is roughly 1.5 to 2 times the depth (z). The coarse cutting milling pattern is usually placed about 1 μm away from the capping layer. Once coarse cutting is completed on both sides of the capping layer, the ion beam current is lowered to 0.79 nA and a similar milling process is repeated on both sides of the capping layer. However, during this step, the milling pattern is incrementally moved closer to the capping layer until they are touching. This fine-cutting stage is used to clean up both sides of the FIB section before moving on with the lift out process (Fig. 2.5b-c). Following fine-cutting, a side cut is performed at 30 kV, 0.79 nA which detaches one side of the FIB section from the surrounding matrix material (Fig. 2.5d). Next, the bottom of the section is detached from the bulk material, mostly composed of meteorite matrix, with an undercut (30
kV, 0.79 nA). The undercut is an L-shaped pattern that is drawn over the entire bottom of the FIB section and extends part of the way up the side of the FIB section so that the FIB section is still supported by a small portion (~1 to 2 μm) of the matrix (Fig. 2.5e). The FIB section is now ready for the final liftout process.

The lift out process is completed using a micromanipulator, commercially referred to as EasyLift on the ThermoScientific FIB used for this dissertation. The micromanipulator uses a tungsten needle, which is inserted into the field of view and moved toward the section. Once in contact with the edge of the section, the needle is welded to the section by depositing ~500 nm of Pt using the Pt GIS. Once the needle is welded to the section, the next step is to detach the section from the bulk substrate. The ion beam current is increased, and the final cut is made to fully detach the section from the matrix. The needle is then moved slowly in (z) to lift the FIB section from the trench. Following lift out, the section is welded to a Cu TEM grid and the needle is cut free from the section using the Ga+ beam (Fig. 2.5f). Once both sides of the section are secured with a Pt weld, the section can be thinned to electron transparency (<100 nm). The thinning process involves milling small amounts of material from both faces of the FIB section using the ion beam (30 kV, 0.23 nA) until the desired thickness is achieved for TEM (< 100 nm, Fig. 2.5g-h). All samples reported in the results chapters of this dissertation were extracted from meteorite thin sections using the same FIB-SEM procedure discussed above.
2.4 TEM Chemical and Microstructural Analysis

2.4.1 Image Formation

In the TEM, a high-energy beam of electrons is transmitted through an electron transparent sample to form an image. Multiple types of electron sources are available on commercial TEMs, but relevant here is the field emission gun (FEG) that produces electrons when an electric potential is applied between the source and two anodes. The first anode provides the extraction voltage needed to pull electrons out of the tip and the second anode accelerates the electrons. Different acceleration voltages can be used depending on the instrument and whether the sample is beam sensitive. For example, using higher acceleration voltages will provide higher resolution, but can also cause greater beam damage than lower acceleration voltage instruments. All measurements completed for this dissertation were done using an acceleration voltage of 200 kV. Figure 2.6 outlines the path of an electron from the beginning of its journey at the electron source to the final image.

After an electron is emitted from the source, it passes through a series of condenser lenses and the condenser aperture. Figure 2.7 outlines the major angles in the TEM including the convergence angle of the beam (α), which defines the angle of incidence of electrons on the sample, the collection semi-angle (β) which can be controlled by apertures and detectors to collect a certain portion of scattered electrons, and the scattering semi-angle (θ), which is used to define scattering angles controlled by the sample. The size of the condenser aperture controls the convergence angle of the beam and also restricts the number of electrons allowed to pass through the sample. In conventional TEM mode, the electron beam is parallel to the optic axis of the microscope, and so the convergence and is small (<1 mrad). Alternatively, in scanning TEM
Figure 2.6: General ray diagram of a TEM showing locations of the lenses and apertures with respect to the sample plane from Williams and Carter (2009).
Figure 2.7: Schematic of major angles in the TEM including the angle of incidence/convergence ($\alpha$), the collection angle ($\beta$), and scattering angles from the sample ($\theta$) from Williams and Carter (2009).
(STEM) mode, the electron beam is converged relative to the optic axis to create a focused probe and scanned across the sample surface. The convergence angle in STEM mode changes based on the probe size and aperture. On the Hitachi HF5000 used in this work, the convergence angle was \( \sim 18 \) mrad using a 136 pm probe and STEM aperture 3. Following transmission through the sample, electrons then pass through the objective lens and a diffraction pattern is formed in its back focal plane (Fig. 2.6). The diffracted beams are combined to form an image on the image plane of the objective lens and the intermediate and projector lenses magnify and project the image. In TEM mode, the object plane is the image plane of the objective lens and bright-field images can be formed and collected when an aperture is used to select only the direct beam. In diffraction mode, the back focal plane of the objective lens acts is the object plane for the intermediate lens, and diffraction patterns can be collected and measured to identify phase and orientation of crystals. In STEM mode, bright-field (BF) and HAADF images can be formed when detectors are place on-axis, or in a plane conjugate to the back focal plane, respectively. HAADF images are useful because they are atomic-number \( (Z) \) contrast images, where the contrast (intensity) in the image is proportional to \( Z^2 \). Therefore, high-\( Z \) materials appear bright, compared to lower-\( Z \) surrounding materials.

Electrons have both particle and wave characteristics. When an electron interacts with a sample, its wave characteristics, such as amplitude and phase can change and result in image contrast. Waves interfere constructively (reinforce one another) when they are in phase and interfere destructively (cancel each other out) when they are out of phase. When scattering occurs in a sample (discussed further in section 2.4.2), those electrons that are elastically scattered are usually coherent and remain in phase after interacting with the sample (Fig. 2.8). Alternatively,
inelastically scattered electrons are incoherent and have no phase relationship after interacting with the sample.

Phase contrast arises when more than one beam is contributing to the image as a result of differences in the phase of electron waves when they interact with the sample. These images are formed when all diffracted electrons are allowed to interfere with each other and transmit to the image plane. Phase contrast images can be used to gain information on the atomic structure of a sample as the phase of the electron wave is determined by atomic positions in the sample. Phase contrast or high-resolution TEM (HRTEM) images contain atomic-scale information such as lattice fringes, which provide information on long-range atomic order including spacing between lattice planes (d-spacing) and their orientation in crystalline samples. Additionally, phase contrast images can also show structural defects and perturbations in the form of Fresnel fringes and moiré fringes.

Alternatively, amplitude contrast arises from variations in mass or thickness (or both) in the sample. Thickness variation results in contrast as the electron beam interacts with more or less material and therefore more or less mass. In order to form an amplitude-contrast image, an objective aperture is required to restrict diffracted waves from interfering with one another such that only amplitude information is obtained in the image. BF images are obtained when only the direct beam is selected for image formation. Alternatively, dark-field (DF) images are obtained when the scattered beams are selected to contribute to the image. Both BF and DF images can also be obtained in STEM mode using dedicated detectors.
Figure 2.8: Schematic of electron scattering in a thin specimen from Williams and Carter (2009).
2.4.2 Elastic and Inelastic Scattering

As the electron beam is transmitted through the sample, electrons interact with each other and atomic nuclei in the sample. Elastic scattering occurs when the incident electrons do not lose energy as a result of interactions with either a single atom or many atoms collectively in a given sample. In the case of a single, isolated atom, elastic scattering can include electron-electron interactions that result in small scattering angles, or high-angle scattering results from electron-nucleus interactions. These elastically scattered electrons contribute contrast to TEM images as discussed above. Additionally, elastic scattering is also important in electron diffraction, where the electron wave interacts with the sample as a whole. Electron diffraction will be discussed in section 2.4.3.

Alternatively, inelastic scattering occurs when the interactions of incident beam with the sample result in a loss of energy. When a high-energy electron comes into contact with an atom, it first encounters the loosely-bound electron cloud before passing through to the more tightly-bound inner electrons, and finally the nucleus. The further the electron penetrates into the atomic structure, the greater the amount of energy that may be lost as a result of such an interaction. Loosely bound valence electrons called secondary electrons can be ejected from the sample and collected by a detector. Such secondary electrons provide useful information on the surface of the sample. Inelastic scattering is key to techniques including electron energy-loss spectroscopy (EELS) and EDS, the latter of which will be discussed in detail in section 2.4.4.

Inelastic scattering results in the emission of characteristic X-rays and energy-loss electrons important for understanding sample chemistry. In order to produce characteristic X-rays, high-energy electrons must interact with the inner-shell or core electrons of an atom (Fig. 2.2). If
the interaction results in more than the critical amount of energy (the critical ionization energy, $E_c$) being transferred to the inner-shell electron, that electron is ejected, leaving the atom in an ionized state. The atom can return to its ground state by filling the hole in the inner shell with an electron from the outer shell. Such a process results in the generation of an X-ray (Fig. 2.2). The associated energy of the X-ray is characteristic of the energy difference between the two electron shells, which is unique to the atom. X-rays and their associated energies can be collected by EDS and provide useful information on the chemical composition of the sample. Similarly, the amount of energy loss from the incident high-energy electrons because of inelastic scattering can also be collected using EELS to gain information about the chemistry and structure of the sample. The materials studied in this dissertation were measured for their composition using EDS.

2.4.3 Selected Area Electron Diffraction

Electron diffraction patterns are used to gain information about the crystal structure of a sample including long-range atomic order, phase, and crystal orientation. A selected-area electron diffraction (SAED) pattern is formed when a selected-area aperture is inserted into the image plane of the objective lens (Fig. 2.6). This field-limiting aperture restricts the illuminated area of the sample that contributes to the diffraction pattern. To collect a diffraction pattern in the TEM, the microscope is put into diffraction mode, which projects the back focal plane of the objective lens onto the viewing screen. Electron diffraction is important in materials science for determining the crystallinity and phase of a sample. Diffraction patterns can be formed using parallel or converged beam illumination. The work included in this dissertation exclusively used parallel illumination, which in crystalline samples, forms a series of diffraction spots, or reflections. The positions of
these reflections and the distances and angles between them relate directly to their structures. Bragg diffraction describes how waves behave when they reflect off atomic planes in a sample (Fig. 2.9). The waves reflected off adjacent scattering centers must have a path difference equal to an integral number of wavelengths ($n\lambda$) in order to remain in phase. The path difference ($AB + BC$, Fig. 2.9) in TEM is the difference between electron waves reflected from two planes and such planes are separated by a distance $d$. The Bragg angle ($\theta_B$) defines the angle of the incident plane wave and the scattered plane wave. The path difference $AB$ and $BC$ are equal to $d \sin \theta_B$, so the total path difference is $2d \sin \theta_B$. Therefore, Bragg’s law can be written as follows (equation 2.3):

$$n \lambda = 2d \sin \theta_B$$

$$\frac{\lambda}{d} = 2 \sin \theta \sim \theta$$

**Figure 2.9:** Schematic demonstrating the Bragg description of diffraction, where an incident plane wave reflects off two adjacent planes separated by a distance $d$ from Williams and Carter (2009).
The magnification of a diffraction pattern is described by its camera length \((L)\), which can be calculated using the spacing \((R)\) between the direct and scattered beam and the angle of scattering \((2\theta)\), Figure 2.10) assuming the small angle approximation as follows (equation 2.5):

\[
\frac{R}{L} = \tan 2\theta \sim \theta
\]

**Figure 2.10:** Schematic demonstrating camera length \((L)\) concept, from Williams and Carter (2009).
Each diffraction pattern can be identified and indexed. Indexing a diffraction pattern associates each reflection with a specific plane \((hkl)\) or set of planes \(\{hkl\}\). From this information, the orientation, or zone axis \([UVW]\) can be determined, which defines the direction along the intersection of two or more planes (Williams & Carter, 2006). Indexing diffraction patterns allows for the identification of mineral phases and their orientation in a sample, which in the case of presolar grains in this dissertation, can be compared to thermodynamic model predictions to infer their origins.

The distance between reflections measured in a diffraction pattern, called the d-spacing, provides information on the distance between atomic planes in the crystal. The d-spacing is characteristic for a crystal structure based on its unit cell and symmetry. Equation 2.6 can be used to calculate the d-spacing for a given diffraction pattern, which combines equations 2.4 and 2.5 from Bragg’s law and the camera length to give:

\[
R_d = \lambda L
\]

where \(R\) is the experimentally measured distance between reflections in pixels and \(\lambda L\) is the camera constant (Å-px), which combines the wavelength (\(\lambda\)) of the electrons accelerated through the sample and the camera length (\(L\)) used to collect the diffraction pattern. In the case of polycrystalline or amorphous diffraction patterns, \(R\) is the distance measured from an origin to the reflection or ring. The calculated d-spacings for a given sample can be compared with structural databases to identify candidate mineral phases and associated crystal planes \((hkl)\). The zone axis of a given diffraction pattern can be calculated by taking the cross-product of two planes \((h_1k_1l_1)\) and \((h_2k_2l_2)\) as follows (equation 2.7):

\[
(h_1k_1l_1) \times (h_2k_2l_2) = (k_1l_2 - k_2l_1) - (h_1l_2 - h_2l_1) + (h_1k_2 - h_2k_1) = [UVW]
\]
The diffractions patterns reported in this dissertation were indexed by manually measuring patterns using Adobe Photoshop and calculating the associated d-spacings and also measured using the Crystallographic Image Processing Software Package (CRISP; Hovmöller, 1992). CRISP can be used to index diffraction patterns based on calibrated camera constants and provides d-spacings, associated Miller indices and candidate zone axes. The CRISP software contains a customizable database of minerals to which it compares measurements. Using such information, simulated diffraction patterns were generated, based on candidate zone axes output by CRISP, with the CrystalMaker software package to confirm indexing. CRISP is not a substitute for measuring diffraction patterns manually, but is an efficient way to narrow down candidate phases and is a tool that was used in addition to EDS to identify presolar grain phases in this dissertation.

2.4.4 Energy Dispersive X-ray Spectroscopy

Structural information obtained using electron diffraction is complemented by chemical information obtained using EDS. As mentioned above, EDS relies on characteristic X-rays produced through inelastic scattering processes as the electron beam interacts with the sample. Once the characteristic X-ray is collected by the detector, a charge pulse proportional to the energy of the X-ray is generated and converted to a voltage. The voltage is amplified and isolated from other pulses before being electronically identified as resulting from an X-ray with a specific energy and digitally stored in its assigned channel. The data are displayed as a spectrum that plots counts versus the X-ray energy in keV.

EDS measurements can include several different types of analyses such as point analyses, linescans, and spectrum images or data cubes from which two-dimensional chemical maps can be
derived that show the distribution of elements in a given field of view. Quantification of EDS data can provide details on the chemical composition of the sample including atomic and weight percent compositions and stoichiometry. The Cliff-Lorimer technique is commonly used for quantitative EDS calculations (Cliff and Lorimer, 1975). In a binary system with two elements (A and B), the Cliff-Lorimer equation (2.8) relates the concentrations of element ‘A’ and ‘B’ (C_A, C_B) with their intensities (I_A, I_B) as follows:

\[
\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}
\]  

(2.8)

\[
C_a + C_b = 1
\]  

(2.9)

where \( k_{AB} \) is the \( k \)-factor, a sensitivity factor that varies according to the microscope, EDS system, and the analytical conditions used. Generally, \( k \)-factors for different elements are determined for a given instrument using standards with a known composition. The EDS quantification in this dissertation, however, is standardless and therefore uses theoretical \( k \)-factors to calculate the compositions of presolar grains and surrounding matrix materials as reported in Chapters 3, 4, and 5.
CHAPTER 3. COORDINATED CHEMICAL AND MICROSTRUCTURAL ANALYSES OF PRESOLAR SILICATE GRAINS FROM AGB/RGB STARS AND SUPERNOVAE IN THE CO3.0 CHONDRITE DOMINION RANGE 08006


Abstract

We report the structural and chemical analyses of six presolar silicate grains identified in situ in the CO3.0 carbonaceous chondrite Dominion Range (DOM) 08006. Two of the grains have O-isotopic compositions consistent with origins in the circumstellar envelopes of low-mass (<2M☉) Asymptotic Giant Branch (AGB)/Red Giant branch (RGB) stars, although without Mg-isotopic data, origins in supernovae (SNe) cannot be ruled out. The other four grains have O-isotopic compositions consistent with origins in the ejecta of type-II SNe. Transmission electron microscopy (TEM) analyses reveal that all grains are crystalline (single crystal or polycrystalline) and have varied compositions. The analyzed AGB/RGB grains include an Fe-rich crystalline olivine with an Fe-sulfide inclusion and a chemically zoned olivine grain that also contains an Fe-oxide rim. The grains derived from SNe include two polycrystalline assemblages with structures that overlap with both olivine and pyroxene, an assemblage composed of both a single crystal of forsterite as well as polycrystalline forsterite, and an orthopyroxene grain with an embedded Fe-sulfide crystal. The thermodynamic origins of both AGB/RGB and SN grains are also diverse. The
structure and compositions of two grains are consistent with equilibrium thermodynamic predictions of condensation, whereas four are not, suggesting formation through nonequilibrium or multi-step processes. Our observations of presolar silicate grains suggest that the circumstellar envelopes of AGB/RGB stars and the ejecta of SNe can produce grains with comparable structures and compositions.

3.1 Introduction

During the latter stages of stellar evolution, dust is produced in circumstellar envelopes and in the ejecta of stellar explosions such as supernovae (SNe). These circumstellar dust grains are transported away from the star, enter the interstellar medium (ISM), and can be incorporated into newly forming stellar and planetary systems. A portion of grains that condensed in stellar environments traveled through the ISM and were incorporated into our solar system. Some of these ‘presolar’ grains survived solar-system formation and are identifiable by their anomalous isotopic compositions in primitive solar-system materials such as meteorites, micrometeorites, interplanetary dust particles, and more recently, cometary samples returned by the NASA Stardust mission. Recorded within the chemistry and crystal structure of these materials are the nucleosynthetic processes and thermodynamic properties of the environments in which they condensed (e.g., Zinner 2014; Floss & Haenecour 2016; Nittler & Ciesla 2016). Thus, analysis of the isotopic and chemical compositions, as well as the crystal structure of circumstellar grains can therefore provide ground-truth information on nucleosynthetic processes, the thermodynamic conditions in circumstellar environments and stellar explosions, as well as their subsequent transport and alteration histories in the ISM and on meteorite parent bodies.
Silicates are the most abundant type of dust present in circumstellar envelopes of evolved O-rich stars and the ISM (Kemper et al., 2004; Speck et al., 2000; Tielens et al., 1998). The majority (>90%) of silicate dust formed in circumstellar envelopes is believed to be amorphous with Fe-bearing olivine compositions, though some circumstellar envelopes have more substantial fractions of crystalline dust (Tielens et al. 1998; Speck et al. 2000; Molster & Kemper 2005). Similarly, observations have also suggested that silicates in the ISM are also Fe-bearing and mainly (>99%) amorphous due to ion radiation, shock waves from SNe, and grain-grain collisions (Jones and Nuth, 2011). Of the fraction that are crystalline, observations suggest forsteritic (Mg$_2$SiO$_4$) compositions, but a small portion occur as pyroxenes such as diopside (CaMgSi$_2$O$_6$) and enstatite (MgSiO$_3$) (Kemper et al., 2004).

Astronomical observations also provide some insight into the composition of dust in the ejecta of SNe and suggest an abundance of amorphous silicates (e.g., Arendt et al. 1999; Rho et al. 2008, 2009). For example, infrared (IR) observations of the Cassiopeia A (Cas A) supernova (SN) remnant show clear evidence for dust formation (Arendt et al. 1999). The dust mass of Cas A is estimated to be 0.020 to 0.054 solar mass (M$_\odot$) and infrared spectrograph (IRS) spectra of Cas A obtained by Spitzer Space Telescope observations show features consistent with abundant Mg-silicates as well as other species including SiO$_2$, SiC, metallic Fe, oxides, and sulfides (Rho et al. 2008; Arendt et al. 2014). Similarly, Spitzer observations of the young SN remnant 1E0102-72.3 show evidence for newly formed dust, with dust mass estimated to be 0.007 to 0.015 M$_\odot$ and spectral features consistent with MgSiO$_3$ and Si are observed (Rho et al. 2009).

Presolar grains are among the building blocks of our solar system and are therefore of particular interest for models of solar-system formation. A SN shock was suggested to have
triggered solar-system formation (Cameron & Truran 1977), and the presence of some short-lived radionuclides in the early solar system suggests contribution of material from a nearby SN (e.g., MacPherson et al. 1995; Tachibana & Huss 2003; Busso et al. 2003; Nittler & Dauphas 2006). The contribution of material from a nearby SN explosion is also supported by isotopic evidence in presolar grains. Such evidence includes the initial presence of short-lived $^{44}$Ti and $^{49}$V (Amari et al. 1992, 1995; Hoppe et al. 1996, 2000; Nittler et al. 1996; Hoppe & Besmehn 2002; Besmehn & Hoppe 2003) which have origins in SNe (Timmes et al. 1996), $^{28}$Si excesses, and large inferred $^{26}$Al/$^{27}$Al ratios which cannot be explained by other stellar origins (e.g., Amari et al. 1995; Hoppe et al. 1996, 2000; Nittler et al. 1995; Lin et al. 2002). Additionally, the relative abundances of SN oxide and silicate grains varies among different primitive materials. SN grains make up ~25-30% of the presolar oxide and silicate population in micrometeorites and interplanetary dust particles, whereas they compose only ~10% of presolar oxides and silicates in primitive carbonaceous chondrites (Floss & Haenecour 2016c). Work by Hoppe et al. (2015) notes that there could be a correlation between grain size and the fraction of O-rich SN grains in primitive meteorites, where the ≤150 nm size fraction of SN grains in their study made up ~33% of the total number of grains. This heterogeneous distribution of SN oxide and silicate grains among primitive planetary materials is thought to suggest that grains were injected into the early solar nebula from a nearby SN and incorporated in varied amounts into parent bodies forming in different parts and/or at different times in the solar nebula (Yada et al. 2008).

Detailed chemical and mineralogical analyses of presolar silicates from AGB stars, RGB stars, and SNe using transmission electron microscopy (TEM) have provided insight into their origins. Studies reveal structures and morphologies that include amorphous grains, single crystals,
aggregates, and polycrystalline assemblages, with compositions including olivine, pyroxene, and intermediate compositions between the two (Floss et al., 2006; Messenger et al., 2005; Messenger et al., 2003; Nguyen et al., 2016; Nguyen et al., 2010; Nguyen et al., 2007; Stroud et al., 2014; Vollmer et al., 2009; Vollmer et al., 2013; Vollmer et al., 2007; Zega et al., 2020). These studies reveal complex formation histories, with evidence for equilibrium condensation suggested by single, stoichiometric crystals, deviations from equilibrium suggested by nonstoichiometric, amorphous, Fe-rich phases, and potentially multistep condensation suggested by polycrystalline assemblages. Evidence for secondary alteration processes in the ISM, solar nebula, and on the parent body are also observed in some grains (e.g., Vollmer et al. 2009; Nguyen et al. 2010, 2016; Floss and Stadermann 2012; Leitner et al. 2016; Zega et al. 2020).

The majority of silicate grains analyzed for their detailed structure and chemistry are derived from AGB/RGB origins. SN silicates are thought to comprise ~10% of anomalous grains in meteorites (Haenecour et al. 2018), though recent work suggests this abundance could be much higher (13% to 20%), as some Group-1 and Group-2 grains originally thought to be from AGB/RGB origins could be from SNe (Leitner & Hoppe 2019; Verdier-Paoletti et al. 2019; Hoppe et al. 2021). Therefore, there is a need for further analyses of SN silicates in order to understand the thermodynamic conditions of dust formation within the ejecta of SNe and their subsequent transport and preservation in solar-system materials. Here we report the coordinated analyses of six presolar silicate grains, two of which are thought to have formed in the circumstellar envelopes of AGB stars, and four of which are thought to have formed in the ejecta of SNe. The silicate grains were identified in situ in order to compare the structure and chemistry of grains derived
from different stellar origins from the same meteorite and to understand their thermodynamic origins. Initial results were reported in Seifert et al. (2018, 2019, 2020).

### 3.2 Sample and Experimental Methods

A petrographic thin section of the CO3.0 Dominion Range (DOM) 08006 carbonaceous chondrite obtained from the meteorite curatorial facility at NASA Johnson Space Center was examined. DOM 08006 is composed of an unequilibrated mixture of anhydrous silicates, metal, and sulfides (Davidson et al. 2019) and is classified as one of the most pristine meteoritic samples available for study due to its lack of evidence of alteration processes. DOM 08006 contains one of the highest abundances of O-rich presolar grains reported to date in meteorites (~257 ppm, Haenecour et al. 2018; Nittler et al. 2018; Davidson et al. 2019), similar to abundances reported in a recent study of Asuka 12169 (~236 ppm, Nittler et al. 2021). Raster-ion imaging of select matrix regions and fine-grained rims around chondrules (FGRs) was performed with the Cameca NanoSIMS 50 at Washington University in St. Louis and previously reported by (Haenecour et al., 2018)). That work identified 55 presolar grains containing anomalous oxygen isotopic compositions. Following the NanoSIMS measurements, the grains were also measured with the PHI 700 Auger nanoprobe at Washington University in St. Louis, where quantitative major element compositions of the grains were derived from Auger spectra. Auger maps were acquired for select grains based on their isotopic and elemental compositions. Information on the NanoSIMS and Auger analysis can be found in (Floss and Stadermann, 2012; Haenecour et al., 2018). We selected six of these grains based on their size (100 nm < x < 1 μm) and suggested
AGB/RGB or SN origins, as indicated by their isotopic compositions, for detailed analysis using TEM.

Electron transparent cross-sections (<100 nm in projected thickness) of the selected grains were prepared for detailed structural and chemical analysis using the Thermo Fisher Scientific (formerly FEI) Helios G$^3$ focused-ion beam scanning-electron microscope (FIB-SEM) located in the Kuiper Materials Imaging and Characterization Facility (KMICF) at the Lunar and Planetary Laboratory (LPL), University of Arizona. The procedure for producing electron-transparent cross sections of presolar grains was described in many papers (Nguyen et al., 2007; 2016; Stroud et al., 2004; Zega et al., 2007, 2011, 2014, 2015, 2020). Briefly, we first go through an alignment procedure to ensure that we capture the anomalous region of interest, initially identified with NanoSIMS, in our FIB transect. The ImageAlign software (e.g., Floss et al. 2006; Floss & Stadermann 2009a, 2012) is used to correlate and align NanoSIMS and Auger data, including both ion and secondary electron (SE) images, with SE images from the FIB-SEM to confirm the location of the anomalous grain. The ImageAlign application works by aligning features between two images. All the NanoSIMS raster ion images and SE Auger images are imported into the software and morphologic features are matched between the two datasets until they are aligned. Once the images are aligned, we trace the O-isotope anomaly in the NanoSIMS image and the corresponding area is automatically traced in the SE image. We repeat this process a second time with two SE images from the Auger nanoprobe, one with the traced O-anomaly and a higher resolution SE image to ensure precise location of the anomaly. The alignment software is capable of aligning images of different magnification and/or orientation. Thirdly, the alignment procedure is repeated with SE images from the Auger nanoprobe and the higher resolution SE image from the FIB-SEM.
Finally, these alignments are then confirmed one more time by manually overlaying the SE NanoSIMS images, SE FIB-SEM images, and O-isotope maps (see Appendix A, Figs. S1-S4). We note that this alignment is not only completed by one person, but is a group effort and includes extensive discussion of the best plan for FIB extraction. Next, using the electron beam in the FIB, we deposited a protective Pt fiducial marker on top of the grain as well as 100 nm thick markers on either side of the grain fiducial. The purpose of the fiducial markers are to: (i) provide an initial protective layer for the grains of interest prior to final deposition of the C capping layer; (ii) mark their location in cross section as an endpoint indicator for ion milling; and (iii) facilitate identification of the grain in cross section in the TEM. We note that the NanoSIMS and Auger analyses confirmed that the presolar grain was not completely sputtered during the NanoSIMS measurements. Prior to FIB extraction and subsequent TEM analyses, the crystallinity, shape, and the extent to which the anomalous region permeates below the surface of the section are unknown. We therefore do not presume the extent of the carrier of the isotopic anomaly below the sample surface or whether it is a single phase, multiple grains, or polycrystalline. The correct placement of the Pt fiducial markers is therefore essential to locating the anomalous region of interest in the TEM. Following the deposition of the Pt fiducial markers, a C capping layer (~3 μm thick) was deposited over the Pt markers using the Ga⁺ ion beam to further protect the grain from ion implantation and radiation damage during the ion milling process. Generally, C is deposited transecting the longest dimension of the grains to maximize the cross-sectional area that we can analyze in the TEM. Cross sectioning involved stairstep cuts previously described in the aforementioned papers, in situ extraction, and thinning to < 100 nm.
The FIB sections were analyzed using the Hitachi HF5000 scanning TEM (S/TEM) in the KMICF at LPL. The HF5000 is equipped with a cold-field emission gun, a 3\textsuperscript{rd}-order spherical-aberration corrector for STEM mode, bright-field (BF), dark-field (DF), and SE STEM detectors, and an Oxford Instruments X-Max N 100 TLE EDS system with dual 100 mm\textsuperscript{2} windowless silicon-drift detectors providing a large solid angle (Ω = 2.0 sr) for rapid EDS mapping of samples in minutes instead of hours. It is also equipped with a Gatan OneView 4k × 4k pixel CMOS camera for the acquisition of TEM images and electron-diffraction patterns.

Grain composition was obtained through EDS mapping and standardless quantification based on the Cliff-Lorimer method (Cliff and Lorimer, 1975) with theoretical correction (k) factors. Information on the long-range atomic order and crystal structure was determined using selected-area electron-diffraction (SAED) patterns. All SAED patterns were measured manually with Adobe Photoshop and with the Crystallographic Image Processing Software Package (CRISP, Hovmöller 1992) based on calibrated camera constants. Additionally, the indexing of experimental SAED patterns were verified by comparison to simulated diffraction patterns using the CrystalMaker software package.

3.3 Results

3.3.1 DOM-49

The O-isotopic compositions of all grains were reported in (Haenecour et al., 2018), but we note them here to place constraints on their stellar origins. NanoSIMS analysis shows that DOM-49 is enriched in $^{17}$O relative to solar-system values with $^{17}$O/$^{16}$O = 5.3 ± 0.2 (×10\textsuperscript{-4}) and $^{18}$O/$^{16}$O = 2.05 ± 0.04 (×10\textsuperscript{-3}). It plots in the Group-1 field of O-rich presolar grains (Fig. 3.1) as
defined by Nittler et al., (1997, 2008) and contains an oval shaped O-anomaly measuring 235 × 195 nm (Fig. 3.2a, arrow). Auger nanoprobe analysis shows that the composition of the grain is consistent with a ferromagnesian silicate. Additional information on major-element compositions for each grain can also be found in (Haenecour et al., 2018).

STEM imaging of the region below the Pt marker reveals an oval-shaped domain, indicated by a dashed line in Fig. 3.2b with orthogonal dimensions of 170 × 83 nm. HAADF contrast is mostly uniform except for a relatively brighter rounded feature in the center measuring 30 × 27 nm, indicated by an arrow in Fig. 3.2c. EDS mapping of the bulk of the domain reveals spatial correlations among Fe, O, Si, Mg, and also Ca and Al. (Fig. 3.2 d-g and j-k, respectively). Mg is concentrated in the left and right portions of the domain and Ca is concentrated at the top and right. The bright feature located in the middle of the domain reveals spatial correlations among Fe, Ni, and S (Fig. 3.2 d, h-i). Comparison of the HAADF (Fig. 3.2 c) and SE (not shown) images of the Fe, Ni, S region suggest that the feature is not on the surface. We were not able to obtain an SAED pattern from this region due to its small size, however, the elemental composition extracted from an EDS spectrum can be found in Table 3.1. Zone-axis SAED patterns were obtained from the right and left sides of DOM-49, indicated by the dashed circles in Fig. 3.2c and indexing is consistent with a single crystal of olivine (Fig. 3.2 l-m). Standardless quantification of an EDS spectrum extracted from the grain indicates an Fe-rich olivine composition of (Mg0.44, Fe1.03, Ca0.05, Ni0.09, Al0.1)(Si1.12)O4 (Table 3.1).
Figure 3.2: NanoSIMS and TEM data on DOM-49. (a) NanoSIMS $\delta^{17}$O (delta notation denotes the deviation of an isotopic ratio of an element $R$ from a standard $[\delta R = ((R_{measured}/R_{standard}) - 1) \times 1000]$, where $R$ is the ratio of the heavy to light isotope) map of DOM-49, with legend at right of image in units of per mil (‰). (b) BF STEM image with dashed line indicating DOM-49 below Pt fiducial marker (we note that dashed line is not meant to be absolute, but rather guide the reader to the ROI). (c) HAADF STEM image with arrow indicating brighter contrast center. (d-k) False color EDS maps for Fe, O, Si, Mg, Ni, S, Ca, Al, respectively. (l-m) SAED pattern from region denoted by (l) and (m) in HAADF image.
### Table 3.1 Grain compositions determined using EDS expressed in wt\% and cation count.

<table>
<thead>
<tr>
<th>Grain</th>
<th>DOM-49 (Fe, Ni, S region)</th>
<th>DOM-49 (Shell)</th>
<th>DOM-59 (Core)</th>
<th>DOM-59 (Fe, Ni, S region)</th>
<th>DOM-22 (R)</th>
<th>DOM-22 (Shale)</th>
<th>DOM-35 (L)</th>
<th>DOM-35 (R)</th>
<th>DOM-39 (Fe, Ni, S region)</th>
<th>DOM-50 (Fe, Ni, S region)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe-sulfide</td>
<td>Fe-sulfide</td>
<td>Fe-sulfide</td>
<td>Fe-sulfide</td>
<td>Fe-sulfide</td>
<td>Fe-sulfide</td>
<td>Fe-sulfide</td>
<td>Fe-sulfide</td>
<td>Fe-sulfide</td>
<td>Fe-sulfide</td>
</tr>
<tr>
<td></td>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>36.84</td>
<td>28.98</td>
<td>44.59</td>
<td>44.15</td>
<td>41.17</td>
<td>n.d.</td>
<td>43.95</td>
<td>43.05</td>
<td>n.d.</td>
<td>39.78</td>
</tr>
<tr>
<td>Si</td>
<td>18.16</td>
<td>17.41</td>
<td>19.72</td>
<td>20.20</td>
<td>20.01</td>
<td>n.d.</td>
<td>19.87</td>
<td>18.83</td>
<td>n.d.</td>
<td>21.71</td>
</tr>
<tr>
<td>Mg</td>
<td>6.12</td>
<td>5.65</td>
<td>32.03</td>
<td>27.16</td>
<td>18.16</td>
<td>n.d.</td>
<td>27.66</td>
<td>27.02</td>
<td>n.d.</td>
<td>7.75</td>
</tr>
<tr>
<td>Fe</td>
<td>33.05</td>
<td>35.78</td>
<td>3.67</td>
<td>1.16</td>
<td>18.20</td>
<td>48.04</td>
<td>6.70</td>
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<td>1.06</td>
<td>n.d.</td>
<td>1.99</td>
<td>n.d.</td>
</tr>
<tr>
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<td>n.d.</td>
<td>4.67</td>
<td>12.77</td>
<td>n.d.</td>
<td>1.32</td>
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**Cation**

| O     | 4                         | n.d.           | 4               | 4                        | 12        | n.d.           | 4         | 4         | 3                        | n.d.                     |
| Si    | 1.12                      | n.d.           | 1.01            | 1.04                    | 3.32      | n.d.           | 1.03      | 1.0       | 9.3                      | n.d.                     |
| Mg    | 0.44                      | n.d.           | 1.89            | 1.62                    | 3.48      | n.d.           | 1.66      | 1.65      | 0.38                     | n.d.                     |
| Fe    | 1.03                      | n.d.           | 0.09            | 0.03                    | 1.52      | n.d.           | 0.17      | 0.27      | 0.52                     | 1.37                     |
| Ca    | 0.05                      | n.d.           | n.d.            | 0.27                    | n.d.      | n.d.           | 0.03      | n.d.      | n.d.                     | n.d.                     |
| Al    | 0.10                      | n.d.           | n.d.            | 0.15                    | n.d.      | n.d.           | 0.05      | 0.06      | 0.09                     | n.d.                     |
| Ni    | 0.09                      | n.d.           | n.d.            | 0.13                    | 3.22      | n.d.           | 0.10      | 0.22      | n.d.                     | n.d.                     |

O-18\textsuperscript{1}O, 16\textsuperscript{1}O compositions from Haencour et al. (2018). All analyses normalized to 100%.

L and R refer to left and right sides of grain.

n.d. = not detected.
3.3.2 DOM-59

NanoSIMS analysis of DOM-59 reveals a crescent-shaped O-anomaly measuring 310 × 390 nm (Fig. 3.3 a-b). It is characterized by enrichment in $^{17}$O and depletion in $^{18}$O relative to solar-system values, with $^{17}$O/$^{16}$O = 11.6 ± 0.5 ($\times 10^{-4}$) and $^{18}$O/$^{16}$O = 0.69 ± 0.03 ($\times 10^{-3}$) and plots in the Group-2 field (Fig. 3.1). Auger nanoprobe mapping shows correlations among Mg, Fe, Si and O suggesting that the grain is a ferromagnesian silicate (Fig. 3.3 d-h).

Figure 3.3: Auger nanoprobe data on DOM-59. (a-b) NanoSIMS $\delta^{17}$O and $\delta^{18}$O maps of DOM-59, with legend at left of image in units of per mil ($\%$). (c) SE image of DOM-59 with anomalous region outlined and FIB transect highlighted by dashed line. (d-h) false color Auger elemental maps as indicated by upper left corner of image.
STEM imaging below the Pt fiducial marker reveals an irregularly shaped grain with orthogonal dimensions of 670 × 596 nm (Fig. 3.4 a-b). HAADF imaging shows a brighter contrast rim (Fig. 3.4b) that is visible by a textural change outside the grain, as indicated by arrows in Fig. 4a. In an effort to get the FIB section as thin as possible for TEM analysis, part of the capping layer and grain were milled through during final thinning. However, the majority of the grain remained undamaged and half of the grain remained covered by the capping layer. EDS mapping reveals spatial correlations among several elements. The bulk of the grain contains spatial correlations among Mg, Si, and O (Fig. 3.4 d-f), whereas the center of the grain contains spatial correlations among O, Si and Ca (Fig. 3.4 d-e,g) and lesser amounts of Mg (Fig. 3.4f). The rim shows spatial correlations between Fe and O with minor Si and Mg (Fig. 3.4 c-f). We note that the overall FIB section of DOM-59 has a more compact structure than the other FIB sections of DOM 08006. We observe heterogeneous distributions of iron in the section with vein-like structures that appear to surround aggregates of grains. SAED patterns acquired across DOM-59 indicate that the grain is crystalline and indexing of a zone-axis pattern is consistent with forsterite (a representative pattern is shown in Fig. 3.4h). We were not able to obtain a distinct SAED pattern from the Ca-rich center of DOM-59. An EDS spectrum was extracted from the Mg-rich surface region and standardless quantification indicates a forsterite composition with \((\text{Mg}_{1.89}, \text{Fe}_{0.09})\text{Si}_{1.01}\text{O}_4\) (Table 3.1). An EDS spectrum was also extracted from the Ca-rich core of the grain and standardless quantification suggests a C-rich olivine composition with \((\text{Mg}_{1.62}, \text{Fe}_{0.03}, \text{Ca}_{0.27})\text{Si}_{1.04}\text{O}_4\) (Table 3.1).
**Figure 3.4:** TEM data on DOM-59. (a) BF STEM image with dashed line indicating location of DOM-59 (we note that dashed line is not meant to be absolute, but guide the reader to the ROI) and arrows indicating textural change outside of DOM-59. (b) HAADF STEM image of DOM-59, with Pt marker indicated. (c-g) False color EDS maps of Fe, O, Si, Mg, Ca, respectively. (h) SAED pattern acquired from region (h) as shown in the HAADF image.
3.3.3. *DOM-22*

NanoSIMS analysis reveals an oval-shaped O-anomaly with orthogonal dimensions of 195 × 195 nm indicated by an arrow in Fig. 3.5a. The anomaly is characterized by enrichment in $^{18}\text{O}$ relative to solar-system values with $^{17}\text{O}/^{16}\text{O}= 3.8 \pm 0.2 \times 10^{-4}$ and $^{18}\text{O}/^{16}\text{O}= 2.47 \pm 0.05 \times 10^{-3}$ and plots in the Group-4 field (Fig. 3.1). Auger nanoprobe analysis indicates a ferromagnesian silicate composition (Haenecour et al., 2018).

STEM imaging shows that DOM-22 is not a discrete grain, precluding identification of a single-phase carrier of the O-isotope anomaly. We therefore consider the region below the Pt fiducial marker as the O-anomalous presolar ‘grain’ DOM-22 (Fig. 3.5 b-d). HAADF images reveal a bright, high-contrast, elongated feature in the center of the field of view (indicated by arrow and dashed outline in Fig. 3.5c) suggesting a higher average atomic number material than the bulk, measuring 118 × 50 nm. EDS mapping below the Pt fiducial marker reveals that the bulk of the domain spatially correlates with Fe, O, Si, Mg, with minor Al (Fig. 3.5 e-h, k). The high-contrast region in the center of the field of view shows correlations among Fe, Ni, and S (Fig. 3.5e, i-j). EDS also reveals that other parts of the domain spatially correlate with Fe, Ni, and S, however, their small sizes preclude single-crystal SAED patterns from being acquired. SAED patterns were acquired across DOM-22 and indicate that the bulk of the domain is fine-grained, polycrystalline, and has d-spacings that overlap with both olivine and pyroxene (Table 3.2, Fig. 3.5m). Standardless quantification of EDS spectra from the fine-grained ferromagnesian silicate domain indicates a composition of $\text{Mg}_{3.48}$, $\text{Fe}_{1.52}$, $\text{Ni}_{0.13})(\text{Si}_{3.32}$, $\text{Al}_{0.15})\text{O}_{12}$ (Table 3.1). Due to the overlapping d-spacings with olivine and pyroxene, the cation composition was quantified based on 12 O atoms, which is the least common multiple of the three and four oxygens per formula.
Figure 3.5: NanoSIMS and TEM data on DOM-22. (a) NanoSIMS $\delta^{18}$O map of DOM-22, with legend at right of image in units of per mil ($\%$). (b) BF STEM image with DOM-22 located below Pt fiducial marker. (c) HAADF STEM image with bright contrast feature indicated by arrow. (d) SE STEM image with Pt fiducial marker labeled. (e-l) False color EDS maps of DOM-22 for Fe, O, Si, Mg, Ni, S, Al, Pt, respectively. (m) SAED pattern acquired from region (m) shown in BF image with rings labeled 1-4. (n) SAED pattern acquired from region (n) shown in BF image.
unit specific to pyroxene and olivine, respectively. The calculated composition most closely matches a mixture of olivine and pyroxene. In comparison, a zone-axis SAED pattern was acquired from the high-contrast Fe, Ni, S rich feature (Fig. 3.5n) in the center of the field of view and can be indexed to pentlandite. Standardless quantification of the pentlandite crystal indicates a composition of (Fe\textsubscript{6.68}, Ni\textsubscript{3.22})S\textsubscript{6.69} (Table 3.1). Comparison of the pentlandite crystal with the SE image shows that a portion appears to protrude from the surface of DOM-22 (indicated by arrow and dashed outline in Fig. 3.5d). However, the entirety of the feature observed in the BF and HAADF images is not visible on the surface, which suggests the feature permeates through the polycrystalline domain DOM-22. The NanoSIMS measurements of DOM-22 only provide isotopic information for grains located at the surface of the meteorite thin section. The pentlandite

<table>
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<td>320</td>
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<td>0.95 (ol, px)</td>
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See Figs. 3.5, 3.6, and 3.8 for locations of rings in SAED patterns.
crystal occurs below the surface that NanoSIMS measured, therefore precluding the definitive identification of the pentlandite as a presolar grain within the anomalous region of DOM-22.

3.3.4 DOM-35

NanoSIMS analysis reveals an oval shaped O-anomaly measuring 235 × 235 nm, indicated by an arrow in Fig. 3.6a. It is characterized by enrichments in both $^{17}$O and $^{18}$O relative to solar system values with $^{17}$O/$^{16}$O = 4.0 ± 0.2 ($\times 10^{-4}$) and $^{18}$O/$^{16}$O = 3.34 ± 0.07 ($\times 10^{-3}$). The isotopic composition of DOM-35 plots in the Group-4 field (Fig. 3.1). Auger nanoprobe analysis indicates a ferromagnesian silicate composition (Haenecour et al. 2018).

STEM imaging does not reveal a grain with distinct boundaries, and so we evaluate the domain located directly below the Pt fiducial marker. The domain measures of 264 × 210 nm in orthogonal dimensions (Fig. 3.6 b-c). EDS mapping shows spatial correlations among Fe, Si, O, Mg and localized Ca (Fig. 3.6d-h). A zone-axis SAED pattern was acquired from the left portion of the domain and is consistent with a single crystal of forsterite (Fig. 3.6j). In comparison, an SAED pattern acquired from the right portion is polycrystalline with d-spacings consistent with forsterite (Table 3.2, Fig. 3.6k). EDS spectra were extracted from both the left and right parts of DOM-35. Standardless quantification indicates a Mg-rich forsterite with a composition of $(\text{Mg}_{1.66}, \text{Fe}_{0.17}, \text{Ca}_{0.03}, \text{Al}_{0.05})(\text{Si}_{1.03})\text{O}_4$ for the single crystal region on the left side and a more Fe-rich forsterite with a composition of $(\text{Mg}_{1.65}, \text{Fe}_{0.27}, \text{Al}_{0.06})(\text{Si}_{1.00})\text{O}_4$ for the polycrystalline region on the right side (Table 3.1).
Figure 3.6: NanoSIMS and TEM data on DOM-35. (a) NanoSIMS δ18O map of DOM-35, with legend at right of image in units of per mil (‰). (b-c) BF and HAADF images with DOM-35 highlighted by dashed oval (we note that dashed oval is not meant to be absolute, but rather guide the reader to the ROI). (d-i) False color EDS maps of DOM-35 for Fe, O, Si, Mg, Ca, Pt, respectively. The high contrast feature in the BF and HAADF images (b-c) spatially correlates with Pt (i) and is the result of Pt redeposition during the final thinning of the FIB section. (j) SAED pattern acquired from region labeled (j) in HAADF image. (k) SAED pattern acquired from region labeled (k) in HAADF image with rings labeled 1-6.
3.3.5 DOM-39

NanoSIMS analysis of DOM-39 reveals a circular O-anomaly measuring 275 nm in diameter, indicated by arrows in Fig. 3.7 a-b. It is characterized by enrichments in both $^{17}$O and $^{18}$O, with $^{17}$O/$^{16}$O = 6.4 ± 0.3 ($\times 10^{-4}$) and $^{18}$O/$^{16}$O = 2.64 ± 0.07 ($\times 10^{-3}$). The O-isotopic composition of DOM-39 plots near to the boundary between Groups 1 and 4, but is closer to the Group-4 field (Fig. 3.1), which is consistent with the classification described in Haenecour et al. (2018). Auger nanoprobe analysis reveals a ferromagnesian silicate composition (Haenecour et al. 2018).

STEM imaging of the region below the Pt fiducial marker reveals an oval-shaped domain, indicated by dashed line in Fig. 3.7c, with orthogonal dimensions of 296 × 160 nm (Fig. 3.7 c-e). BF and HAADF images show a high-contrast footprint-shaped feature in the upper-left corner of the field of view that extends into the top left part of the domain and measures ~50 × 130 nm (Fig. 3.7 c-d). We note that the footprint feature is too small to be distinguishable on NanoSIMS maps at the resolution used for routine imaging (~100nm spatial resolution) of the meteorite thin section, thus precluding isotopic measurements and definitive determination of its presolar origins. However, comparison with the SE image (Fig. 3.7e) indicates that the footprint-shaped feature is not on the surface of the cross-section exposed by FIB and appears to be within the anomalous region. Additionally, this FIB section was thinned twice due to Pt redeposition over the region of interest. After both thinning sessions, the feature does not appear on the surface and therefore is included within the thickness of the section. We note that the random orientation of the footprint feature observed in the TEM images is dependent on multiple factors including how the thin sections were cut from the original meteorite sample and also how we chose to section the anomalous region.
Figure 3.7: NanoSIMS and TEM data on DOM-39. (a-b) NanoSIMS δ¹⁷O and δ¹⁸O maps of DOM-39, with legend at right of image in units of per mil (‰). (c) BF STEM image with DOM-39 indicated by dashed line below Pt fiducial marker (we note that dashed line is not meant to be absolute, but rather guide the reader to the ROI). (d-e) HAADF and SE STEM images of DOM-39 below Pt fiducial marker. (f-l) False color EDS maps of DOM-39 for Fe, O, Si, Mg, Ni, S, Al, respectively. (m) SAED pattern acquired from region labeled (m) in HAADF image. (n) SAED pattern acquired from region labeled (n) in HAADF image.
The footprint-shaped feature also contains a rim (cf., Fig. 3.7 c-d, e). EDS mapping of DOM-39 reveals spatial correlations among Fe, O, Si, Mg, with minor Al, (Fig. 3.7 f-i,l). The footprint shaped region correlates strongly with Fe, and contains local Ni and S concentrated at its center (Fig. 3.7 f, j-k). The rim around the footprint spatially correlates with Fe and O (Fig. 3.7 f-g, Appendix A, Fig. S5). A zone-axis SAED pattern was acquired from the center of DOM-39 and indexes to orthopyroxene (Fig. 3.7m). An EDS spectrum was extracted from the grain and standardless quantification is consistent with a composition of (Mg0.38, Fe0.52, Ni0.1)(Al0.09, Si0.93)O3 (Table 3.1). Zone-axis SAED patterns were also obtained across the footprint region (see Appendix A, Fig. S5) and measurement of such patterns reveal d-spacings close to the pyrrhotite-6C structure (Fig. 3.7n, Table 3.2). However, standardless quantification of the footprint region is not consistent with pyrrhotite stoichiometry, as it is enriched in Fe and depleted in S with a composition (Fe1.37, Ni0.22)S0.405 (Table 3.1). Henceforth, we refer to the crystal as an Fe-sulfide.

3.3.6 DOM-50

NanoSIMS analysis of DOM-50 reveals a circular O-anomaly measuring 195 nm, indicated by arrow in Fig. 3.8a. DOM-50 is characterized by enrichment in 18O, with 18O/16O= 2.56 ± 0.05 (×10^{-3}) and 17O/16O= 3.6 ± 0.2 (×10^{-4}) and the isotopic composition plots in the Group-4 field (Fig. 3.1). Auger nanoprobe analysis reveals a ferromagnesian silicate composition (Haenecour et al. 2018). STEM imaging of the region below the Pt fiducial marker reveals an oval-shaped domain, indicated with dashed line in Fig. 3.8b, with orthogonal dimensions of 187 × 91 nm (Fig. 3.8 b-c). EDS mapping of the bulk of the domain reveals spatial correlations among Fe, O, Si (Fig. 3.8 d-f), and localized Mg, as well as a significant amount of Pt redeposition covering the top half of
DOM-50 (Fig. 3.8 g-h). The maps indicate that Fe and O are concentrated towards the bottom of the domain and Si and Mg are concentrated towards the right side. A SAED pattern was acquired from the center of the domain, indicating DOM-50 is polycrystalline with d-spacings that overlap with both olivine and pyroxene (Table 3.2, Fig. 3.8i). Standardless quantification of the polycrystalline region extracted from an EDS spectrum based on 12 O atoms is consistent with a composition of $(\text{Mg}^{2+}_{2.05}, \text{Fe}^{2+}_{4.22}, \text{Ca}_{0.10}, \text{Ti}_{0.18})(\text{Si}^{4+}_{1.78}, \text{Fe}^{3+}_{1.72})\text{O}_{12}$ (Table 3.1).
Figure 3.8: NanoSIMS and TEM data on DOM-50. (a) NanoSIMS $\delta^{18}$O maps of DOM-50, with legend at right of image in units of per mil ($‰$). (b) BF STEM image with DOM-50 indicated by dashed oval below Pt fiducial marker (we note that dashed oval is not meant to be absolute, but rather guide the reader to the ROI). (c) HAADF STEM image of DOM-50. (d-h) False color EDS maps of DOM-50 for Fe, O, Si, Mg, Pt, respectively. (i) SAED pattern acquired from region labeled (i) in HAADF image with rings labeled 1-5.
3.4 Discussion

The isotopic compositions of oxygen-rich presolar grains define broad trends in three-oxygen isotope space that can be reproduced by nucleosynthetic models of stellar evolution (Nittler et al. 1997). The comparison of the isotopic data to such models has therefore led to detailed insights into nucleosynthesis in RGB, AGB stars, as well as stellar explosions such as novae and SNe (Nittler et al., 1997, 2008). Comparison of grain isotopic data with nucleosynthetic models of stellar evolution is used to determine the type, mass, and metallicity of the progenitor star from which the grains originated in addition to mixing processes that occurred within them (Boothroyd and Sackmann, 1999; Boothroyd et al., 1994). Similarly, the isotopic compositions of grains derived from stellar explosions are reproducible with nucleosynthetic models of SNe (Choi et al., 1998; Nittler et al., 2008).

O-rich circumstellar grains can be divided into four groups based on their O-isotopic compositions, which are indicative of different stellar origins. Group 1 grains are characterized by enrichment in $^{17}$O relative to solar-system values and many also have slight depletions in $^{18}$O. These Group-1 grains are thought to have condensed in the circumstellar envelopes of low-mass RGB or AGB stars experiencing dredge-up processes (Boothroyd and Sackmann, 1999; Nittler et al., 1997; Nollet et al., 2003). Dredge up involves convective mixing that transports the products of main-sequence nucleosynthesis to the circumstellar envelope. The nuclides make their way to the surface of the star where solid dust grains can condense according to their thermodynamic stabilities, incorporating the products from main-sequence nucleosynthesis. The O-isotopic compositions of grains derived from AGB/RGB origins can be used to trace the mass and metallicity of their progenitor stars by comparison with model predictions (Boothroyd and
The $^{17}\text{O}/^{16}\text{O}$ ratio is related to stellar mass, and the $^{18}\text{O}/^{16}\text{O}$ ratio following the first dredge-up is related to metallicity. We note, however, that recent work by Leitner & Hoppe (2019); Verdier-Paoletti et al. (2019) and Hoppe et al. (2021) suggests that a portion of Group 1 and Group 2 (discussed below) presolar silicate grains may originate in SNe, intermediate-mass AGB stars, and super-AGB stars as determined by Mg-isotopic analyses consistent with such origins.

Group 2 grains are characterized by enrichments in $^{17}\text{O}$ and large depletions in $^{18}\text{O}$ relative to solar system values. Group 2 grains were attributed to origins in < 2 $M_\odot$ AGB stars (Boothroyd and Sackmann, 1999; Boothroyd et al., 1994; Nittler et al., 1997; Nollet et al., 2003). However, more recent nucleosynthetic models suggest that some grains could have origins in intermediate mass (4 to 8 $M_\odot$) AGB stars (Lugaro et al., 2017). The large $^{18}\text{O}$ depletions are not predicted by standard models and require an extra mixing process, which has been referred to as ‘cool-bottom processing’ or ‘hot bottom burning’ depending on whether the star is of low or intermediate mass, respectively. These mixing processes are used to explain the isotopic compositions observed in these grains (Nollett et al., 2003; Wasserburg et al., 1995). Such mixing destroys $^{18}\text{O}$ via the reaction $^{18}\text{O}(p, \alpha)^{15}\text{N}$ and therefore, the $^{18}\text{O}$ composition of Group 2 grains cannot be compared to model predictions to infer metallicity.

Group 4 grains are characterized by enrichments in $^{18}\text{O}$ and some have enrichments in $^{17}\text{O}$ above solar system values. These grains are thought to have condensed in the ejecta of type-II core-collapse SNe (Choi et al., 1998; Nittler et al., 2008). The enrichments in $^{18}\text{O}$ are thought to result from partial He burning in the He/C zone of massive stars via $^{14}\text{N}(\alpha, \gamma)^{18}\text{F}(e^+,\nu)^{18}\text{O}$. Some Group 4 grains that have $^{17}\text{O}$ compositions above solar composition that are suggested to follow
the galactic chemical evolution trend and indicate a progenitor star with higher than solar metallicity. The Mg, Si, and Fe isotopic compositions of some Group 4 grains are not compatible with high metallicity stars, however, they are reproducible with nucleosynthetic models of SNe (Choi et al., 1998; Nittler et al., 2008).

In addition to grains providing information on the nucleosynthetic processes of their progenitor stars, they can also help us constrain the conditions in which they condensed in their host circumstellar envelopes. Comparison of the chemical compositions and crystal structures of the grains to equilibrium and nonequilibrium thermodynamic model predictions (e.g., Gail & Sedlmayr 1999; Ebel & Grossman 2000; Ferrarotti & Gail 2001; Lodders, 2003) helps us to infer the temperatures at which mineral phases will condense from a gas, typically defined as solar composition or some variation thereof, under a presumed set of total pressures (e.g., Stroud et al. 2004; Vollmer et al. 2007, 2009, 2013; Zega et al. 2011, 2014, 2015; Nguyen et al. 2007, 2010, 2016). Solar composition can be a reasonable assumption for circumstellar environments, especially in grains whose isotopic composition indicates formation in a solar-metallicity star (e.g., Nittler et al. 2008; Lugaro et al. 2017). Regarding the pressures expected in circumstellar envelopes, we note that models of C stars estimate a range of pressures, with the photospheric region ranging from $10^{-3}$ to $10^{-5}$ bar and the envelope expected to have even lower pressures (Lodders & Fegley 1995). Additionally, models of the circumstellar outflows of O-rich AGB stars estimate a range of pressures, between $10^{-10}$ to $10^{-6}$ bar (Gail & Sedlmayer 1999, Jeong et al. 2003). Therefore, comparison of the grain data to thermodynamic model predictions can provide first-order constraints on the thermodynamic conditions under which these grains condensed around their host stars.
Given the energetic nature of SNe environments (e.g., Arnett et al. 1989; Hughes et al. 2000), comparison of grain data with equilibrium thermodynamic models specific to the solar nebula could pose challenges. However, there are some models of dust condensation specific to SNe environments. For example, (Fedkin et al., 2010) used model compositions of thin layers of ejecta within the main burning zones of type-II SNe computed by (Rauscher et al., 2002) to predict the chemical compositions of minerals that condensed via equilibrium processes in 15-, 21- and 25M☉ SNe. There are also models that predict dust condensation via kinetic processes that take into account nucleation and grain growth (Cherchneff and Dwek, 2010; Nozawa et al., 2003; Todini and Ferrara, 2001) and can provide information such as the compositions of grains, their sizes, the zone of formation within the SN structure and the timescale of condensation following the SN explosion. We note that the grain sizes predicted by kinetic models of dust condensation in SNe are much smaller than those typically observed in the laboratory. Additionally, kinetic models show differences in condensation temperatures depending on how the time evolution of the gas temperature is calculated. For example, Todini & Ferrera (2001) use observational data from SN1987A in their calculations of the time evolution of gas temperature. Alternatively, Nozawa et al. (2003) calculate the evolution of the gas temperature using a multifrequency radiative transfer code together with the energy equation. Below we discuss the grain properties, how they compare to nucleosynthetic and thermodynamic models, and infer their origins.
3.4.1 Origins of AGB/RGB Grains

3.4.1.1 DOM-49

STEM images of DOM-49 do not reveal a distinct grain below the Pt fiducial marker that indicates the location of the O-anomalous region. While SAED patterns from the domain show that it is crystalline, we cannot pinpoint an individual grain that is the carrier of the O-anomaly and therefore we consider the domain shown (Fig. 2b-c) as the presolar ‘grain’. Comparing the O-isotope data with model predictions for AGB/RGB stars, DOM-49 is consistent with a close to solar metallicity RGB or AGB star of roughly 1.3 \( M_\odot \) (Boothroyd and Sackmann, 1999; Boothroyd et al., 1994). The olivine solid solution is predicted to condense via equilibrium processes at 1444 K and pure forsterite is expected at 1354 K assuming a total pressure of \( 10^{-3} \) and \( 10^{-4} \) bars respectively (Ebel and Grossman, 2000; Lodders, 2003). However, Fe-rich phases are not predicted to condense via equilibrium processes from a gas of solar composition (Ebel and Grossman, 2000; Lodders, 2003). Therefore, the nonstoichiometric and Fe-rich nature of DOM-49 suggests it could have formed via nonequilibrium processes.

Crystalline and amorphous olivine presolar grains from AGB stars were previously studied in meteorites and IDPs using TEM and are reported to contain varied amounts of Fe (Messenger et al. 2005; Busemann et al. 2009; Vollmer et al. 2009; Stroud et al. 2009, 2014; Nguyen et al. 2016; Nittler et al. 2018; Zega et al. 2020). The Fe contents of the amorphous grains are notably higher than the Fe contents in the crystalline grains. High Fe contents are consistent with models of nonequilibrium condensation, which show that amorphous olivine grains can contain higher Fe contents than crystalline olivine grains that formed through equilibrium condensation (Gail & Sedlmayr 1999; Ferrarotti & Gail 2001; Ebel & Grossman 2000; Lodders 2003). Additionally,
astronomical observations of O-rich stars suggest Fe-rich olivine is more commonly amorphous than crystalline (Molster et al. 2002a, 2002b). Multiple scenarios were suggested to explain the incorporation of Fe into presolar crystalline olivine grains. One suggestion is that the olivine grain first formed as an amorphous grain with an Fe-rich composition and was later crystallized by thermal annealing processes in stellar wind (Nguyen et al. 2016). Alternatively, Messenger et al. (2005) suggested that higher Fe contents could be obtained if the olivine grain formed at high temperatures under oxidizing conditions, which would allow for a greater availability of FeO that could be incorporated into the olivine. Finally, these grains could have formed through non-equilibrium processes to obtain higher Fe contents, as mentioned above, or could incorporate Fe during parent body alteration.

The nonstoichiometric composition and crystalline structure of DOM-49 could suggest a scenario where the olivine grain formed first as an amorphous grain through nonequilibrium processes before being thermally annealed to a crystalline grain. Whether or not a single crystal would form from an amorphous grain would depend on its initial size and the availability of nucleation sites (Varshneya 1993, Callister & Rethwisch 2014). Alternatively, the higher Fe content could have been incorporated into the olivine at high temperatures under oxidizing conditions where FeO is more abundant. Parent body alteration is also a possibility, but given that DOM 08006 experienced minimal alteration (Davidson et al. 2019), none of which is observed in the FIB section containing DOM-49, and that the Fe content is relatively homogeneous argues against parent-body alteration.

While we were not able to determine definitively the mineral phase of the Fe, Ni, S region given its small size, iron sulfides are predicted to condense at lower temperatures than silicate
minerals such as olivine and pyroxene (Ebel and Grossman, 2000; Lodders, 2003). Therefore, the presence of a low-temperature phase within a silicate grain suggests DOM-49 formed through a nonequilibrium process. Presolar silicates with iron sulfides were previously reported with compositions similar to glass with embedded metal and sulfides (GEMS, Messenger et al. 2003; Floss et al. 2006; Vollmer et al. 2009; Keller & Messenger 2011; Bradley et al. 2014). However, DOM-49 lacks nanocrystalline kamacite and pyrrhotite and the amorphous structure indicative of GEMS grains (Bradley 1994; Dai & Bradley 2001). Thus, a GEMS-like material can be ruled out.

As noted above, recent work by Leitner & Hoppe (2019), Verdier-Paoletti et al. (2019) and Hoppe et al. (2021) suggests that some Group-1 presolar silicate grains thought to originate in AGB/RGB stars could instead have condensed in SNe ejecta. While we do not have Mg isotopic data to confirm a SN origin, we discuss the possibility here. The nonstoichiometric, Fe-rich composition of DOM-49 suggests a kinetic origin. Kinetic models of dust condensation in SNe predict Mg-silicates to condense in SNe ejecta around 1400 to 1500 K (Nozawa et al. 2003) and also around 1100 K (Todini & Ferrara 2001). Fe-sulfides such as FeS are predicted to condense at lower temperatures of 1000 to 1100 K (Nozawa et al. 2003). The presence of a low-temperature Fe, Ni, S phase within the silicate would therefore be consistent with mixing in the SN ejecta, where transport and changing thermodynamic conditions led to the formation of the assemblage observed in DOM-49. Without further isotopic analyses, it is not possible to confirm whether an AGB/RGB or SN origin is more plausible for DOM-49. However, we note that only a small fraction (~3-12%) of Group-1 silicates are thought to have SN origins (Leitner & Hoppe 2019) and so the statistics would appear to favor an AGB/RGB origin.
3.4.1.2 DOM-59

STEM images reveal DOM-59 is a discrete presolar grain that conforms to forsterite structure and chemistry. Comparison of the O-isotopic composition of DOM-59 with model predictions is consistent with an origin in an AGB star of roughly 1.65 M⊙ (Boothroyd and Sackmann, 1999; Boothroyd et al., 1994). While we cannot confirm the metallicity of the progenitor star of Group-2 grains, we note that solar composition was used to reproduce the trends defined by Group-2 grains to understand their origins in AGB stars (e.g., Nittler et al. 2008; Lugaro et al. 2017).

Comparison of grain data with equilibrium thermodynamic model predictions provides constraints on the origin of DOM-59. The TEM data show that DOM-59 is an olivine, both structurally (Fig. 3.4h) and compositionally within error (Fig. 4g). The olivine solid solution is predicted to condense from a cooling gas of solar composition at 1444 K and 1240 K assuming total pressures of 10^{-3} and 10^{-6} bars respectively (Ebel & Grossman 2000). The spatial relationships that we observe in DOM-59 are consistent with solids sequentially condensing out of a monotonic cooling gas of solar composition. The microstructure observed for DOM-59 is therefore consistent with the Ca-rich core having condensed first, followed by the Mg-rich shell in order to produce the core-shell structure we observe in DOM-59.

As mentioned above for DOM-49, previous studies have reported presolar olivine grains from diverse stellar origins including AGB/RGB stars and supernovae (Messenger et al. 2005; Busemann et al. 2009; Vollmer et al. 2009; Stroud et al. 2009, 2014; Nguyen et al. 2016; Nittler et al. 2018; Zega et al. 2020). These studies include both crystalline and amorphous grains, some of which conform to equilibrium condensation and some that likely formed through
nonequilibrium processes. Core-mantle structures similar to what we observe here for DOM-59 were reported in the literature, including a spinel grain surrounded by Mg-rich silicate (Nguyen et al. 2014b), where the spinel core is thought to have formed through equilibrium processes, while the mantle suggests nonequilibrium formation. An Al-Ca-Ti oxide surrounded by a Ca-rich silicate was also reported but no TEM data are available, leaving its origins ambiguous (Leitner et al. 2018). Recently, two grains with core-mantle structures were reported in DOM 08006 (Nittler et al. 2018; Zega et al. 2020). First, a Ca-Al-rich core surrounded by ferromagnesian silicates was reported (DOM-77, Nittler et al. 2018) and is consistent with equilibrium condensation. Finally, a presolar spinel grain surrounded by solar Mg-silicate was observed (DOM-9, Zega et al. 2020) and is consistent with nonequilibrium condensation. We discuss the implications of the Fe-rich rim that surrounds DOM-59 below.

Fe-rich rims around oxide and silicate presolar grains were previously reported in the Adelaide, Acfer 094 and QUE 99177 meteorites (Floss and Stadermann, 2012; Zega et al., 2020). Vollmer et al. (2009) reported an olivine grain in Acfer 094 with an amorphous Fe-rich rim that was suggested to have formed through amorphization due to sputtering in the ISM. Nguyen et al. (2016) reported an enstatite grain in QUE 99177 with an amorphous Fe-silicate rim and suggested formation through parent-body alteration. The Fe-rims from Acfer 094 and QUE 99177 differ from DOM-59 in that they do not have a compositional gradient. Floss and Stadermann (2012) identified two silicate grains with Fe-rims in the Adelaide meteorite consistent with Fe-diffusion resulting from secondary processes possibly due to short-lived thermal processing of mm- to cm-sized clumps of dust in an oxidizing nebular environment with elevated gas-to-dust ratios. Similarly, TEM analyses by Zega et al. (2020) suggest that Fe-rich rims and heterogenous distributions of Fe
throughout the matrix are indicators of thermal processing of fragments of dust. Such secondary alteration in the solar nebula resulted in material that was processed to varied degrees and incorporated into the Adelaide matrix. Compared to these previously identified Fe-rich rims in silicate and oxide presolar grains, the chemically zoned and diffusion-like structure of the rim around DOM-59 (Fig. 3.4c) is most similar to those observed in the Adelaide meteorite. However, we note that the Adelaide meteorite has experienced significantly more alteration and has a smaller abundance of O-rich presolar grains compared to DOM 08006 (Floss & Stadermann 2012; Haenecour et al. 2018; Nittler et al. 2018; Davidson et al. 2019). In any case, Fe-rich rims around presolar grains and solar-system derived grains within the matrices of their host meteorites are generally regarded as a signature of thermal processing. Whether the rim in DOM-59 formed through such processing is worth exploring.

DOM 08006 was reported to be the most primitive CO chondrite, with very minor evidence for parent body aqueous alteration and terrestrial weathering (Davidson et al. 2019). Such evidence includes metal being altered to magnetite and Fe oxyhydroxide needles, which are not observed here (Davidson et al. 2019). The matrix of other FIB sections in this study do not contain phases characteristic of parent-body alteration, which argues against parent-body processing as having formed the Fe-rich rim around DOM-59. Thus, the origin of the Fe-rich rim more likely involved processing that was pre-accretionary in the solar nebula or host circumstellar envelope.

One other possible formation pathway for the Fe-rim in DOM-59 includes condensation of the Fe-rim around the compositionally zoned olivine grain. Presolar Fe-bearing oxides were previously identified (Floss et al. 2008; Bose et al. 2010a; Zega et al. 2015; Haenecour et al. 2018), and are predicted to condense at lower temperatures than the olivine solid solution (e.g., Ebel &
Thus, it is conceivable that an olivine grain could provide a nucleation site for the Fe-rich rim to condense. Condensation of the rim via equilibrium processes would likely produce a homogeneous distribution of Fe around DOM-59. We note that because a portion of the grain was milled through during the final thinning of the FIB section, we do not know if the Fe-rim originally surrounded the entirety of DOM-59. Given that we also observe Fe-rich veins throughout the FIB section containing DOM-59, we infer that the Fe-rich rim around DOM-59 and the surrounding matrix represent a clump of dust that was altered in the solar nebula in an environment similar to that described by Floss and Stadermann (2012). The lack of Fe-rich rims in the other FIB sections in this study suggests that the alteration may have been inherited by the material accreted onto the parent body asteroid.

As noted above, recent work by Leitner & Hoppe (2019), Verdier-Paoletti et al. (2019) and Hoppe et al. (2021) suggests that a fraction of Group-2 presolar silicate grains could originate in SNe. We do not have Mg isotopic data for DOM-59 to confirm such an origin, but we discuss the possibility here. Equilibrium models of dust condensation of SNe predict olivine to condense between 1576 and 1063 K. Thus, if DOM-59 formed in SN ejecta and the core-mantle structure observed is consistent with equilibrium condensation, the Ca-core likely condensed first, followed by the Mg-rich mantle at lower temperatures. The Fe-rich rim is consistent with nebular origins as discussed above.
3.4.2 Origins of SN Grains

3.4.2.1 DOM-22

The polycrystalline region of DOM-22 has d-spacings common to both olivine and pyroxene (Table 3.2), and precludes the identification of a single grain that is the carrier of the isotopic anomaly. To ensure that we correctly located and marked the O-anomalous region DOM-22, we verified the location of DOM-22 by further correlating images from the NanoSIMS to those in the FIB-SEM prior to sectioning. Therefore, we consider the polycrystalline domain shown (Fig. 3.5b-d) as the presolar ‘grain’. Given the Fe-rich composition of DOM-22 and the presence of Fe-sulfides in the polycrystalline domain, it is difficult to reconcile this microstructure with equilibrium predictions.

Polycrystalline and amorphous presolar silicate grains were identified within meteoritic samples (Nguyen et al., 2010; Stroud et al., 2009; Vollmer et al., 2009; Zega et al., 2020). Stroud et al. (2009) reported forsterite-like nanocrystalline and amorphous material with a nonstoichiometric composition and inferred formation under nonequilibrium conditions. Vollmer et al. (2009) identified a cluster of several amorphous, nonstoichiometric silicate particles that are similar to GEMS and are thought to have formed through nonequilibrium condensation. Nguyen et al. (2010) reported several amorphous grains with nonstoichiometric compositions and suggested the grains could have formed through multistep or nonequilibrium condensation. Zega et al. (2020) identified a polycrystalline assemblage of ferromagnesian silicates that could have formed through multistep condensation followed by mechanical accretion in the host circumstellar envelope. In comparison, the Fe-rich polycrystalline assemblage and nonstoichiometric pentlandite grain of DOM-22 is not consistent with equilibrium condensation. We therefore infer
that DOM-22 formed through nonequilibrium or multistep condensation, the details of which will be discussed below.

The ejecta of SNe are dynamic environments and individual grains formed within them have the ability to record snapshots of the likely rapidly changing conditions within SNe. Astronomical observations of SN remnants displaying heterogeneous compositions and clumpy structures suggest that large-scale mixing likely occurs in their ejecta, which is supported by both the isotopic compositions of SN grains and modeling efforts that describe how such mixing occurs (Arnett et al. 1989; Hughes et al. 2000; Kifonidis et al. 2003; Hammer et al. 2010; Abarzhi et al. 2019). Kinetic models of SN ejecta predict Mg-rich silicates to condense between 1400 to 1500 K (Nozawa et al., 2003), and around 1100 K (Todini and Ferrara, 2001). Both equilibrium and kinetic models predict iron sulfides to condense at lower temperatures (Lodders, 2003) than those suggested for Mg-silicates. Therefore, we consider two possible scenarios for the formation of DOM-22. First, as temperatures cooled in the host SN ejecta, the polycrystalline assemblage could have formed in a stepwise manner, with the ferromagnesian silicate condensing first, followed by the Fe-sulfides at lower temperatures which were then mechanically accreted together with the silicate. Alternatively, the Fe-sulfides condensed first in a cooler region of the SN ejecta and was then transported to a warmer region where the polycrystalline ferromagnesian silicate could condense around it. Given the structure observed in DOM-22, it is difficult to distinguish between these two scenarios and it is also unclear whether the Fe-sulfides contained within the polycrystalline domain are in fact presolar in origin. If the Fe-sulfides are not presolar in origin, they likely formed in the early solar system or in the ISM before being mechanically accreted to the presolar ferromagnesian silicate assemblage either as free-floating objects or on the parent
body asteroid. These observations therefore preclude constraining the precise conditions under which it formed. However, a nonequilibrium, multistep formation mechanism is likely.

3.4.2.2 DOM-35

Equilibrium condensation of forsterite is predicted by Fedkin et al. (2010) in a 15 to 25 $M_{\odot}$ SN between 1063 and 1575 K. Thus, the single crystal forsterite on the left side of DOM-35 is consistent with equilibrium condensation. Fedkin et al. (2010) notes that in the H and He/N zones of the ejecta, the olivine equilibrium mole fraction ($X_{Fe}$) is $<0.002$ above 1000 K, whereas forsterite that occurs in the O-rich zones between 1500 K and 1600 K has $X_{Fe}<0.03$. The polycrystalline portion of DOM-35 is more Fe-rich than the single crystal forsterite, with $X_{Fe}>0.03$. Fedkin et al. (2010) note that to produce more Fe-rich olivine compositions ($X_{Fe}>0.03$) via equilibrium processes in SN dust, mixing is required between different SN layers. It is therefore possible that the polycrystalline portion of DOM-35 condensed via equilibrium processes. As noted above, large-scale mixing likely occurs in the ejecta of SNe and the microstructures observed in DOM-35 are consistent with the single crystal and polycrystalline forsterite being brought together through large-scale mixing processes.

One other SN olivine aggregate ‘B10A’, was identified in an interplanetary dust particle (IDP) and was suggested to have condensed via equilibrium processes in a 15 $M_{\odot}$ SN at 1560 K in a solar metallicity star (Messenger et al., 2005). Similar to DOM-35, B10A also has an Fe-rich composition that required mixing to produce its composition, however its isotopic composition is significantly different. While it is possible that DOM-35 formed under similar thermodynamic
conditions to B10A, the difference in isotopic composition suggests different nucleosynthetic origins.

### 3.4.2.3 DOM-39

The orthopyroxene solid solution is predicted to condense via equilibrium processes in a 15 to 25 M☉ SN between 1090 to 1548 K (Fedkin et al. 2010). However, the Fe-sulfide and orthopyroxene assemblage observed in DOM-39 is difficult to reconcile with monotonic equilibrium cooling. While the orthopyroxene solid solution is not considered in available kinetic models of dust condensation (Todini and Ferrara 2001; Nozawa et al. 2003), pyroxenes have been observed in the Cas A SN remnant (Rho et al. 2009). Kinetic models do consider the pure endmember enstatite, which is suggested to condense between 1400 to 1500 K (Nozawa et al. 2003) and at 1100 K (Todini & Ferrara 2001). Below we explore formation scenarios for both presolar and solar origins of the iron sulfide and the surrounding orthopyroxene.

It is difficult to explain the microstructure observed in DOM-39 without both the Fe-sulfide and the orthopyroxene having presolar origins. A solar origin would require the mechanical accretion of an Fe-sulfide that contains an Fe-oxide rim with the presolar orthopyroxene. In this scenario, the Fe-sulfide would have accreted to the outside of the orthopyroxene, which is not what we observe (Fig. 3.7e). Alternatively, the presolar orthopyroxene could have provided a nucleation site for Fe-sulfide formation in the solar protoplanetary disk. However, the continuous rim that surrounds the Fe-sulfide (Fig. 3.7c-d; Appendix A, Fig. S5) but not the orthopyroxene is not consistent with this scenario.
Fe-sulfides are more volatile than pyroxenes and therefore are predicted to condense at lower temperatures (e.g. ~1000 K) than Mg-rich pyroxenes (e.g. 1400-1500 K, (Lodders, 2003)) through both equilibrium and kinetic processes. However, the nonstoichiometric composition of the Fe-sulfide in DOM-39 is inconsistent with equilibrium predictions, and so condensation via kinetic processes seems more realistic. That the Fe-sulfide grain has a continuous oxide rim but its host orthopyroxene does not suggest that the former formed before the latter. We hypothesize that the continuous rim on the Fe-sulfide was acquired as it was a freely floating object in the ejecta under oxidizing conditions before becoming embedded within the orthopyroxene. This scenario would imply that the embedded Fe-sulfide within the orthopyroxene in DOM-39 is also presolar in origin.

As mentioned above for DOM-22, the conditions within the ejecta of SNe are likely rapidly changing and large-scale mixing is likely occurring. One possible formation scenario for the DOM-39 assemblage is that after acquiring its rim, the Fe-sulfide was transported to a region of the ejecta where conditions were favorable for orthopyroxene to condense around the Fe-sulfide. Alternatively, the entire DOM-39 assemblage could have formed through a nonequilibrium process where the Fe-sulfide and rim formed and subsequently provided a nucleation site for the orthopyroxene to condense. We note that TEM studies on two other SN pyroxene grains were reported in the literature, both of which are amorphous. One of these grains is stoichiometric enstatite, which is consistent with equilibrium condensation followed by amorphization. The second grain is nonstoichiometric with a high-Ca pyroxene composition (Nguyen et al. 2016).
3.4.2.4 DOM-50

The polycrystalline domain of DOM-50 suggests a multiphase carrier of the isotope anomaly. The anomaly was still present in the last NanoSIMS raster ion image and DOM-50 was carefully located and marked by correlating images from the NanoSIMS and FIB-SEM. We are therefore confident that the entire polycrystalline domain is the anomalous presolar ‘grain’. As noted above with DOM-35, more Fe-rich compositions are possible via equilibrium condensation in SNe if there is large-scale mixing in the ejecta (Fedkin et al. 2010). However, the Fe content of DOM-50 exceeds the Fe content required for stoichiometric Fe-rich endmembers of both olivine and pyroxene and therefore cannot be explained by mixing in the SN ejecta in conjunction with equilibrium condensation. Thus, DOM-50 likely formed through nonequilibrium processes in its host SN ejecta. While Fe-rich silicates were previously reported in presolar silicate grains from AGB/RGB origins, Nguyen et al. (2016) reported the only other TEM analysis of an Fe-rich SN silicate to date. The grain, 2_33b, is a GEMS-like Fe-rich silicate and differs from DOM-50 in that it is both nonstoichiometric and amorphous, which is suggestive of formation through nonequilibrium processes.

Previous studies have discussed the origins of Fe in presolar silicate grains (Nguyen et al. 2007, 2010; Floss & Stadermann 2009a; Vollmer et al. 2009; Bose et al. 2010a; Ong & Floss 2015). In altered meteorites, secondary processing plays a role in the origin of Fe in presolar silicates (Ong & Floss 2015). However, in pristine meteorites with a high abundance of presolar grains, such as DOM 08006, the Fe is likely primary (Ong & Floss 2015). Fe-isotopic analyses of Group-4 presolar silicate grains are consistent with the primary origin of Fe in SN silicates (Ong & Floss 2015). The SN silicates analyzed contain $^{54}$Fe/$^{56}$Fe and $^{57}$Fe/$^{56}$Fe ratios consistent with
formation in the outer zones of type-II core collapse SNe (Ong & Floss 2015). We hypothesize that the Fe-rich compositions of both DOM-22 and DOM-50 reported above are primary in origin.

3.4.3 Presolar Grain Constraints on Dust Composition/Formation in SN Ejecta

Previous studies reveal that SN silicates have ferromagnesian compositions and both stoichiometric and nonstoichiometric compositions are reported. Additionally, both amorphous and crystalline structures were reported, with amorphous structures appearing to be higher in abundance (~70%, Nguyen et al. 2016). The SN silicates that we have discussed here are consistent with the previously reported grain diversity in chemistry, including olivine, pyroxene, and intermediate phases, but differ from previous studies in that they all have crystalline structures (either single crystal or polycrystalline) and are more Fe-rich. In comparison, astronomical observations suggest a greater abundance of amorphous silicates with MgSiO₃ and Mg₂SiO₄ compositions in the ejecta of SNe (e.g., Arendt et al. 1999; Rho et al. 2008, 2009). However, astronomical observations do bear some uncertainty, as it can be difficult to distinguish dust formed in the SN ejecta and the ISM. Based on the limited statistics, it is unclear whether there is a bias in the grain data because of the small number of detailed studies on SN silicates or if Fe-rich crystalline silicates in SNe are preferentially preserved and therefore more abundant than previously suggested. As noted above, the Fe-bearing compositions of presolar silicates in unaltered meteorites are likely primary features (Ong & Floss 2015), which would appear to argue against a bias in the grain data. Additionally, two of the SN silicates we discuss contain iron sulfide inclusions that appear to be contained within the isotopically anomalous regions of interest and would represent the first observations of iron sulfides from a SN origin. To date, two other iron sulfides that are not GEMS-like were observed within a presolar silicate and a graphite grain from AGB stars (Haenecour et al. 2016, 2020). Astronomical observations do suggest the presence of iron sulfides such as FeS in circumstellar environments and the ejecta of SNe (e.g., Hony et al. 2003; Rho et al. 2008). Additionally, work by Köhler et al. (2014) suggests that FeS nano-
inclusions in amorphous silicates could provide a reservoir for S in the ISM. Iron sulfides such as FeS are predicted in equilibrium models of dust condensation in a solar composition gas (e.g., Lodders 2003) and in kinetic models of dust condensation in SNe (Nozawa et al. 2003). Iron sulfides were common in the solar protoplanetary disk based on the meteoritic record (Lauretta et al. 1996, 1997, 1998; Scott & Krot 2014) and the CSE of a solar-composition star might be expected to form FeS if it experiences equilibrium or kinetic condensation. In short, we might expect presolar sulfides to occur in CSEs of solar-metallicity stars in the galaxy. However, why a single crystal of presolar troilite or pyrrhotite has not been identified to date is unclear, but we suspect it could be related to the ability of sulfide materials to survive ISM transport and solar-system formation (Heck et al. 2012; Hoppe et al. 2012; Zhao et al. 2013). To date, that the only candidate presolar Fe-sulfide grains identified are present as small inclusions inside of other presolar grains would appear to be consistent with sulfides having a higher susceptibility to processing and destruction than other types of presolar grains (Haenecour et al. 2016). A higher susceptibility to processing is supported by previous laboratory work that suggests FeS grains produced around evolved stars and injected into the ISM will be destroyed more quickly than crystalline silicate grains (Keller & Rahman 2011). It remains to be seen whether single-crystal presolar sulfide grains will be identified in future presolar-grain studies.

Comparing the analyses of SN silicates with previous studies from AGB/RGB origins reveals similarities in the variety of mineralogies and structures observed. Including this work, of the SN silicates analyzed using TEM, half are amorphous and half are crystalline (single crystal or polycrystalline, Messenger et al. 2005; Floss et al. 2006; Nguyen et al. 2016). Similarly, TEM analyses of AGB/RGB silicates show comparable distributions of amorphous and crystalline
grains, with about 46% of grains being amorphous, about 44% being crystalline (single crystal or polycrystalline), and the remainder are composite grains (Messenger et al. 2003; Vollmer et al. 2007, 2009, 2013; Nguyen et al. 2007, 2010, 2013, 2014a, 2016; Busemann et al. 2009; Floss & Stadermann 2009a; Keller & Messenger 2011; Stroud et al. 2013, 2014; Haenecour et al. 2020; Nittler et al. 2020; Zega et al. 2020). Additionally, both stellar sources show evidence for equilibrium and nonequilibrium formation processes. As with previous TEM studies of presolar grains from AGB/RGB stars and SNe, it does not appear that there are significant differences in silicate grains derived from the different stellar origins, which suggests that the circumstellar envelopes of AGB/RGB stars and the ejecta of SNe can have similar local thermodynamic landscapes.

3.5 Conclusions

This work reports detailed chemical and mineralogical analyses of six presolar silicate grains from the CO3.0 carbonaceous chondrite DOM 08006. O-isotopic compositions of two of the grains are consistent with formation in the circumstellar envelopes of evolved AGB/RGB stars and the remaining four grains are consistent with origins in the ejecta of type-II core collapse SNe. TEM data reveal that all of the analyzed grains are crystalline. One of the AGB grains is a Fe-rich olivine with an Fe-Ni sulfide inclusion that likely formed under nonequilibrium conditions around a low-mass (~1.3M☉) star with close to solar metallicity. The second AGB grain is a chemically zoned olivine grain that contains a Ca-rich core, Mg-rich shell, and an Fe-oxide rich rim. The core-shell structure is consistent with equilibrium condensation from a cooling gas of solar composition in a low-mass (~1.65M☉) AGB star with the Ca-rich core and Mg-rich shell condensing
sequentially. We infer that the Fe-rich rim formed through nebular processing in an oxidizing environment, but a nonequilibrium process cannot be ruled out. Two of the SN grains are polycrystalline and have compositions consistent with a mixture of olivine and pyroxene and likely formed through nonequilibrium processes. The third SN grain contains both single crystal and polycrystalline forsterite that were likely brought together through large-scale mixing processes and formed between 1063 K and 1575 K in a 15 to 25 M☉ SN. The fourth SN grain is a crystalline orthopyroxene grain with an embedded Fe-sulfide that appears to be contained within the anomalous hotspot. This observation would, to our knowledge, be the first report of a presolar Fe-sulfide within a SN silicate grain. Given that the Fe-sulfide contains a complete rim, it must have formed before incorporation into the surrounding orthopyroxene, which suggests transport in the SN ejecta and is not consistent with monotonic equilibrium cooling. Despite the differences between circumstellar shells of AGB/RGB stars and the ejecta of SNe, our examination of these preserved stardust grains suggests that each of these distinct astrophysical environments can condense similar types of dust with comparable structures and compositions.

3.6 Acknowledgements

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CHAPTER 4. AN IN SITU INVESTIGATION OF THE PRESERVATION AND ALTERATION OF PRESOLAR SILICATE GRAINS IN THE MILLER RANGE 07687 CHONDRITE


Abstract
Dust grains that formed around ancient stars and in stellar explosions seeded the early solar protoplanetary disk. While most of such presolar grains were destroyed during solar system formation, a fraction were preserved in primitive materials such as meteorites. These grains can provide constraints on stellar origins and secondary processing such as aqueous alteration and thermal metamorphism on their parent asteroids. Here, we report on the nature of aqueous alteration in the Miller Range (MIL) 07687 chondrite through the analysis of four presolar silicates and their surrounding material. The grains occur in the Fe-rich and Fe-poor lithologies, reflecting relatively altered and unaltered material, respectively. The O-isotopic compositions of two grains, one each from the Fe-rich and Fe-poor matrix, are consistent with formation in the circumstellar envelopes of low-mass Asymptotic Giant Branch (AGB)/Red Giant Branch (RGB) stars. The other two grains, also one each from the Fe-rich and Fe-poor matrix, have O-isotopic compositions consistent with formation in the ejecta of type-II supernovae (SNe). The grains derived from AGB/RGB stars include two polycrystalline pyroxene grains that contain Fe-rich rims. The SNe grains include a polycrystalline Ca-bearing pyroxene and a polycrystalline assemblage consistent
with a mixture of olivine and pyroxene. Ferrihydrite is observed in all focused ion beam (FIB) sections, consistent with parent-body aqueous alteration of the fine-grained matrix under oxidizing conditions. The Fe-rich rims around presolar silicates in this study are consistent with Fe-diffusion into the grains resulting from early-stage hydrothermal alteration, but such alteration was not extensive enough to lead to isotopic equilibration with the surrounding matrix.

4.1 Introduction

Presolar grains are particles of dust that form in the circumstellar envelopes (CSE) of evolved stars and in the ejecta of stellar explosions such as novae and supernovae (SNe). These grains are transported away from their host stars via stellar winds, injected into the interstellar medium (ISM), and can be incorporated into stellar and planetary systems. Following their formation, a fraction of such grains were transported through the ISM and incorporated into the molecular cloud from which our solar system formed. Presolar grains can be identified based on their anomalous isotopic compositions and are found preserved in primitive materials including meteorites, micrometeorites, interplanetary dust particles, and cometary samples returned from the Stardust and Hayabusa2 missions. A variety of presolar grain types have been identified including SiC, graphite, nanodiamond, nitrides, and various oxides and silicates. Silicates are the second most abundant presolar grain type after nanodiamond, followed by SiC, spinel, graphite, corundum, and nitride (e.g., Nguyen et al., 2007; Nguyen & Messenger, 2011; Nittler & Ciesla, 2016; Hoppe et al. 2022).

Previous isotopic work comparing C-rich presolar grain abundances among chondrite groups highlights the ability of presolar grains to record nebular and parent body alteration
processes (Huss & Lewis, 1995; Huss, 1997; Huss et al., 2003). Presolar silicate grains are less refractory than C-rich presolar grains and are therefore more susceptible to aqueous alteration, thermal metamorphism, and isotopic equilibration (Floss & Stadermann, 2012; Haenecour et al., 2020). Given their high susceptibility to such alteration, presolar silicates can serve as useful tracers of the earliest stages of nebular and parent body processing (Bose et al., 2014; Haenecour et al., 2018, 2020; Nguyen et al., 2010, 2016; Nittler et al., 2018; Zega et al., 2020). Though these previous studies provided information about the preferential destruction of presolar grains among chondrite groups, more detailed structural and chemical information can be used to understand the thermodynamic origins and alteration histories of presolar silicates, including how they are preserved in solar system materials, the mechanisms by which they are altered, and the extent to which they are affected by alteration processes.

The MIL 07687 chondrite was originally classified as a CO3 chondrite. Previous work noted differences between MIL 07687 and typical CO chondrites (Righter & Satterwhite, 2009; Weisberg et al., 2009; Brearley, 2012, 2013b; Davidson et al., 2014b; Prestgard et al., 2021). Such differences include a lack of fine-grained chondrule rims, fewer refractory inclusions, and more matrix than typical CO chondrites. Analyses of the Cr₂O₃ content of ferroan olivine by Davidson et al. (2014a) indicate a petrographic grade similar to that of the ungrouped Acfer 094 chondrite, whereas Haenecour et al. (2020) found lower Cr₂O₃ values that indicate minor thermal metamorphism, which is inconsistent with the thermal history of Acfer 094. Recent bulk oxygen isotopic, spectroscopic, and thermogravimetric analysis (TGA) measurements by Prestgard et al. (2021) suggests an ungrouped classification, though the authors note that a CO or CM classification cannot be ruled out. Such a classification is consistent with previous suggestions that
MIL 07687 is an ungrouped carbonaceous chondrite with affinities to the CO group (Brearley, 2012, 2013b; Davidson et al., 2014a; Haenecour et al., 2020).

The MIL 07687 chondrite contains a high abundance of matrix that is dominated by two distinct matrix lithologies, Fe-rich and Fe-poor (Haenecour et al., 2020). The Fe-rich regions contain a unique style of aqueous alteration that is dominated by a fibrous Fe-oxide phase. In contrast, the Fe-poor regions are relatively unaltered, porous, and contain a fine-grained mixture of olivine, pyroxene, amorphous silicates, and Fe-sulfides (Haenecour et al., 2020). The overall O-rich presolar grain abundance of MIL 07687 is 137 ± 13 ppm, which is consistent with previous observations of other moderately altered carbonaceous chondrites. Here we report on the focused-ion beam (FIB) extraction and detailed transmission electron microscopy (TEM) analyses of four presolar silicate grains from the Miller Range 07687 CO3 chondrite. Two grains were selected from the Fe-rich matrix regions and two grains from the Fe-poor matrix regions to investigate how and to what extent presolar silicate grains are affected by parent-body processing at the TEM scale and to understand their thermodynamic origins. Initial results were reported in Seifert et al. (2021a, 2021b, 2022a, 2022b).

4.2 Sample and Experimental Methods

A polished thin section of the Miller Range (MIL) 07687 chondrite obtained from the Meteorite Curation Facility at NASA Johnson Space Center was analyzed. Isotopically anomalous grains were identified in matrix-rich regions of MIL 07687 using the Cameca NanoSIMS 50 at Washington University in St. Louis and are reported in Haenecour et al. (2020). They identified 107 O-rich presolar grains across nine matrix regions of MIL 07687. Following NanoSIMS
analysis, Auger spectra were acquired on all grains to determine their major element compositions using the PHI 700 Auger nanoprobe at Washington University in St. Louis. We note that discrepancies between the compositions reported by Auger and those reported here using TEM are likely the result of the two techniques sampling different material. The Auger nanoprobe only measures the top ~10 nm of the sample surface, while the TEM measurements provide compositional information in cross-section well below the sample surface. Auger maps were also obtained for one grain in this study based on its morphology and chemical composition. Additional details pertaining to the NanoSIMS and Auger analyses can be found in Haenecour et al. (2020).

Electron transparent (<100 nm in projected thickness) cross-sections of four grains were prepared using the Thermo Fisher Scientific (formerly FEI) Helios G3 focused-ion beam scanning-electron microscope (FIB-SEM) located in the Kuiper Materials Imaging and Characterization Facility (KMICF) at the Lunar and Planetary Laboratory (LPL), University of Arizona. The general procedure for producing electron transparent cross-sections of presolar grains is described in several previous papers (e.g., Holzapfel et al., 2009; Seifert et al., 2022c; Zega et al., 2007, 2011, 2014b, 2015, 2020; Haenecour et al., 2019, 2020). Briefly, we first go through an alignment procedure, described in detail in Seifert et al. (2022c), to ensure that we capture the presolar grain identified in the NanoSIMS with our FIB transect. Next, using the electron beam we deposited protective Pt fiducial markers on top of the grain and rectangular 200 nm × 100 nm thick markers on either side of the grain fiducial to assist in the thinning process. Following the deposition of the Pt fiducial markers, a C capping layer (~3 um thick) is deposited using the Ga⁺ ion beam and cross-sectioning follows previously described stair-step cuts, in situ extraction, and thinning to electron transparency at 30 kV, 0.23 nA.
The prepared FIB sections were analyzed using the Hitachi HF5000 scanning TEM (S/TEM) in the KMICF at LPL. The HF5000 is equipped with a cold-field emission gun, a 3rd-order spherical-aberration corrector for STEM mode, bright-field (BF), dark-field (DF), and SE STEM detectors, and an Oxford Instruments X-Max N 100 TLE EDS system with dual 100 mm² windowless silicon-drift detectors providing a large solid angle (Ω = 2.0 sr). It is also equipped with a Gatan OneView 4k × 4k pixel CMOS camera for the acquisition of TEM images and electron-diffraction patterns. The compositions of the presolar grains were obtained through EDS mapping followed by standardless quantification based on the Cliff-Lorimer method using theoretical (k) factors (Cliff & Lorimer, 1975). Selected-area electron-diffraction (SAED) patterns were used to gain information on long-range atomic order and crystal structure. SAED patterns were measured both manually with Adobe Photoshop as well as using the Crystallographic Image Processing Software Package (Hovmoller, 1992) based on calibrated camera constants.

4.3 Results

4.3.1 Presolar Grains from Fe-poor Matrix Regions

4.3.1.1 MIL 2a7-25 o1

The O-isotopic compositions of all grains in this study were previously reported in Haenecour et al. (2020), but we include them here for completeness and to discuss stellar origins. NanoSIMS analysis reveals MIL 2a7-25 o1 contains enrichment in $^{18}$O relative to solar system values with $^{18}$O/$^{16}$O (x10$^{-3}$) = 3.34 ± 0.07 and $^{17}$O/$^{16}$O (x10$^{-4}$) = 3.92 ± 0.23 (Appendix B Fig. S1). The O-isotopic composition of MIL 2a7-25 o1 places it in the Group 4 field of presolar grains (Fig. 4.1) as defined by Nittler et al., (1997, 2008). Auger nanoprobe analysis reveals MIL 2a7-25
STEM imaging of the whole FIB section reveals matrix that is porous and fine-grained (<500 nm, Fig. 4.2a). Elongated, fibrous grains with sizes from ~500 nm to 1 μm in length crosscut the matrix in the FIB section (Fig. 4.2a). EDS mapping reveals that O, Si, Mg, Fe, and Al are spatially correlated with each other across the FIB section. There are also localized regions where Ca, S and Ni spatially correlate (Fig. 4.2b–i). The fibrous grains observed in the FIB section spatially correlate with Fe and O. The 200–500 nm of matrix immediately surrounding MIL 2a7-25 o1 is polycrystalline and consists of a mixture of olivine and pyroxene. The remaining matrix contained within the FIB section is porous and fine grained and is composed of a mixture of crystalline and amorphous silicate material and Fe-sulfides. The center of the FIB section is crystalline and is separated from the surrounding matrix which is dominated by amorphous material by an Fe-oxide boundary (cf., Fig. 4.2a white arrows and 4.2e). SAED patterns obtained across the Fe-oxide boundary are consistent with ferrihydrite; one representative pattern is shown in Fig. 4.2j.

STEM imaging below the Pt fiducial marker does not reveal a grain that is distinct from the surrounding matrix, but rather a fine-grained domain (Fig. 4.3a–b). EDS mapping of the region below the Pt fiducial marker reveals that the domain contains O, Si, Fe, and Mg (Fig. 4.3c–f). The center of the domain contains local Fe, S and Ni enrichment relative to the surrounding material (white arrows, Fig. 4.3e, g–h) and is depleted in O, Si, and Mg. SAED patterns were obtained across the fine-grained domain and reveal that MIL 2a7-25 o1 is polycrystalline (a representative SAED pattern is shown in Fig. 4.3i). Given its small size, we were not able to obtain a distinct
Figure 4.2: TEM data on the FIB section containing MIL 2a7-25 o1. (a) STEM-HAADF image of the entire FIB section, with textural change in matrix outlined by white dashed line. Field of view of EDS measurements outlined by yellow dashed box. White arrows indicate Fe-oxide boundary between crystalline and amorphous matrix. (b–i) False color EDS maps of the entire FIB section for O, Si, Mg, Fe, Al, Ca, S and Ni. Dashed white line indicates same textural change in matrix as defined in panel (a). (j) SAED pattern from region denoted by (j) in panel (a).
Figure 4.3: TEM data on MIL 2a7-25 o1. (a-b) HAADF and BF-STEM images of MIL 2a7-25 o1 below Pt fiducial marker. (c–h) False color EDS maps for O, Si, Fe, Mg, S and Ni, respectively. White arrows indicate local enrichment of Fe, Ni, and S. (i) SAED pattern from region denoted by (i) in HAADF image. EDS spectrum data in Table 4.2 also acquired from region (i).
diffraction pattern from the region of Fe, S and Ni enrichment. Measurement of the SAED patterns reveal d-spacings that overlap with both olivine and pyroxene (Table 4.1), precluding identification of a single-phase carrier of the O-anomaly. Therefore, here and elsewhere in the manuscript, we consider the entire polycrystalline silicate domains below the Pt fiducial markers as the ‘presolar grains’ that carry the O-anomaly. Given that the measured d-spacings of the polycrystalline domain MIL 2a7-25 o1 overlap with olivine and pyroxene, the cation composition was quantified based on 12 O atoms, which is the least common multiple of the three and four oxygens specific to pyroxene and olivine, respectively. An EDS spectrum was extracted from the bulk of MIL 2a7-25 o1 and standardless quantification indicates a composition of (Mg_{4.34}Fe_{0.61}S_{0.11}Ni_{0.07})(Si_{3.23}Al_{0.13})O_{12} (Table 4.2), which is consistent with a mixture of olivine and pyroxene.
Table 4.1. d-spacings of polycrystalline presolar grains in this study as determined by SAED.

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<tr>
<th>Grain</th>
<th>Ring Number</th>
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<tr>
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Table 4.2. Grain compositions determined using EDS expressed in wt% oxide and cation count.

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<tr>
<th>Grain Phase Structure</th>
<th>Fe-poor Matrix Grains</th>
<th>Fe-rich Matrix Grains</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MIL 2a7-25 o1</td>
<td>MIL 7a1-1 o1</td>
</tr>
<tr>
<td>Olivine/Pyroxene Polycrystalline</td>
<td>Pyroxene Polycrystalline</td>
<td>Pyroxene Polycrystalline</td>
</tr>
<tr>
<td>\textsuperscript{17}O/\textsuperscript{16}O (x10\textsuperscript{-4})</td>
<td>3.92 ± 0.23</td>
<td>8.40 ± 0.12</td>
</tr>
<tr>
<td>\textsuperscript{18}O/\textsuperscript{16}O (x10\textsuperscript{-3})</td>
<td>3.34 ± 0.07</td>
<td>1.72 ± 0.02</td>
</tr>
<tr>
<td>Oxide</td>
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<td></td>
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<td>MgO</td>
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<tr>
<td>FeO</td>
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<td>25.28</td>
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<tr>
<td>SiO\textsubscript{2}</td>
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<td>53.16</td>
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<tr>
<td>CaO</td>
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<td>n.d.</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
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<td>n.d.</td>
</tr>
<tr>
<td>SO\textsubscript{3}</td>
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<td>n.d.</td>
</tr>
<tr>
<td>NiO</td>
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<td>n.d.</td>
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<tr>
<td>Cation</td>
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<td>Mg</td>
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<td>Fe</td>
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<td>Ca</td>
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<tr>
<td>Al</td>
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<td>S</td>
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<td>Ni</td>
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<tr>
<td>O</td>
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O-isotopic compositions from Haenecour et al. (2020). All analyses normalized to 100%. 3σ errors on wt% oxide quantification.
n.d. = not detected.
4.3.1.2 MIL 7a1-1 o1

NanoSIMS analysis reveals MIL 7a1-1 o1 is enriched in $^{17}$O relative to solar system values with $^{17}$O/$^{16}$O ($\times10^{-4}$) = 8.40 ± 0.12 and $^{18}$O/$^{16}$O ($\times10^{-3}$) = 1.72 ± 0.02 (Appendix B Fig. S1). The O-isotopic composition of MIL 7a1-1 o1 places it in the Group 1 field of presolar grains (Fig. 4.1) as defined by Nittler et al., (1997, 2008). Auger nanoprobe analysis reveals that MIL 7a1-1 o1 is a ferromagnesian silicate.

STEM imaging of the FIB section reveals a fine-grained, porous matrix with elongated, fibrous grains that vary in size, ranging from about 600 nm to 1.8 μm in length (Fig. 4.4a). EDS mapping of the entire FIB section reveals that O, Si, Mg, and Fe are spatially correlated with each other across the FIB section (Fig. 4.4b–h). Localized Ca is present in the lower left portion of the FIB section and there are local regions where Fe, Ni and S spatially correlate with each another. The fibrous grains contain mainly O and Fe, with lesser amounts of Mg and Si, and localized S and Ni. The matrix contained within the FIB section is dominated by polycrystalline ferromagnesian silicate material with lesser amounts of localized Fe-sulfides (Fig. 4.4e, g). An SAED pattern obtained from one of the Fe-oxide fibers is polycrystalline (Fig. 4.4i) and measurement is consistent with ferrihydrite (Table 4.3).
Figure 4.4: TEM data on FIB section containing MIL 7a1-1 o1. (a) HAADF-STEM image of whole FIB section containing MIL 7a1-1 o1. Yellow box indicates field of view of EDS maps. (b–h) False color EDS maps of the entire FIB section for O, Si, Mg, Fe, Ca, S, and Ni, respectively. (i) SAED pattern from region denoted by (i) in HAADF image in panel (a).
<table>
<thead>
<tr>
<th>Figure</th>
<th>Ring Number</th>
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<td>4.11h</td>
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See Figs. 4.5i, 4.9i and 4.11h for locations of rings in SAED patterns.
STEM imaging below the Pt fiducial marker reveals a shallow domain that is distinct from the surrounding matrix (Fig. 4.5a–b). EDS mapping shows spatial correlations among O, Si and Mg and localized Fe at the edge of the domain (Fig. 4.5 c–f). Pt is also observed extending into the center of the domain (Fig. 4.5a–b), which is consistent with a hole being filled with Pt during the fiducial-marker deposition. Prior to extraction, this hole was observed by secondary-electron imaging in the FIB-SEM. SAED patterns acquired across the domain reveal that MIL 7a1-1 o1 is polycrystalline and d-spacing measurements are consistent with a Mg-rich pyroxene (Fig. 4.5g, Table 4.1). An EDS spectrum was extracted from MIL 7a1-1 o1 and is consistent with a composition of (Mg1.21Fe0.79)(Si2.0)O6 (Table 4.2). High-resolution TEM (HRTEM) imaging at the boundary between the Fe-poor bulk of MIL 7a1-1 o1 and the Fe-rich rim confirms the polycrystallinity of MIL 7a1-1 o1 (Fig. 4.6a) and indicates that the Fe-rich rim at the edges of MIL 7a1-1 o1 is not structurally distinct from the Fe-poor bulk of the domain. A higher magnification EDS map showing the distribution of Fe across the Fe-poor and Fe-rich boundary in MIL 7a1-1 o1 is shown in Fig. 4.6b. Measurement of lattice fringes in the Fe-poor and Fe-rich domains reveal d-spacings of 1.81 Å and 2.02 Å, consistent with the (622) and (422) planes in orthopyroxene, respectively.
Figure 4.5: TEM data on MIL 7a1-1 o1. (a) HAADF-STEM image of MIL 7a1-1 o1 below Pt fiducial marker. (b) BF-STEM image of MIL 7a1-1 o1. Dashed box indicates region where HRTEM image in Figure 6a was obtained. (c–f) False color EDS maps for O, Si, Fe, and Mg, respectively. (g) SAED pattern from region denoted by (g) in HAADF image. EDS spectrum data in Table 4.2 also acquired from region (g).
Figure 4.6: HRTEM data on MIL 7a1-1 o1. (a) HRTEM image of the region outlined by dashed box in Figure 5b. (b) False color EDS map of Fe for the same field of view as the HRTEM image.
4.3.2 Presolar Grains from Fe-rich Matrix Regions

4.3.2.1 MIL 10a2-6 o1

NanoSIMS analysis reveals MIL 10a2-6 o1 is enriched in both $^{17}\text{O}$ and $^{18}\text{O}$ relative to solar system values with $^{17}\text{O}/^{16}\text{O} \times 10^{-4} = 4.86 \pm 0.15$ and $^{18}\text{O}/^{16}\text{O} \times 10^{-3} = 2.56 \pm 0.03$ (Appendix B Fig. S1). The O-isotopic composition of MIL 10a2-6 o1 places it in the Group 4 field (Fig. 4.1) of presolar grains as defined by Nittler et al., (1997, 2008). Auger mapping reveals that MIL 10a2-6 o1 contains O, Si, Fe, and Ca, which is consistent with a Ca-bearing ferromagnesian silicate (Fig. 4.7b–f).

STEM imaging of the entire FIB section reveals that the matrix is porous (Fig. 4.8a). The top of the FIB section is dominated by a fine-grained material that has a spongy texture (Fig. 4.8a, dashed outline) and SAED patterns from this region are consistent with polycrystalline pyroxene. The remainder of the FIB section is dominated by elongated, fibrous grains that range in size from ~400 nm to 1.4 μm in length and lesser amounts of silicate material. EDS mapping of the FIB section reveals localized Ca and spatially correlated O, Si, Mg, Fe, minor Ni and S (Fig. 4.8b–h). The fibrous grains contain Fe and O. A polycrystalline SAED pattern was obtained from one Fe-oxide fiber (Fig. 4.8i) and measurement is consistent with ferrihydrite (Table 4.3).

STEM imaging reveals an irregularly shaped, fine-grained domain below the Pt fiducial marker (indicated by dashed line in Fig. 4.9a–b). HAADF imaging shows three oval-shaped, high-contrast features located near the top of the domain. STEM-EDS reveals O, Si, Mg, Ca, Al and S are spatially correlated with each other in the domain (Fig. 4.9c–e, g–i). The high-contrast features visible in the HAADF image are consistent with holes filled with Pt from the fiducial marker.
Figure 4.7: Auger spectroscopy data on MIL 10a2-6 o1, indicated by red circle. (a) SE image of MIL 10a2-6 o1 with FIB transect indicated by dashed yellow line. (b–f) Grayscale Auger maps for O, Si, Mg, Fe and Ca, respectively.
Figure 4.8: TEM data on the FIB section containing MIL 10a2-6 o1. (a) HAADF-STEM image of the whole FIB section containing MIL 10a2-6 o1. Dashed outline indicates fine-grained material distinct from porous matrix. Arrows indicate fibrous ferrihydrite. Yellow box indicates field of view of EDS maps. (b–h) False color EDS maps for O, Si, Mg, Fe, Ca, S, and Ni, respectively. (i) SAED pattern from region labeled (i) in HAADF image.
deposition. These holes were visible in the Auger SE image (Fig. 4.7a) and in the SE images acquired in the FIB-SEM (not shown) prior to FIB lift out. An Fe-rich composition is present at the bottom edge MIL 10a2-6 o1 and also around the bright oval-shaped holes (Fig. 4.9f). SAED patterns were obtained around the fine-grained domain and indicate that MIL 10a2-6 o1 is polycrystalline (Fig. 4.9j) and measurement of one representative pattern indicates d-spacings consistent with a pyroxene (Table 4.1). An EDS spectrum was extracted from MIL 10a2-6 o1 and standardless quantification is consistent with a composition of \((\text{Mg}_{0.55}\text{Fe}_{0.98}\text{Ca}_{0.24}\text{S}_{0.13}\text{Ni}_{0.03})(\text{Si}_{1.77}\text{Al}_{0.17})\text{O}_6\) (Table 4.2).
Figure 4.9: TEM data on MIL 10a2-6 o1. (a-b) HAADF and BF-STEM images below Pt fiducial marker with MIL 10a2-6 o1 outlined by dashed line in panel (b). White arrows in panel (a) indicate holes filled with Pt. (c–i) False color EDS maps for O, Si, Mg, Fe, Ca, Al, and S, respectively. White arrows in panel (c) again indicate holes at grain surface. (j) SAED pattern from region denoted by (j) in BF image. EDS spectrum data in Table 3 also acquired from region (j).
4.3.2.2 MIL 10b2-5 o1

NanoSIMS analysis reveals MIL 10b2-5 o1 is enriched in $^{17}$O relative to solar system values with $^{17}$O/$^{16}$O ($\times10^{-4}$) = 5.65 ± 0.10 and $^{18}$O/$^{16}$O ($\times10^{-3}$) = 1.81 ± 0.02 (Appendix B Fig. S1). The O-isotopic composition of MIL 10b2-5 o1 places it in the Group 1 field of presolar grains (Fig. 4.1) as defined by Nittler et al., (1997, 2008). Auger nanoprobe analysis reveals that MIL 10b2-5 o1 is a ferromagnesian silicate.

STEM imaging of the entire FIB section reveals a notably less porous matrix than other FIB sections in this study (Fig. 4.10a). EDS mapping of the whole FIB section reveals O, Si, Mg, S and Al correlate with each other and there are also localized regions containing Fe and O (Fig. 10b–g). The matrix contained in the FIB section is dominated by polycrystalline and amorphous silicate material and a few small (~80 nm) Fe-sulfides are also present (Fig. 4.10e, f). SAED patterns acquired from the regions enriched in Fe and O are consistent with ferrihydrite (Table 4.3), one representative pattern is provided in Fig. 4.10h. The ferrihydrite in this FIB section is more compact and vein-like compared to the fibrous grains observed in the other FIB sections in this study and appears to have filled void space between matrix grains.

STEM imaging below the Pt fiducial marker reveals a fine-grained domain (dashed line, Fig. 4.11b). EDS mapping of the region reveals that O, Si, Mg, and Al correlate with each other in the domain (Fig. 4.11c, e–g). Local Mg hotspots occur on the right side of the domain, with the Mg/Si ratio increasing from the left to the right of the domain (~0.15 to 0.36 at %). Additionally, there is an Fe-rich composition at the edges of the domain (Fig. 4.11d). SAED patterns acquired across the domain reveal that MIL 10b2-5 o1 is polycrystalline, with d-spacings consistent with a
Figure 4.10: TEM data on the FIB section containing MIL 10b2-5 o1. (a) HAADF-STEM image of the whole FIB section containing MIL 10b2-5 o1. White arrows indicate ferrihydrite. Yellow dashed box indicates field of view of EDS maps. (b–g) False color EDS maps for O, Si, Mg, Fe, S, and Al, respectively. (h) SAED pattern from region labeled (h) in HAADF image.
Figure 4.11: TEM data on MIL 10b2-5 o1. (a-b) HAADF and BF-STEM images of MIL 10b2-5 o1 as indicated by dashed line in panel (b) below Pt fiducial marker. Dashed box in panel (a) indicates region where HRTEM image in Figure 12a was obtained. (c–g) False color EDS maps for O, Fe, Mg, Si, and Al, respectively. (h) SAED pattern from region labeled (h) in BF image. EDS spectrum data in Table 3 also acquired from region (h).
pyroxene (Fig. 4.11h, Table 4.1). The polycrystalline nature of MIL 10b2-5 o1 is confirmed via HRTEM (Fig. 4.12a). An EDS spectrum was extracted from MIL 10b2-5 o1 and is consistent with a composition of \((\text{Mg}_{0.27}\text{Fe}_{1.43}\text{S}_{0.17})(\text{Si}_{1.72}\text{Al}_{0.18})\text{O}_6\) (Table 4.2). A higher magnification EDS map of the region outlined by the dashed box in Fig. 4.11a highlights the Fe-rich composition at the edges of MIL 10b2-5 o1. The same field of view is captured in the HRTEM image (Fig. 4.12a), which shows that the Fe-rich composition is not structurally distinct from the bulk of MIL 10b2-5 o1. Measurements of the lattice fringes present in the Fe-enriched regions indicate d-spacings of 3.20 Å and 2.55 Å, consistent with the (411) and (131) crystal planes in orthopyroxene.
Figure 4.12: HRTEM data on MIL 10b2-5 o1. (a) HRTEM image of region outlined by dashed box in Figure 11a. Dashed outline indicates MIL 10b2-5 o1 region of interest with Fe-rich and Fe-poor, domains labeled. (b–c) False color EDS map for Pt and Fe with the same field of view as panel (a).
4.4 Discussion

4.4.1 Aqueous Alteration in the Matrix of MIL 07687

Ferrihydrite is a poorly crystalline to amorphous hydrous Fe-oxide mineral with the chemical formula $5\text{Fe}_2\text{O}_3\cdot9\text{H}_2\text{O}$ (e.g., Schwertmann & Fischer, 1973; Schwertmann et al. 1987; Schwertmann, 1988; Schwertmann & Taylor, 1989; Janney et al. 2000; Bland et al., 2006; Waychunas, 1991). Ferrihydrite is found in a variety of geologic settings and also in several carbonaceous chondrite groups, including CI, CV, CM, CO and the ungrouped carbonaceous chondrite Acfer 094 and can be attributed to both terrestrial weathering and parent-body aqueous alteration (e.g., Brearley, 1997; Greshake, 1997; Keller & Buseck, 1990; Lee et al., 1996; Leroux et al., 2015; Morlok et al., 2006; Tomeoka & Buseck, 1988). In geologic settings, ferrihydrite is formed by the hydrolysis and precipitation of dissolved Fe (e.g., Combes et al. 1989; Schwertmann & Taylor, 1989; Waychunas, 1991). In meteoritic samples, ferrihydrite is reported to be one of the first alteration phases to form as a result of corrosion of primary meteoritic minerals such as troilite, olivine, and pyroxene during terrestrial weathering (Bland et al., 2006). However, as discussed in Haenecour et al. (2020), though MIL 07687 has a CE weathering grade (severe rustiness, evaporite minerals visible; Weisberg et al., 2009), no other Antarctic carbonaceous chondrite exhibits terrestrial weathering similar to the aqueous alteration observed in MIL 07687. The alteration observed in MIL 07687 is therefore likely a result of alteration on the parent body asteroid (Haenecour et al. 2020).

As noted by previous authors (Brearley, 2012, 2013; Davidson et al., 2014a; Haenecour et al., 2020; Prestgård et al., 2021) the unique alteration present in the MIL 07687 chondrite suggests a heterogeneous distribution of water on the parent body, leading to localized regions of relatively
altered and unaltered material. We hypothesize that the interaction of fluids with matrix materials resulted in the dissolution of Fe-metal, Fe-sulfides such as troilite, and Fe-bearing silicate minerals such as olivine, and pyroxene via the following reactions (e.g. Bland et al., 2006):

(i) Fe-metal: \( \text{Fe}^0 + 2\text{H}_2\text{O}(l) \rightarrow \text{Fe}^{2+}(aq) + 2\text{OH}^-(aq) + \text{H}_2(g) \)

(ii) Troilite: \( \text{FeS}(s) + \text{H}_2\text{O}(l) + 3\text{O}^2-(g) \rightarrow \text{Fe}^{2+}(aq) + \text{H}_2\text{SO}_4(aq) \)

(iii) Olivine: \( (\text{Mg, Fe})_2\text{SiO}_4(s) + 4\text{H}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{Fe}^{2+}(aq) + \text{H}_4\text{SiO}_4(aq) \)

(iv) Pyroxene: \( (\text{Mg, Fe})\text{SiO}_3(s) + 2\text{H}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{Fe}^{2+}(aq) + \text{H}_4\text{SiO}_4(aq) \)

The dissolution of such minerals makes Fe\(^{2+}\) available for oxidation, followed by hydrolysis to form ferrihydrite via the following reaction:

(i) \( 10\text{Fe}^{3+}(aq) + 24\text{H}_2\text{O}(l) \rightarrow 5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}(s) + 30\text{H}^+(aq) \)

Thus, we hypothesize that Fe that was not incorporated into ferrihydrite was likely mobile through the matrix and resulted in the Fe-rich compositions at the edges of MIL 7a1-1 o1, MIL 10a2-6 o1, and MIL 10b2-5 o1. Similar alteration textures to those observed in MIL 07687 are reported in previous work by Keller & Buseck (1990), Hanowski & Brearley (2001) and Suttle et al. (2022). Keller & Buseck (1990) identified poorly crystalline ferrihydrite that formed through the release of Fe from olivine and metal during alteration processes in the Lancé CO3 chondrite. Hanowski & Brearley (2000) identified Fe-rich aureoles in CM chondrites that formed as a result of the in situ alteration of metal grains. Suttle et al. (2022) performed laboratory alteration experiments on chips of the CO3 chondrite Kainsaz to simulate hydrothermal processing under alkaline and oxidizing conditions on carbonaceous chondrite parent bodies. Their study showed that Fe-oxyhydroxides form early in the alteration process at low temperatures (50 °C), compared to phyllosilicates, Ni-rich sulfides, Fe-sulfate, and calcite that form later. They also observed the
formation of reaction fronts, where minimally altered material is in direct contact with heavily altered material, similar to the textures observed in MIL 07687 and suggesting that fluids rapidly react with matrix materials (Suttle et al., 2022). Given that we observe ferrihydrite, a metastable precursor, as the dominant alteration phase in the FIB sections in this study and none of the later-stage alteration minerals, such as goethite or phyllosilicates, our data suggest that the alteration experienced by MIL 07687 was early-stage and restricted by the availability of water-bearing fluid. Similar to previous studies, we do not observe evidence of phyllosilicates in the matrix of MIL 07687, which suggests that alteration occurred under oxidizing conditions that resulted in the formation of ferrihydrite over phyllosilicates (Haenecour et al., 2020).

Among the FIB sections in this study, those extracted from the Fe-poor matrix retain unequilibrated matrix material including Fe-sulfides and both amorphous and crystalline silicate material, evidence that this lithology is less altered than the Fe-rich matrix. However, the amount of alteration between the FIB sections from the Fe-poor regions is also variable. In the FIB section containing MIL 2a7-25 o1 (Fig. 4.2) we hypothesize that the distinct boundary of ferrihydrite separating the predominantly crystalline and predominantly amorphous material could indicate a partially arrested alteration reaction, where the extent of alteration was limited by the availability of fluid. We note that the alteration could have also stopped due to changes in the composition of the fluid, however, we do not observe any other alteration products that would suggest such a change in the fluid. In comparison, the FIB section containing MIL 7a1-1 o1 appears to have experienced more alteration as evidenced by abundant ferrihydrite and its Fe-rich rim, though Fe-sulfides are preserved in part of the matrix suggesting that alteration was not extensive enough to dissolve all Fe-sulfides.
The FIB sections extracted from the Fe-rich matrix regions are extensively altered. The FIB section containing MIL 10a2-6 o1 is dominated by ferrihydrite and does not retain discrete Fe-sulfide grains, but contains a more equilibrated distribution of S and Ni, suggesting that these elements were mobile during aqueous alteration. That the matrix surrounding MIL 10a2-6 o1 is texturally distinct from the remaining matrix in the FIB section suggests that this fine-grained material likely experienced less alteration, preserving the isotopically anomalous composition of MIL 10a2-6 o1. Similarly, the FIB section containing MIL 10b2-5 o1 also shows a more equilibrated distribution of S and is dominated by a vein-like ferrihydrite. That the ferrihydrite in this section is vein-like rather than fibrous and the FIB section has a compact structure that lacks porosity suggests that pore spaces were filled during dissolution and reprecipitation of matrix mineral phases, consistent with the observations made by Suttle et al. (2022).

4.4.2 Alteration of Presolar Silicate Grains in the MIL 07687 Chondrite

Presolar silicate grains are easily altered and can therefore be used as tracers of nebular and parent-body alteration processes (Floss & Brearley, 2015; Floss & Stadermann, 2012). However, the presolar grain abundances reported for the Fe-rich and Fe-poor matrix regions in the MIL 07687 chondrite are the same within error (Haenecour et al., 2020). Nonetheless, our TEM observations show that even the FIB sections extracted from the relatively Fe-poor matrix contain evidence for alteration processes. Fe-rich rims surrounding O-rich presolar grains were reported in multiple chondrites including Adelaide, Acfer 094, QUE 99177, DOM 08006, NWA 801 and Isheyevo (Vollmer et al., 2009; Floss & Stadermann, 2012; Nguyen et al., 2016; Sanghani et al., 2022; Seifert et al., 2022c; Zega et al., 2020) and several formation paths were suggested. In Acfer
an amorphous, Fe-rich rim was observed around an olivine grain and the authors argued that it formed through amorphization due to sputtering in the ISM (Vollmer et al., 2009). An enstatite grain with an amorphous Fe-rich rim was reported in QUE 99177 and the authors argued that the Fe-enrichment in the rim was the result of parent-body alteration (Nguyen et al., 2016). Two silicate grains with Fe-rich rims in the Adelaide meteorite were observed and consistent with Fe-diffusion resulting from short-lived thermal processing of mm-to cm-sized clumps of dust in an oxidizing nebular environment (Floss and Stadermann, 2012). Zega et al. (2020) reported similar findings, suggesting that Fe-rich rims could result from thermal processing of fragments of dust. In the DOM 08006 chondrite, Seifert et al. (2022c) reported a forsterite grain with an Fe-rich rim and the authors argued that it formed through thermal processing of a clump of dust, similar to that of Floss & Stadermann (2012) and Zega et al. (2020). Finally, a nonstoichiometric olivine-like grain and an enstatite grain with Fe-rich rims were identified in the NWA 801 and Isheyevo chondrites, and were attributed to aqueous alteration (Sanghani et al., 2022).

The MIL 07687 chondrite is reported to have experienced aqueous alteration, which is consistent with our TEM observations, and little to no thermal alteration (Haenecour et al., 2020). Given that signatures of aqueous alteration are present in all the FIB sections in this study, we hypothesize that aqueous alteration led to the dissolution of Fe-bearing silicate and Fe-sulfide materials in the matrix, as discussed above, leading to the mobilization of Fe through the matrix and diffusion into MIL 7a1-1 o1, MIL 10a2-6 o1, and MIL 10b2-5 o1. Mobility of Fe through the matrix is supported by the higher Fe content measured in the altered matrix presolar grains compared to the relatively unaltered matrix presolar grains. Similarly, Haenecour et al. (2020) report that grains in the altered matrix regions have a higher median Fe content compared to the
unaltered regions, but are comparable within error. Therefore, it is plausible that the Fe originates from fluid-mineral interactions in the surrounding matrix, resulting in the formation of ferrihydrite and the Fe-rich rims surrounding three of the presolar silicates in this study.

Our TEM data suggest that even though three of the grains in this study show signs of processing, such alteration was not extensive enough to replace primary presolar grain phases with alteration phases or lead to complete isotopic equilibration with the surrounding matrix material. However, we cannot rule out minor isotopic exchange as a result of hydrothermal fluid interactions with the anomalous presolar silicates. Such interaction could result in the measured isotopic composition recorded via NanoSIMS analysis to be less anomalous (relative to solar system values) than the original isotopic composition of the grains following circumstellar condensation.

We note that Bose et al. (2018) modeled the time-scale and temperatures of Mg-Fe diffusivity in orthopyroxene in the Adelaide meteorite and concluded a diffusion time-scale of <214,000 years at temperatures of 500 to 600 °C. Zega et al. (2020) used such information to estimate the likelihood of isotopic equilibration of a presolar spinel in Adelaide and found that over the suggested timescale of ~214,000 years, O diffusion length scales range from approximately 30 to 200 pm at 500 °C and 1 to 6 nm at 600 °C. Given the size (~570 nm) of the presolar spinel that they measured, they concluded that the grain is larger than the calculated diffusion length scales by a factor of ~20 to ~19,000 for temperatures of 600 °C and 500 °C respectively, suggesting that isotopic equilibration was unlikely. The Adelaide meteorite is more thermally altered than MIL 07687, which likely experienced temperatures less than those of Adelaide (<600 °C). Indeed, as noted above, laboratory experiments on the CO3 chondrite Kainsaz by Suttle et al (2022) indicate the formation of ferrihydrite, the primary alteration phase in MIL 07687, via hydrothermal
processing at temperatures ranging from 50 °C to 150 °C, which is in agreement with temperatures reported for thermal metamorphism of CO3 chondrites (~200°C, Huss et al., 2006), to which MIL 07687 has affinities. Alteration at low temperature is also in agreement with the Cr$_2$O$_3$ measurements by Haenecour et al. (2020) that suggest little to no thermal alteration in MIL 07687. Given that hydrothermal alteration likely occurred at such low temperatures in MIL 07687, any diffusion of oxygen likely proceeded more slowly than those suggested by Bose et al. (2018) for Fe and Mg, over timescales $>214,000$ years. In order to get some sense of the likelihood of the O-isotopic equilibration at such low temperatures in MIL 07687, we followed a methodology similar to Zega et al. (2020) to calculate the timescale of diffusion of oxygen in a pyroxene. Not all of the parameters necessary for such a calculation are known for pyroxene, but for the sake of completeness, we made some simplifying assumptions. We assumed a range of correlation factors and that the activation energy and collision-frequency factor for diopside is a reasonable proxy (Ryerson & McKeegan 1994). Based on these assumptions, our calculations yield timescales that exceed the age of the solar system. Therefore, O-isotopic exchange between the presolar silicates in this study and the surrounding matrix is unlikely at low temperatures over the length-scales observed in this study.

We note the possibility that polycrystalline assemblages could result from the alteration of originally amorphous grains that experienced more advanced aqueous alteration processes or thermal annealing. Advanced aqueous alteration could result in formation of nanocrystalline phyllosilicate material, as suggested for amorphous matrix grains in the CM chondrite Y-791198 (Chizmadia et al., 2008). In the case of thermal annealing, the transition of a stoichiometric amorphous grain to a stoichiometric polycrystalline assemblage is unlikely given that amorphous
grains are not controlled by equilibrium thermodynamics. However, thermal annealing of amorphous grains with non-stoichiometric compositions could result in a polycrystalline assemblage as reported by Nguyen et al. (2016). The presolar grain assemblages observed here were not replaced by phyllosilicates and do not exhibit evidence of being extensively hydrated, making an amorphous to polycrystalline transition via aqueous alteration unlikely. All grains in this study are nearly stoichiometric, making an amorphous to polycrystalline transitions through thermal annealing unlikely, however it is a possibility that we cannot rule out. We also note the possibility that polycrystalline assemblages could result from the breakdown of a single crystal, resulting in an assemblage that is finer-grained and nanocrystalline. In this scenario, the pyroxene grains in this study could have originally formed in their host circumstellar environment as a single crystal, and following accretion on the parent body, were subsequently aqueously altered, leading to the breakdown of the single crystal to form a nanocrystalline assemblage. This scenario is a possibility that we are unable to rule out, however, such a scenario would likely have resulted in significant isotopic exchange between the presolar grain and the altering fluid, perhaps preventing identification of the presolar grain. We discuss the thermodynamic origins of the polycrystalline presolar grain assemblages below.

4.4.3 Stellar Origins of O-rich Presolar Grains

The O-isotopic compositions of O-rich presolar grains can be reproduced with nucleosynthetic models of stellar evolution and SNe (Choi et al., 1998; Nguyen & Messenger, 2014; Nittler et al., 1997, 2008). Comparison of isotopic data with such models has led to detailed insight into nucleosynthesis in AGB/RGB stars and in stellar explosions such as novae and SNe.
The comparison of isotopic data from presolar grains with nucleosynthetic models of stellar evolution can be used to determine the type, mass, and metallicity of the progenitor star from which grains originate.

O-rich presolar grains are divided into four groups based on their O-isotopic compositions, which represent distinct stellar origins that have been discussed in detail in numerous publications (Nittler et al., 1997, 2008). We briefly discuss the origins of Group 1 and Group 4 grains below.

Group 1 grains are thought to originate in the circumstellar envelopes of low-mass RGB or AGB stars experiencing dredge-up processes that bring the products of main-sequence nucleosynthesis to the circumstellar envelope (Boothroyd & Sackmann, 1999; Nittler et al., 1997; Nollett et al., 2003). Such grains are characterized by enrichment in $^{17}\text{O}$ relative to solar-system values and may also have slight depletions in $^{18}\text{O}$. The $^{17}\text{O}/^{16}\text{O}$ ratio is linked to stellar mass and the $^{18}\text{O}/^{16}\text{O}$ ratio is linked to metallicity. Recent Mg-isotopic analyses suggest that a fraction of Group 1 and Group 2 silicates originally thought to be derived from low-mass RGB/AGB stars could instead originate in SNe, intermediate-mass AGB stars, or super-AGB stars (Hoppe et al., 2021; Leitner & Hoppe, 2019; Verdier-Paoletti et al., 2019). Additionally, novae have been considered a possible source for extreme Group 1 grains, though work by Hoppe et al. (2021) and Leitner & Hoppe (2019) suggest novae origins are less likely for many of these grains.

Group 4 grains are attributed to origins in the ejecta of type-II core-collapse SNe (Choi et al., 1998; Nittler, 2008) and are characterized by enrichments in $^{18}\text{O}$ relative to solar system values that are thought to result from partial He burning via $^{14}\text{N}(\alpha, \gamma)^{18}\text{F}(\beta^+,\nu)^{18}\text{O}$. Some Group 4 grains also have enrichments in $^{17}\text{O}$ relative to solar system values that are suggested to follow the galactic
chemical evolution trend, indicating that their progenitor stars had a metallicity higher than solar. Though the Mg, Si, and Fe isotopic compositions of Group 4 grains are not compatible with high-metallicity stars, they are reproducible with nucleosynthetic models of SNe (Choi et al., 1998; Nguyen & Messenger, 2014; Nittler, 2008; Vollmer et al., 2008).

The detailed analysis of presolar grains can also provide information on the conditions under which they condensed in their host circumstellar envelopes or SNe ejecta. The chemical compositions and crystal structures of presolar grains can be compared with thermodynamic model predictions to infer the pressure and temperature conditions under which they formed (e.g. Nguyen et al., 2007a, 2010, 2016; Seifert et al., 2022c; Stroud et al., 2004; Vollmer et al., 2007, 2009, 2013; Zega et al., 2011, 2014a, 2015, 2020). Such models predict when certain minerals will condense from a gas, generally defined as solar composition, under an assumed set of total pressures. Similarly, thermodynamic models specific to dust condensation in SNe are available in the literature and can be used to understand the thermodynamic origins of grains originating in SNe. Comparisons of presolar grain data with thermodynamic model predictions can provide first-order constraints on the thermodynamic conditions under which these grains condensed in their host circumstellar envelope or ejecta.

4.4.3.1 Stellar Origins of Grains Preserved in Fe-poor Matrix Regions

4.4.3.1.1 MIL 2a7-25 o1 (Group 4-Supernova)

The polycrystalline nature of MIL 2a7-25 o1 makes constraining the exact conditions under which it formed difficult. Polycrystalline and amorphous presolar grains were previously reported and are thought to suggest nonequilibrium or multistep condensation processes (Nguyen et al.,
2010; Vollmer et al., 2009; Zega et al., 2020). Equilibrium models of dust condensation in SNe predict orthopyroxene to condense between 1090 and 1548 K and olivine to condense between 1063 and 1575 (Fedkin et al., 2010). Fedkin et al. (2010) used model compositions of type II SNe layers computed by Rauscher et al. (2002) to predict the minerals that will condense in each respective zone. We note that dust condensation occurs after SN explosion and that astronomical observations suggest that material from different SN zones mixes in the ejecta (Abarzhi et al., 2019; Arnett et al., 1989; Hammer et al., 2010; Hughes et al., 2000; Kifonidis et al., 2003). The temperature range noted above for orthopyroxene and olivine suggests contributions from the H envelope, the He/N, and the O-rich zones, with the highest temperatures present in the O-rich zones. Using the SN modeling data of Rauscher et al. (2002), previous studies have estimated the O-isotopic compositions of the H envelope, and the He/N, He/C, and O-rich zones (e.g., Nittler et al. 2008; Haenecour et al. 2013 (see Fig. 1)). Comparing the O-isotopic composition of MIL 2a7-25 o1 with the estimated O-isotopic compositions of the different SN zones suggests contributions from the H envelope and the He/N and He/C zones, with little contribution from the O-rich zones. We note, however, that the Fedkin et al. (2010) model does not predict orthopyroxene or olivine as a condensate in the He/C zone. It is therefore most probable that the condensation temperatures for the outer-most SN zones are most relevant here, suggesting temperatures of 1090 K to 1110 K for orthopyroxene and 1138 K to 1145 K for olivine.

However, the Fe-Ni-S composition at the center of MIL 2a7-25 o1 is not consistent with solids condensing sequentially from a gas via equilibrium processes. Both equilibrium and nonequilibrium models predict iron sulfides to condense at temperatures below those predicted for silicates such as olivine and pyroxene (e.g., Lodders, 2003; Nozawa et al., 2003). We therefore
consider multiple scenarios for the formation of the MIL 2a7-25 o1 assemblage. First, MIL 2a7-25 o1 could have formed in a stepwise manner as temperatures cooled in the host SN ejecta. In this scenario, nanocrystalline olivine and pyroxene condensed first, followed by the Fe-Ni-S material, which was then mechanically accreted together with the silicate material. Second, SNe are thought to be dynamic environments that experience large-scale mixing processes (Abarzhi et al., 2019; Arnett et al., 1989; Hammer et al., 2010; Hughes et al., 2000; Kifonidis et al., 2003). It is also possible that the Fe-Ni-S material condensed first in a cooler region of the ejecta and was transported to a warmer region that was more favorable for the condensation of nanocrystalline olivine and pyroxene. However, we note that in such a scenario, sulfides would not be stable for a long period of time at temperatures suitable for silicate formation. Therefore, silicate material would need to nucleate before significant sublimation of the sulfide to preserve the microstructure we observe here.

4.4.3.1.2 MIL 7a1-1 o1 (Group 1-AGB/RGB)

Comparison of the O-isotopic composition of MIL 7a1-1 o1 with nucleosynthetic model predictions indicates an origin in a close-to-solar metallicity AGB/RGB star of approximately 1.5 M☉ (Boothroyd & Sackmann, 1999; Boothroyd et al., 1994). Comparison of the grain data with thermodynamic model predictions can provide first-order constraints on the origins of MIL 7a1-1 o1. Equilibrium thermodynamic models predict the orthopyroxene solid solution to condense from a gas of solar composition at 1366 K and pure enstatite to condense at 1316 K and assuming total pressures of 10^{-3} and 10^{-4} bar respectively (Ebel & Grossman, 2000; Lodders, 2003). Given that MIL 7a1-1 o1 is a stoichiometric pyroxene, we hypothesize that nanocrystalline pyroxene grains
formed through equilibrium processes and mechanically accreted to form the assemblage we observe. That MIL 7a1-1 o1 was extracted from an Fe-poor matrix region and still shows indications of processing suggests that alteration in the MIL 07687 chondrite is fine-scale and heterogeneous. Several other presolar pyroxenes from AGB stars are reported in the literature, all of which have varied degrees of crystallinity. Nguyen et al. (2016) identified two pyroxene grains, one of which is a twinned clinoenstatite thought to have formed through equilibrium processes at high temperatures, while the other is an enstatite grain consisting of a nanocrystalline core and amorphous Fe-rich shell that likely resulted from the ISM irradiation of a single crystal of enstatite. Vollmer et al. (2007) identified a MgSiO₃ grain with a perovskite structure that likely formed as a result of shock processing of a silicate precursor. Vollmer et al. (2013) identified a single crystal of orthopyroxene that likely condensed under equilibrium conditions in a locally non-solar gas. Nittler et al. (2019) reported a crystalline enstatite grain that amorphized quickly under the electron beam, suggesting partial hydration.

As noted above, recent Mg isotopic work suggests that some Group 1 grains originally thought to condense in the circumstellar envelopes of AGB/RGB stars could have instead condensed in the ejecta of SNe or in the stellar winds of red/blue supergiants (Hoppe et al., 2021; Leitner & Hoppe, 2019; Verdier-Paoletti et al., 2019). Only a small fraction (10–25%) of Group 1 silicates are thought to have SN or red/blue supergiant origins and we do not have Mg-isotopic data to confirm such origins, nevertheless, we discuss the possibility of a SN origin here based on available thermodynamic model predictions. Equilibrium thermodynamic models of dust condensation specific to SNe predict the orthopyroxene solid solution to condense between 1090 and 1548 K in a 15 to 25 M☉ SN (Fedkin et al., 2010). If MIL 7a1-1 o1 has SN origins,
nanocrystalline pyroxene grains likely condensed in a stepwise manner as temperatures cooled in the ejecta and mechanically accreted to form the assemblage we observe. Following parent body accretion, MIL 7a1-1 o1 was subsequently aqueously altered as discussed in detail below.

4.4.3.2 Stellar Origins of Grains Preserved in Fe-rich Matrix Regions

4.4.3.2.1 MIL 10a2-6 o1 (Group 4-Supernova)

Equilibrium models of dust condensation in supernovae predict Ca-bearing pyroxene to condense between 1082 and 1560 K (Fedkin et al., 2010). These condensation temperatures indicate that Ca-bearing pyroxene is a predicted condensate in the H envelope and the He/N and O-rich SN zones. As with MIL 2a7-25 o1, if we compare the O-isotopic composition of MIL 10a2-6 o1 with the estimated O-isotopic compositions of different SN zones in Haenecour et al. (2013), MIL 10a2-6 o1 is consistent with contributions mainly from the H envelope and the He/N zone, with little contribution from the O-rich zones. Therefore, given that Ca-bearing pyroxenes are not predicted in the He/C zone, the condensation temperatures (1082 K to 1163 K) for the outermost H envelope and the He/N zone are most probable in the case of MIL 10a2-6 o1. Kinetic models of supernovae do not consider Ca-bearing pyroxenes but predict that Mg-silicates condense between 1400 and 1500 K and also around 1100 K (Nozawa et al., 2003; Todini & Ferrara, 2001). As mentioned above, polycrystalline and amorphous presolar grains were previously identified and are thought to suggest either nonequilibrium or multistep condensation processes (Nguyen et al., 2010; Seifert et al., 2022c; Vollmer et al., 2009; Zega et al., 2020). We note that three other TEM studies on SN pyroxene grains were reported in the literature. The first of these grains is a single crystal of nearly stoichiometric orthopyroxene that contains an embedded nonstoichiometric
Fe-sulfide (Seifert et al., 2022c). The second grain is a stoichiometric enstatite, which likely condensed first as a crystalline grain before being subsequently amorphized (Nguyen et al., 2016). The third grain is also amorphous, but contains a nonstoichiometric, high-Ca pyroxene composition (Nguyen et al., 2016). Given that MIL 10a2-6 o1 is a nearly stoichiometric pyroxene, we hypothesize that as temperatures cooled in the host supernova ejecta, nanocrystalline pyroxene grains condensed to form the assemblage we observe. That MIL 10a2-6 o1 contains an Fe-rich composition at its edges suggests that it was altered following its formation as discussed above.

4.4.3.2.2 MIL 10b2-5 o1 (Group 1-AGB/RGB)

Comparison of the O-isotopic composition of MIL 10b2-5 o1 with nucleosynthetic models of stellar evolution suggest origins in a close-to-solar metallicity AGB/RGB star of approximately 1.35 \( M_\odot \) (Boothroyd & Sackmann, 1999; Boothroyd et al., 1994). The orthopyroxene solid solution is predicted to condense from a gas of solar composition at 1366 K and 1190 K between total pressures of \( 10^{-3} \) and \( 10^{-6} \) bar, respectively (Ebel & Grossman, 2000). MIL 10b2-5 o1 conforms to pyroxene both structurally and compositionally, and we hypothesize that nanocrystalline pyroxene grains condensed through equilibrium processes and mechanically accreted to form the assemblage we observe. The Fe-rich rim surrounding MIL 10b2-5 o1 is indicative of parent-body alteration, which is further explored in the above discussion sections.

As noted above in the discussion of MIL 7a1-1 o1, recent Mg-isotopic work suggests that a fraction of Group 1 grains thought to originate in AGB/RGB stars could have origins in the ejecta of SNe (Hoppe et al., 2021; Leitner & Hoppe, 2019; Verdier-Paoletti et al., 2019). We do not have Mg-isotopic data to confirm such origins, but we discuss the possibility here. The orthopyroxene
solid solution is predicted to condense via equilibrium processes between 1548 and 1090 K in a 15 to 25 M☉ SN (Fedkin et al., 2010). If MIL 10b2-5 o1 has origins in the ejecta of a SN, nanocrystalline pyroxene grains likely condensed in a stepwise manner before being mechanically accreted together. Following parent body accretion, MIL 10b2-5 o1 was subsequently altered as discussed above.

4.4.4 Astronomical Observations and Presolar Silicate Grains

Silicates are a key dust component in circumstellar envelopes, the ISM, and the ejecta of SNe. Infrared (IR) observations of SN ejecta indicate abundant amorphous silicates (e.g., Arendt et al. 1999; Rho et al. 2008, 2009). Specifically, observations of Cassiopeia A and 1E0102-72.3 SN remnants indicate the presence of Mg-silicates (Arendt et al. 2014; Rho et al. 2008, 2009). In circumstellar environments, astronomical observations suggest that a significant fraction of silicates (>90%) are amorphous with Fe-bearing olivine compositions (Molster & Kemper 2005; Speck et al. 2000; Tielens et al. 1998). Alternatively, there are also stellar sources that are dominated (~97%) by crystalline silicates (Jiang et al. 2013). Of the silicates that are crystalline, both olivine and pyroxene grains are observed, with largely Mg-rich endmember compositions (Molster et al. 2002a, 2002b). However, crystalline enstatite (MgSiO3) grains account for more than two-thirds of crystalline silicate dust (Jiang et al. 2013). The width of spectral peaks was also suggested to provide information on crystallinity, i.e., single-crystal silicate grains without defects have much sharper peaks in IR spectra compared to grains with defects that are likely polycrystalline (Molster et al., 2002). These observations suggest that single crystal grains are produced around evolved stars, where gas temperatures cool slowly as dust grains condense.
Alternatively, polycrystalline assemblages could be produced around young stars, with crystalline silicates forming at the inner edge of the accretion disk where they experience partial melting, rapid cooling, and recrystallize to include defects (Molster et al. 2002).

In comparison, presolar silicate grains have been analyzed in the laboratory for their detailed structure and chemistry. Such measurements reveal a range of structures including amorphous grains, single crystals, and polycrystalline assemblages (Messenger et al. 2003, 2005; Floss et al. 2006; Vollmer et al. 2007, 2009, 2013; Nguyen et al. 2007, 2010, 2014, 2016; Busemann et al. 2009; Floss & Stadermann 2009a; Zega et al. 2020; Keller & Messenger 2011; Stroud et al., 2014; Takigawa et al. 2014; Nittler et al. 2020, Sanghani et al. 2022; Singerling et al. 2022; Seifert et al. 2022). Presolar silicates are also compositionally variable including olivine, pyroxene, and phases intermediate between the two. Many presolar silicate grains have Fe-rich compositions inconsistent with astronomical observations that suggest mainly Mg-rich endmember compositions. In pristine chondrites with minimal evidence of secondary alteration, the Fe-rich nature of some grains is thought to be primary in origin, suggesting that Fe-rich silicates are more abundant than previously suggested by astronomical observations. Alternatively, in other grains from less pristine chondrites, the Fe enrichment is thought to be the result of secondary processing such as aqueous alteration and thermal metamorphism (e.g., Floss & Stadermann 2012), as is the case for the grains in this study. A survey of the literature cited above suggests that of the crystalline silicates analyzed using TEM, olivine compositions appear to be more abundant than pyroxene. However, as noted above, astronomical observations indicate a dominance of crystalline pyroxene over olivine in circumstellar environments. We note that this is likely a sampling bias, as only a small fraction (<100 grains) of all identified presolar silicates have been
analyzed using TEM. Further detailed studies are necessary to better understand the diverse structures and chemistries present in presolar silicates, especially across chondrite groups.

### 4.5 Conclusions

This work reports detailed chemical and microstructural analyses of four presolar silicate grains from the uniquely altered MIL 07687 chondrite. Two grains were extracted from the Fe-rich altered matrix; two others were extracted from the Fe-poor relatively unaltered matrix. The O-isotopic compositions of two grains are consistent with origins in the ejecta of type-II core-collapse SNe and two grains are consistent with origins in the circumstellar envelopes of AGB/RGB stars. All grains in this study are polycrystalline and likely formed through multistep processes. The grains from the Fe-poor matrix regions include a polycrystalline assemblage with a composition consistent with a mixture of olivine and pyroxene and a polycrystalline pyroxene that contains an Fe-rich rim. The grains from the Fe-rich matrix regions include two polycrystalline pyroxene grains, one of which is Ca-bearing, and both of which contain Fe-rich rims. The Fe-rich rims that surround three of the four grains in this study are consistent with parent-body aqueous alteration processes, which is supported by abundant ferrihydrite observed in the matrix of the FIB sections. The analysis of presolar silicates in the MIL 07687 chondrite provides a view of aqueous alteration in-progress. Despite clear interaction with a fluid on the parent-body, all grains retained an isotopically anomalous composition, demonstrating that presolar silicates can withstand mild aqueous alteration.
4.6 Acknowledgements

The research completed here was supported by NASA grant 80NSSC19K0509. We also acknowledge NASA grants NNX12AL47G, NNX15AJ22G, and National Science Foundation grant 1531243 for funding instrumentation in the Kuiper Materials Imaging and Characterization Facility at LPL. We thank Krysten Villalon and Larry Nittler for constructive reviews that greatly improved the manuscript.
CHAPTER 5. AN IN SITU STUDY OF PRESOLAR GRAINS AND THE FINE-GRAINED MATRICES OF THE METEORITE HILLS 00526 AND QUEEN ALEXANDRA RANGE 97008 UNEQUILIBRATED ORDINARY CHONDRITES


Abstract

A fraction of presolar dust grains that formed around ancient stars and in stellar explosions survived the formation of the solar system and are preserved in meteorites. The ordinary and carbonaceous chondrites are thought to originate from distinct reservoirs in the inner and outer solar system, respectively, and can provide information on how the solar protoplanetary disk was seeded with presolar dust. To date, very few presolar grains from ordinary chondrites have been analyzed in situ. Here, we report on the in situ structure and chemistry of four presolar grains and the nature of alteration in the matrices of the Meteorite Hills (MET) 00526 L3.05 and Queen Alexandra Range (QUE) 97008 L3.05 ordinary chondrites. The presolar grains in MET 00526 include one single crystal olivine grain, and one olivine grain that contains both amorphous and polycrystalline material. The single crystal olivine likely has origins in the circumstellar envelopes of asymptotic giant branch (AGB) stars and the amorphous/polycrystalline olivine has an O-isotopic composition consistent with supernova origins. The presolar grains from QUE 97008 include one crystalline, stoichiometric olivine and one crystalline, stoichiometric pyroxene grain, both of which have O-isotopic compositions consistent with origins in the circumstellar envelopes.
of low-mass AGB/RGB stars. The olivine grains have Fe-rich compositions indicating Fe-
diffusion into the silicates as a result of secondary processing. The matrices of both unequilibrated
ordinary chondrites (UOCs) are mineralogically diverse and contain evidence of both altered and
unaltered material. Several FIB sections contain Ni-rich sulfides, abundant Fe-rich olivine, and
Fe-Mg zoning in matrix silicates, all of which are consistent with hydrothermal processing. The
Fe-rich olivine grains are the dominant alteration phase in both UOCs and likely replaced primary
amorphous silicates in the presence of an Fe-rich fluid during hydrothermal alteration on the parent
asteroid.

5.1 Introduction

Presolar grains are particles of dust that formed in the circumstellar envelopes of ancient
stars and in stellar explosions such as novae and supernovae. These grains seeded the early solar
protoplanetary disk and are preserved in small abundances (ppm) in a variety of planetary materials
including meteorites, Antarctic micrometeorites, interplanetary dust particles, and cometary dust
returned from the Stardust mission. Presolar grains were identified in a variety of chondrite groups,
with the largest abundance to date reported in carbonaceous chondrites (e.g., Floss and Haenecour,
2016c; Nittler and Ciesla, 2016). In comparison, few studies have focused on searching for and
analyzing presolar grains in ordinary chondrites but those that are available reveal diverse
abundances of C- and O-anomalous presolar grains.

Presolar grain abundances in ordinary chondrites, were, until recently, significantly lower
than those in carbonaceous chondrites. However, previous work by Floss & Haenecour (2016a)
reported the highest abundance of O-rich presolar grains in non-carbonaceous chondrites to date.
in the L3.05 Meteorite Hills (MET) 00526 unequilibrated ordinary chondrite (UOC). MET 00526 contains an overall abundance of O-rich presolar grains of 275 ± 50 ppm (Floss and Haenecour, 2016a). Such abundances make MET 00526 the first ordinary chondrite with a presolar grain abundance comparable to the highest abundances reported in carbonaceous chondrites, i.e., ~257 ppm in Dominion Range 08006 and ~236 ppm in Asuka 12169, (Haenecour et al., 2018; Nittler et al., 2021). However, recent work by Barosch et al. (2022a) found a much lower presolar grain abundance of ~151 ppm in MET 00526. Similarly, recent work on the Queen Alexandra Range (QUE) 97008 unequilibrated ordinary chondrite indicates a presolar grain abundance of 145 ± 30 ppm, comparable to many primitive carbonaceous chondrites (Floss and Haenecour, 2016b).

Isotopic work suggests that the carbonaceous and non-carbonaceous chondrites formed from distinct reservoirs in the outer and inner solar system, respectively (Kruijer et al., 2019; Nanne et al., 2019). The differences in abundances of presolar grains between chondrite groups could suggest that the inner and outer solar system did not receive the same inventory of presolar grains or that inner solar system materials do not preserve these grains very efficiently. The high abundance of presolar grains observed in MET 00526 and QUE 97008 suggests that the ordinary chondrites could have been seeded with comparable abundances of presolar grains compared to other chondrite groups. Similarly, the recent work of Barosch et al. (2022a) suggests a homogeneous distribution of presolar grains in the solar nebula. If all chondrite groups were seeded with comparable quantities of presolar grains, then secondary processing must play a key role in the observed abundances of presolar grains in ordinary chondrites. The detailed chemical and microstructural analysis of presolar grains in MET 00526 and QUE 97008, both of which are relatively primitive L chondrites (petrologic type 3.05), provides the opportunity to understand
how well such grains are preserved in inner solar system materials and their alteration histories, including the mechanisms by which ordinary chondrites are altered.

To date, only one study has focused on the in situ TEM analysis of presolar grains in unequilibrated ordinary chondrites (Singerling et al., 2022). That study found well-crystallized, stoichiometric presolar SiC and spinel grains and the majority of the presolar silicates in Semarkona are poorly crystallized with non-stoichiometric compositions (Singerling et al., 2022). Here we expand on this recent work with detailed analysis of presolar grains identified in the MET 00526 and QUE 97008 UOCs and their relationship to surrounding matrix material to understand their origins and preservation.

5.2 Samples and Methods

Polished thin sections of the MET 00526 and QUE 97008 UOCs obtained from the Meteorite Curation Facility at NASA Johnson Space Center were analyzed. The Cameca NanoSIMS 50 instrument at Washington University was used for C and O raster ion imaging measurements of multiple fine-grained matrix regions. Initial results are reported in Floss & Haenecour (2016a,b). That work identified 12 C-rich presolar grains and 32 O-rich presolar grains in MET 00526, giving overall abundances of $65 \pm 25$ ppm for SiC and $275 \pm 50$ ppm for O-rich presolar grains. In the QUE 97008 chondrite, 16 C-rich presolar grains and 23 O-rich presolar grains were identified, giving overall abundances of $125 \pm 30$ ppm for SiC and $145 \pm 30$ ppm for O-rich presolar grains. Details of the NanoSIMS analysis will be reported in a forthcoming manuscript. Both O-rich and C-rich presolar grains were selected in this study to investigate the origins, preservation, and alteration of grains from diverse stellar origins.
Electron-transparent sections (<100 nm in projected thickness) of five grains, three from MET 00526 and two from QUE 97008 and three matrix sections were prepared using the Thermo Fisher Scientific (formerly FEI) Helios G³ focused-ion beam scanning-electron microscope (FIB-SEM) located in the Kuiper Materials Imaging and Characterization Facility (KMICF) at the Lunar and Planetary Laboratory (LPL), University of Arizona. We followed previously described procedures for producing electron-transparent cross-sections of presolar grains, which is described in detail in the literature (Haenecour et al., 2019, 2020; Holzapfel et al., 2009; Leitner et al., 2012a, 2016b; Nguyen et al., 2007, 2016; Seifert et al., 2022; Stroud et al., 2004; Vollmer et al., 2009, 2007, 2013; Zega et al., 2007, 2011, 2014b, 2015, 2020).

Following preparation, the FIB sections were analyzed using the Hitachi HF5000 scanning TEM (S/TEM) in the KMICF at LPL. The HF5000 is equipped with a cold-field emission gun, a 3rd-order spherical-aberration corrector for STEM mode, bright-field (BF), dark-field (DF), and SE STEM detectors, and an Oxford Instruments X-Max N 100 TLE EDS system with dual 100 mm² windowless silicon-drift detectors providing a large solid angle (Ω = 2.0 sr). TEM images and electron-diffraction patterns were acquired with a Gatan OneView 4k × 4k pixel CMOS camera. The compositions of presolar grains and matrix material were obtained using energy dispersive X-ray spectroscopy (EDS) mapping followed by standardless quantification based on the Cliff-Lorimer method using theoretical k-factors. Information on long-range atomic order and crystal structure were obtained using selected-area electron-diffraction (SAED). The SAED patterns were measured using the Crystallographic Image Processing Software Package (Hovmoller, 1992) based on calibrated camera constants and also measured manually using Adobe Photoshop.
5.3 Results

5.3.1 TEM analysis of Matrix Sections

5.3.1.1 MET 00526 Matrix #1

STEM-HAADF imaging of the FIB section reveals a low porosity (<1%) matrix that is dominated by high-contrast grains that fill space between larger matrix grains and amorphous silicates (Fig. 5.1a-b). EDS mapping of the FIB section reveals that the majority of the matrix contains O, Si, Mg, and Fe (Fig. 5.1c). There are also localized regions that contain Cl, Ca, S, and Ni (Fig. 5.1c). A few larger grains at the left and right sides of the FIB section are enriched in Mg, Si, and O (Fig. 5c-e). In particular, one rounded grain on the right side of the FIB section appears zoned in HAADF images (Fig. 5.1e). EDS mapping confirms a chemically zoned grain, with a Mg-rich center and more Fe-rich exterior. One Fe-Ni metal grain is present on the left side of the FIB section (Fig. 5.1a). Several other grains in the matrix are consistent with Fe-sulfides and Fe-oxide (Fig. 5.1a). The high contrast grains that dominate the matrix have compositions consistent with Fe-rich olivine (cf., Fig. 5.1a, c). Measurement of SAED patterns obtained from the Mg-rich grains on the left and right side of the FIB section are consistent with pyroxene and forsterite, respectively (yellow boxes Fig 5.1a, 5.1f-g). Multiple domains with needle-like morphology are visible in the FIB section. One such region is highlighted in Figure 5.1h. EDS mapping of the region reveals spatial correlations among O, Fe, Cl, S, and Ni (Fig. 5.1i).
**Figure 5.1:** TEM data on MET 00526 matrix section #1. a) False-color layered EDS map of the whole FIB section with color scheme indicated at the top of the panel. b) HAADF-STEM image of entire FIB section. c) HAADF-STEM image of region denoted by yellow box on left side of FIB section in panel (a). d) HAADF-STEM image of region denoted by yellow box on right side of FIB section in panel (a). e) SAED pattern obtained from region labeled (e) in panel (c). f) SAED pattern obtained from region labeled (f) in panel (d). g) HAADF-STEM image of region denoted by yellow box in panel (d). h) False-color layered EDS map of region in panel (g) with color scheme indicated at the top of the panel.
5.3.1.2 QUE 97008 Matrix #1

STEM imaging of the FIB section reveals a compact matrix with many high-contrast grains distributed throughout (arrows, Fig. 5.2a). EDS mapping of the FIB section reveals that the matrix is dominated by O, Si, Mg, Al and Na and the high-contrast grains contain varied amounts of Fe, Ni, and S (Fig. 5.2b) with compositions consistent with pyrrhotite and pentlandite. SAED patterns obtained from the section indicate that the matrix contains amorphous silicate material (Fig. 5.2c). One large grain present on the bottom of the FIB section (yellow box, Fig. 5.2a, 2d) appears zoned in HAADF images and EDS mapping confirms such zoning with an Fe-rich composition at its right edge (Fig. 5.2e). A SAED pattern obtained from the grain is consistent with forsterite (Fig. 5.2f). EDS mapping of a circular grain (Fig. 5.2g) on the right side of the FIB section (right yellow box, Fig. 5.2a) reveals that it is enriched in C (Fig. 5.2h). We were not able to obtain an SAED pattern from the spherical grain as the section was not stable under the TEM beam, but its composition, shape, and size are consistent with a C-rich nanoglobule.
Figure 5.2: TEM data on QUE 97008 matrix section #1. a) HAADF-STEM image of the entire FIB section. b) False-color layered EDS map of the whole FIB section with color scheme noted at the top of the panel. c) SAED pattern obtained from region labeled (c) in panel (a). d) HAADF-STEM image of the region denoted by yellow box at the bottom of the FIB section in panel (a). e) False-color layered EDS map of the region in panel (d) with color scheme at top of panel. f) SAED pattern obtained from region labeled (f) in panel (d). g) HAADF-STEM image of region denoted by yellow box on right side of FIB section in panel (a). h) False-color layered EDS map with color scheme noted at top of panel.
5.3.1.3 QUE 97008 Matrix #2

STEM imaging of the FIB section reveals a matrix with ~5% porosity. The right side of the FIB section contains amorphous silicate material mixed with crystalline Fe-rich olivine grains (Fig. 5.3a). A large (~2 μm × 2 μm) circular-shaped grain occurs on the left side of the FIB section (Fig. 5.3a). EDS mapping reveals that the large circular grain on the left side of the FIB section contains O, Si, and Mg, with localized Fe and Na enrichment on the left side (Fig. 5.3b-c). SAED patterns obtained from the large circular grain reveal that it contains an amorphous center (Fig. 5.3d) and also crystalline Fe-rich pyroxene (Fig. 5.3e), and crystalline Mg-rich pyroxene (Fig. 5.3f-g). EDS spectra were extracted from both the Mg-rich and Na-rich regions of the circular grain (labeled “1” and “2” in Fig 5.3a, respectively), the compositions of which are reported in Table 5.1. Standardless quantification of the EDS spectrum extracted from the Mg-rich region is consistent with a stoichiometric pyroxene with composition (Mg$_{1.84}$Fe$_{0.03}$Ca$_{0.05}$)Si$_{2.04}$O$_{6}$ (Table 5.1). The morphology, structure, and chemistry of the circular-shaped pyroxene are consistent with a microchondrule (e.g. Dobrică & Brearley, 2016).
Figure 5.3: TEM data on QUE 97008 matrix section #2. a) HAADF-STEM image of the entire FIB section. Regions labeled “1” and “2” indicate where EDS spectra were extracted from, the results of which are found in Table 5.1. b) Higher magnification HAADF-STEM image of large rounded grain on left side of FIB section. c) False-color layered EDS map of the rounded grain in panel (b) with color scheme noted at top of panel. d-g) SAED patterns obtained from regions labeled (d), (e), (f), (g) in panel (b), respectively.
Table 5.1 Compositions of microchondrules determined using EDS expressed in wt%.

<table>
<thead>
<tr>
<th>Section</th>
<th>Matrix #2 Spectrum 1</th>
<th>Matrix #2 Spectrum 2</th>
<th>QUE c4-4 01 Spectrum 1</th>
<th>QUE c4-4 01 Spectrum 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Pyroxene</td>
<td>Na-bearing</td>
<td>Silicate</td>
<td>Na-bearing</td>
</tr>
<tr>
<td>Structure</td>
<td>Crystalline</td>
<td>Amorphous</td>
<td>Amorphous</td>
<td>Crystalline</td>
</tr>
<tr>
<td>Wt %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>46.78</td>
<td>50.59</td>
<td>49.02</td>
<td>34.38</td>
</tr>
<tr>
<td>Mg</td>
<td>22.31</td>
<td>4.83</td>
<td>4.97</td>
<td>6.78</td>
</tr>
<tr>
<td>Fe</td>
<td>2.89</td>
<td>15.62</td>
<td>16.43</td>
<td>43.52</td>
</tr>
<tr>
<td>Si</td>
<td>27.14</td>
<td>18.25</td>
<td>20.90</td>
<td>15.32</td>
</tr>
<tr>
<td>Ca</td>
<td>0.89</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Al</td>
<td>n.d.</td>
<td>0.73</td>
<td>1.16</td>
<td>n.d.</td>
</tr>
<tr>
<td>Na</td>
<td>n.d.</td>
<td>9.98</td>
<td>7.52</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Stoichiometry: $(\text{Mg}_{1.88}\text{Fe}_{0.11}\text{Ca}_{0.05})\text{Si}_{1.98}\text{O}_6$ and $(\text{Mg}_{0.52}\text{Fe}_{1.45})\text{Si}_{1.02}\text{O}_4$.

All analyses normalized to 100%.

n.d. = not detected.

5.3.2 TEM Analysis of Presolar Grains

5.3.2.1 MET 3a2-12 o1

NanoSIMS analysis reveals MET 3a2-12 o1 contains enrichment in $^{18}$O relative to solar system values with $^{18}$O/$^{16}$O (x10$^{-3}$) = 2.21 ± 0.015 and $^{17}$O/$^{16}$O (x10$^{-4}$) = 3.69 ± 0.06 (Fig. 5.4a). The O-isotopic composition of MET 3a2-12 o1 places it in the Group 4 field of O-rich presolar grains as defined by Nittler et al. (1997, 2008).

STEM imaging of the FIB section reveals a fine-grained matrix (Fig. 5.5a). HAADF imaging shows higher contrast grains distributed throughout the FIB section that are separated by a fine-grained, lower contrast groundmass (Fig. 5.5a). STEM imaging (Fig. 5.5b) reveals that MET 3a2-12 o1 is a fine-grained domain below the Pt fiducial marker (yellow box labeled b in Fig. 5.5a).
5.5a). SAED patterns were obtained across the domain and indicate that the left side of MET 3a2-12 o1 is polycrystalline while the right side is amorphous (Fig. 5.5c-d). Measurements of such patterns are consistent with olivine. Unfortunately, the FIB section was lost before we could complete EDS mapping to determine the stoichiometry of MET 3a2-12 o1.

**Figure 5.4:** NanoSIMS δ¹⁸O, δ¹⁷O, δ¹³C isotopic maps for the presolar grains in MET 00526 (a-c) and QUE 97008 (d-e) reported here. Legend at right of images in units of per mil (%o). Delta notation denotes the deviation of an isotopic ratio of an element R from a standard [$\delta R = ((R_{measured}/R_{standard}) -1) \times 1000$], where R is the ratio of the heavy to light isotope. All maps are 10µm field of view.
**Figure 5.5:** TEM data on MET 3a2-12 o1. a) HAADF-STEM image of FIB section containing MET 3a2-12 o1, with yellow boxe indicating grain location. b) HAADF-STEM image of MET 3a2-12 o1, respectively with dashed lines indicating region of interest below the Pt fiducial marker. c-d) SAED patterns obtained from regions labeled (c) and (d) in panel (b).

### 5.3.2.2 MET 3a2-24 o1, c1

NanoSIMS analysis reveals that MET 3a2-24 o1 contains enrichment in $^{17}$O (Fig. 5.4b) and depletions in $^{18}$O relative to solar system values with $^{18}$O/$^{16}$O (x10$^{-3}$) = 0.786 ± 0.08 and $^{17}$O/$^{16}$O (x10$^{-4}$) = 9.45 ± 0.09, placing it in the Group 2 field of O-rich presolar grains as defined by Nittler et al. (1997, 2008). A second grain, MET 3a2-24 c1, was transected in the same FIB section and contains a C-isotopic composition of $^{12}$C/$^{13}$C = 103.19 ± 2.72 (Fig. 5.4c). However, we were not able to relocate MET 3a2-24 c1 in the FIB section, likely indicating that little material from the grain remained following the NanoSIMS analysis. We therefore discuss only the TEM results of MET 3a2-24 o1 and the surrounding matrix contained within the FIB section.

STEM imaging of the overall FIB section reveals a compact matrix that is dominated by fine-grained material and several large (~1-3 μm) grains (Fig. 5.6a, c-d). EDS mapping reveals
that the bulk of the matrix contains O, Si, and Al and localized areas of Mg and Ca enrichment (Fig. 5.6b). SAED patterns collected from three large (~1-3μm) matrix grains are consistent with single crystals of olivine (Fig. 5.6e-g). The olivine grains (indicated by yellow boxes in Fig. 5.6a) are chemically zoned, with Mg enrichment at the center of the grains and an Fe-rich composition at its edges (Fig. 5.6e-g). SAED patterns obtained across the FIB section reveal that the majority of the matrix is fine-grained and nanocrystalline (Fig. 5.6h-i). Fe is present throughout the matrix and is locally enriched in rims surrounding the larger matrix grains (Fig. 5.6b). Small (~50-150 nm) grains that contain Fe, Ni, and S are distributed throughout the matrix.

STEM imaging reveals that MET 3a2-24 o1 is a distinct oval-shaped grain below the Pt fiducial marker (Fig. 5.7a-b). HAADF imaging reveals a brighter contrast region at the top of the grain that is consistent with Pt from the fiducial marker placement. EDS mapping reveals that MET 3a2-24 o1 contains O, Si, Mg and Fe (Fig. 5.7c-f). Al is enriched outside the grain (Fig. 5.7g). Two Ni-bearing sulfides occur adjacent to MET 3a2-24 o1 (white arrows, Fig. 5.7g). A zone axis SAED pattern obtained from the grain reveals that MET 3a2-24 o1 is a single crystal of olivine (Fig. 5.7h). Standardless EDS quantification of an EDS spectrum extracted from MET 3a2-24 o1 indicates a composition of (Mg_{1.01}Fe_{0.99})SiO_4 (Table 5.2).
**Figure 5.6:** TEM data on the FIB section containing MET 3a2-24 o1 and MET 3a2-24 c1. a) HAADF-STEM image of whole FIB section. b) False-color layered EDS map of the whole FIB section with color scheme noted at the top of the panel. c) HAADF-STEM image of region denoted by yellow box on the left side of the FIB section. d) HAADF-STEM image of region denoted by yellow box in the middle of the FIB section. e-f) SAED patterns obtained from regions labeled € and (f) in panel (c). g) SAED pattern obtained from region labeled (g) in panel (d). SAED pattern obtained from region labeled (h) in panel (a).
Figure 5.7: TEM data on MET 3a2-24 o1. a-b) HAADF-STEM and BF-STEM images of MET 3a2-24 o1 below the Pt fiducial marker. c-i) False-color EDS maps for O, Si, Mg, Fe, Al, S, and Ni, respectively. j) SAED pattern obtained from region labeled (j) in panel (b).
Table 5.2 Grain compositions determined using EDS expressed in wt% oxide and cation count.

<table>
<thead>
<tr>
<th></th>
<th>MET 00526 Grain</th>
<th>QUE 97008 Matrix Grains</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Grain</strong></td>
<td>MET 3a2-24 o1</td>
<td>QUE b1-3 o1 Core</td>
</tr>
<tr>
<td><strong>Phase</strong></td>
<td>Olivine</td>
<td>Olivine</td>
</tr>
<tr>
<td><strong>Structure</strong></td>
<td>Crystalline</td>
<td>Crystalline</td>
</tr>
<tr>
<td><strong>O_{17}/O_{16} (x10^{-4})</strong></td>
<td>9.44 ± 0.09</td>
<td>7.26 ± 0.22</td>
</tr>
<tr>
<td><strong>O_{18}/O_{16} (x10^{-3})</strong></td>
<td>0.786 ±0.007</td>
<td>1.84 ± 0.033</td>
</tr>
<tr>
<td><strong>Oxide</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>23.76</td>
<td>17.24</td>
</tr>
<tr>
<td>FeO</td>
<td>41.28</td>
<td>37.01</td>
</tr>
<tr>
<td>SiO₂</td>
<td>34.95</td>
<td>36.25</td>
</tr>
<tr>
<td>CaO</td>
<td>n.d.</td>
<td>9.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td><strong>Cation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>1.01</td>
<td>0.74</td>
</tr>
<tr>
<td>Fe</td>
<td>0.99</td>
<td>0.89</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
<td>1.04</td>
</tr>
<tr>
<td>Ca</td>
<td>n.d.</td>
<td>0.29</td>
</tr>
<tr>
<td>Al</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>O</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

All analyses normalized to 100%.

n.d. = not detected.
5.3.2.3 QUE b1-3 o1

NanoSIMS analysis reveals that QUE b1-3 o1 contains enrichment in $^{17}\text{O}$ (Fig. 5.4d) relative to solar system values with $^{18}\text{O}/^{16}\text{O}$ $(x10^{-3}) = 1.84 \pm 0.03$ and $^{17}\text{O}/^{16}\text{O}$ $(x10^{-4}) = 7.26 \pm 0.22$, placing it in the Group 1 field of O-rich presolar grains as defined by Nittler et al. (1997, 2008).

STEM imaging of the FIB section reveals a matrix with ~6% porosity that contains several larger (500 nm to 1 μm) grains that are separated by fine-grained material (Fig. 5.8a). EDS mapping of the FIB section reveals that the matrix is dominated by O, Si, Mg and Fe, with localized regions of Al, Ca, S and Ni (Fig. 5.8b). Several regions of the FIB section contain crystalline Fe-rich silicates (Fig. 5.8a). One large grain in the upper right of the FIB section is consistent with a Ca-Al-Mg silicate and an Al-oxide is present near the center of the FIB section. We were not able to obtain SAED patterns from these regions, but their compositions are most consistent with a pyroxene and corundum, respectively. A SAED pattern obtained from one large grain at the bottom of the FIB section is consistent with a single crystal of pyroxene (Fig. 5.8c-d). The remaining matrix contains several olivine, pyroxene, and sulfide grains and small regions containing amorphous silicates (Fig. 5.8e).

STEM imaging below the Pt fiducial marker reveals that QUE b1-3 o1 is an elongated domain below the Pt fiducial marker (Fig. 5.9a-b). EDS mapping indicates that QUE b1-3 o1 contains O, Si, Mg, Fe and localized Ca enrichment (Fig. 5.9c-f). A zone axis SAED pattern obtained from QUE b1-3 o1 reveals that it is a single crystal of olivine (Fig. 5.9h). Standardless quantification of an EDS spectrum extracted from the Ca-enriched olivine portion of QUE b1-3
o1 is consistent with a composition of (Mg_{0.74}Fe_{0.89}Ca_{0.29})Si_{1.04}O_{4} while the surrounding “shell” has a composition of (Mg_{0.83}Fe_{1.02}Ca_{0.1})Si_{0.99}O_{4} (Table 5.2).

**Figure 5.8:** TEM data on the FIB section containing QUE b1-3 o1. a) HAADF-STEM image of the overall FIB section containing QUE b1-3 o1. b) False-color layered EDS map of the whole FIB section with color scheme denoted at top of the panel. c) HAADF-STEM image of the region denoted by yellow box in panel (a). d) SAED pattern obtained from region labeled (d) in panel (c). SAED pattern obtained from region labeled (e) in panel (a).
Figure 5.9: TEM data on QUE b1-3 o1. a-b) HAADF-STEM and BF-STEM images of QUE b1-3 o1 below the Pt fiducial marker. c-g) False-color EDS maps for O, Fe, Si, Ca, and Mg, respectively. h) SAED pattern obtained from region labeled (h) in panel (b).

5.3.2.4 QUE c4-4 o1

NanoSIMS analysis reveals that QUE c4-4 o1 contains enrichment in $^{17}$O (Fig. 5.4e) relative to solar system values with $^{18}$O/$^{16}$O ($\times 10^{-3}$) = 1.89 ± 0.02 and $^{17}$O/$^{16}$O ($\times 10^{-4}$) = 4.73 ± 0.15, placing it in the Group 1 field of O-rich presolar grains as defined by Nittler et al. (1997, 2008).

STEM imaging of the FIB section reveals a large (~2μm wide) rounded grain on the left side of the section (white box, Fig. 5.10a). EDS mapping reveals that Na is enriched in the center of rounded grain (Fig. 5.10b) and an SAED pattern obtained from the grain reveals that it is
Figure 5.10: TEM data on the FIB section containing QUE c4-4 o1. a) HAADF-STEM image of the overall FIB section containing QUE c4-4 o1. Regions labeled “1” and “2” indicate where EDS spectra were extracted from, the results of which are found in Table 5.1. b) False-color layered EDS map of the whole FIB section with color scheme noted at top of the panel. c) HAADF-STEM image of the large rounded grain on the left side of the FIB section indicated by dashed white box in panel (a). d) HAADF-STEM image of grain outlined by yellow box in panel (a). e-f) SAED patterns obtained from regions labeled (e) and (f) in panel (c). g) SAED pattern obtained from region labeled (g) in panel (d). h-i) SAED patterns obtained from regions labeled (h) and (i) in panel (a).
amorphous (Fig. 5.10e). An EDS spectrum was extracted from the Na-bearing glass (labeled “1” in Fig. 5.10a), the composition of which can be found in Table 5.2. The morphology, structure, and chemistry of the grain are consistent with a microchondrule (e.g. Dobrică & Brearley, 2016). The microchondrule contains a rim composed of high-contrast grains similar to those observed in other sections in this study in both MET 00526 and QUE 97008 (Figs. 5.1, 5.3, 5.6, 5.8, 5.10c). These high contrast grains are also present in the remainder of the FIB section filling space between other matrix grains (Fig. 5.10a). Measurement of SAED patterns obtained from the high contrast grains are consistent with an Fe-rich olivine (Fig. 5.10f). Standardless quantification of an EDS spectrum extracted from the Fe-rich olivine (labeled “2” in Fig. 5.10a) is consistent with a composition of (Mg0.52, Fe1.45) Si1.02 O4 (Table 5.1). Several Mg-rich olivine grains are present on the right side of the FIB section that contain Fe-enrichment at their edges (Fig. 5.10b, d). An SAED pattern obtained from one zoned silicate on the right side of the FIB section (yellow box) is consistent with a single crystal of olivine (Fig. 5.10g). A few Fe-metals are present at the top of the FIB section (Fig. 5.10b), one of which is consistent with BCC Fe (Fig. 5.10h) and one Fe-oxide is present above the microchondrule. The remaining material between large matrix grains is consistent with amorphous silicate material (Fig. 5.10i).

STEM imaging reveals that QUE c4-4 o1 is an elongated domain below the Pt fiducial marker (Fig. 5.11 a-b). EDS mapping reveals that QUE c4-4 o1 contains O, Si, Mg, and Fe (Fig. 5.11 c-f). Several Ni-rich sulfides are present on the bottom right side of QUE c4-4 o1 (Fig. 5.11g). Measurement of a zone-axis SAED pattern indicates that QUE c4-4 o1 is a single crystal of pyroxene (Fig. 5.11h). Standardless quantification of an EDS spectrum extracted from QUE c4-4 o1 is consistent with a composition of (Mg0.76Fe1.14Al0.16)Si1.93O6 (Table 5.2).
Figure 5.11: TEM data on QUE c4-4 o1. a-b) HAADF-STEM and BF-STEM images of QUE c4-4 o1 below the Pt fiducial marker. c-f) False-color EDS maps for O, Si, Mg, Fe, respectively. g) False-color layered EDS map with color scheme noted at top of panel. h) SAED pattern obtained from region labeled (h) in panel (b).

5.4 Discussion

5.4.1 Evidence for Alteration in the Matrices of MET 00526 and QUE 97008

The MET 00526 and QUE 97008 are both unequilibrated ordinary chondrites (UOCs) with petrologic type 3.05, indicating limited secondary alteration (Grossman and Brearley, 2005). Previous TEM characterization of MET 00526 and QUE 97008 by Dobrică & Brearley (2011) notes similarities in the matrices of both chondrites including Fe-rich olivines that crosscut an amorphous silicate groundmass, evidence for nanocrystalline phyllosilicate material, and the presence of taenite, tetrataenite, sulfides, and Ca phosphates. The main difference noted in
previous work between the two UOCs is the porosity, with QUE 97008 having a more porous matrix than MET 00526, but MET 00526 having a more fine-grained matrix than QUE 97008 (Dobrică and Brearley, 2011). The authors argue that the presence of the nanocrystalline phyllosilicates, Ca phosphates, and Ni-rich sulfides indicate that both chondrites experienced some degree of aqueous alteration, but the alteration was not extensive given that some unaltered primary amorphous material and Mg-rich silicates remain present.

The TEM characterization of the matrices MET 00526 and QUE 97008 reported here have similarities and differences to the results of Dobrică & Brearley (2011). Similar to Dobrică & Brearley (2011), the FIB sections extracted from MET 00526 have low porosity (<1%) and contain an amorphous-to-nanocrystalline silicate groundmass that is crosscut by Fe-rich olivines (Fig. 5.1). In contrast, the FIB sections extracted from QUE 97008 show a range of porosities, with FIB section Matrix #1 lacking porosity (Fig. 5.2), FIB section QUE c4-4 o1 containing minimal porosity (<1%, Fig. 5.10), and FIB sections of Matrix #2 and QUE b1-3 o1 containing the highest porosity (~5-6%, Figs. 5.3, 5.8). Compared to MET 00526, the QUE 97008 FIB sections contain larger (micron-sized) and more abundant matrix grains. A key difference observed in this study is the presence of two microchondrules in the QUE 97008 chondrite, in addition to a carbon-rich globule. The spherical, C-rich globule identified in Matrix #1 (Fig. 5.2g) is similar to C-globules previously reported in several carbonaceous chondrites (Aoki and Akai, 2008; De Gregorio et al., 2013; Garvie and Buseck, 2004; Nakamura-Messenger et al., 2006). The origins of C-rich globules are debated, with several environments proposed for their formation including the ISM, the outermost, cold regions of the solar protoplanetary disk, or on parent body asteroids (Cody et al., 2011; De Gregorio et al., 2010, 2013; Matrajt et al., 2012; Nakamura-Messenger et al., 2006). To
our knowledge, the C-rich globule reported here in QUE 97008 is the first to be observed in an ordinary chondrite to date and suggests that the UOCs can preserve organic C in the form of nanoglobules. One other notable difference is the lack of phyllosilicates in the matrices of both UOCs examined here. Though we did not observe phyllosilicates in any of the FIB sections in this study, we do observe needle-like morphologies (Fig. 5.1, 5.2) that could be indicative of hydrated material. Additionally, other evidence of alteration processes is present including Fe-rich olivine grains, chemical zoning in matrix grains, and Ni-rich sulfides.

5.4.2 Amorphous Silicates in Ordinary Chondrites

Amorphous silicates are present in several FIB sections in this study including MET 00526 Matrix #1 (Fig. 5.1). The chemistry and microstructures observed in QUE 97008 matrix #1 indicate likely primary, unaltered matrix materials because the section is dominated by amorphous silicates and abundant sulfides (Fig. 5.2). Amorphous silicates are key components of the most pristine planetary materials and are also abundant in circumstellar environments (Brearley, 1993; Chizmadia and Brearley, 2008; Dobrică and Brearley, 2020a; Greshake, 1997; Le Guillou and Brearley, 2014; Kemper et al., 2004). They are therefore believed to be primary, unaltered materials that are among the building blocks of the solar system (Bradley et al., 1999; Keller and Messenger, 2011). In addition to their occurrence in the carbonaceous chondrites, amorphous silicates are also reported in the ordinary chondrites (e.g., Alexander et al., 1989; Ashworth, 1977; Dobrică and Brearley, 2020a, b). Early studies (Ashworth, 1977) of Weston (H4) and Chainpur (LL3.4) revealed amorphous silicates in both UOCs, although the greater abundance of amorphous silicates in Chainpur, which has a lower petrologic type, indicated that amorphous silicates are
sensitive to secondary processing. Similar conclusions were made for the Bishunpur (LL3.15) and Semarkona (LL3.0) UOCs where smectite was an observed alteration product of amorphous silicates (Alexander et al., 1989). More recent characterization of the matrix of the Semarkona UOC reveal the widespread occurrence of unaltered amorphous silicates (Dobrică and Brearley, 2020a). That study found similarities between the amorphous silicates found in carbonaceous chondrites and UOCs, but also differences suggesting formation at different times and in different locations in the solar nebula (Dobrică and Brearley, 2020a).

Previous work demonstrates that amorphous silicates are affected by early-stage aqueous alteration to form phyllosilicates, and can also be thermally altered to form Fe-rich olivines, as is observed in recent work on MET 00526 (Chizmadia et al., 2006; Dobrică and Brearley, 2020b; Le Guillou et al., 2015; Nakamura-Messenger et al., 2011). The observation of amorphous silicates in both the MET 00526 and QUE 97008 UOCs in this study confirms that primary, pristine materials are preserved in UOCs. The diversity in the extent of alteration processes across the FIB sections, ranging from pristine amorphous material, to highly altered Fe-rich silicates suggests that alteration processes were localized and not widespread on the MET and QUE parent bodies. Heterogeneous parent body alteration processes that preserve relatively unaltered material is supported by the high abundance of presolar silicate grains in both UOCs.

5.4.3 Effects of Hydrothermal Alteration on UOC Matrices and Presolar Silicates

Fe-rich olivine is the dominant alteration phase observed across FIB sections in this study. These Fe-rich olivine grains crosscut amorphous silicates and surround Mg-rich matrix grains. Fe-rich silicates are not predicted to condense via equilibrium processes (Lodders, 2003) and therefore
could have formed through nonequilibrium processes or as a result of secondary processing. Given that we observe other evidence for secondary alteration including chemical zoning of several matrix olivine grains and Ni-rich sulfides suggests that secondary processing likely affected the matrices of both UOCs in this study. However, the degree of such alteration varies among FIB sections in both MET 00526 and QUE 97008 suggesting that alteration processes on their parent asteroids were heterogeneous.

Fe-rich silicates were observed in the matrices of several chondrite groups (UOCs, CO, CV, CK), especially in chondrites of higher (>3.1) petrologic types (Brearley and Krot, 2013a; Dobrică and Brearley, 2011, 2014, 2020b; Doyle et al., 2015; Krot et al., 2004, 2011). Several previous studies have suggested that Fe-rich olivine grains in the matrices of chondrites result from secondary processes such as hydrothermal alteration or fluid-assisted metamorphism on the asteroid parent body (Dobrică and Brearley, 2020b; Doyle et al., 2015; Krot et al., 2004; Zolotov et al., 2006). The two processes can be differentiated as follows: hydrothermal alteration involves the replacement of pre-existing phases by hydrous phases, while fluid-assisted metamorphism combines metamorphic (e.g., recrystallization) and fluid (dissolution and/or growth of new phases) processes, which can result in anhydrous phases (Brearley and Krot, 2013a). Of relevance to this study are previous observations of Fe-rich olivine in ordinary chondrites. Several previous studies reported minor occurrences of Fe-rich olivines in the UOC Semarkona (LL3.0) which was aqueously altered but not thermally metamorphosed (Alexander et al., 1989; Dobrică and Brearley, 2016; Hutchison et al., 1987). In comparison, the Bishunpur UOC (LL3.15) contains more widespread, fine-grained Fe-rich olivine because it has experienced aqueous alteration and more extensive thermal metamorphism than Semarkona (Alexander et al., 1989).
The formation of Fe-rich olivine appears to be closely linked with thermal metamorphism in the presence of a fluid, which is supported by the observations of Fe-rich olivines reported here for MET 00526 and QUE 97008 and also in previous work by Dobrică et al. (2020b). Recent work by Dobrică & Brearley (2020b) proposed a number of potential formation mechanisms for Fe-rich olivines as a result of hydrothermal alteration, including the replacement of amorphous silicates, precipitation from an SiO-rich fluid, or replacement of phyllosilicates. We do not observe any phyllosilicates in the FIB sections in this study and therefore the replacement of phyllosilicates by Fe-rich olivines is unlikely. The authors note that Fe-rich olivines can form as a result of the interaction between an Fe-rich fluid (Fe_{aq}) and amorphous silicates (SiO_{solid}) in the matrix. Recent hydrothermal alteration experiments support this possibility as Fe-rich olivines were produced using Fe-rich amorphous silicate and Fe powder as the starting materials (Dobrică et al., 2018). Alternatively, Fe-rich olivines can also form through precipitation from an SiO-rich fluid (SiO_{aq}) in the presence of an Fe-rich fluid (Fe_{aq}) (Dobrică and Brearley, 2020b). The Si/Fe ratio dictates whether Fe-rich olivine or phyllosilicates will be produced, with low Si/Fe ratios resulting in the formation of Fe-rich olivine and high Si/Fe ratios resulting in the formation of phyllosilicates (Dobrică and Brearley, 2020b). In the present study, given that we do not observe phyllosilicates, Si/Fe ratios must have remained low, resulting in the widespread formation of Fe-rich olivines in the FIB sections reported here. The microstructures in several FIB sections (particularly Figs. 5.1, 5.3, 5.10) support the idea that amorphous silicates were replaced by Fe-rich olivine grains, though precipitation from an SiO-rich fluid cannot be ruled out.

Fe-Mg chemical zoning in several Mg-rich silicates across both UOCs in this study is also consistent with secondary processing. Such zoning indicates Fe-diffusion into originally Mg-rich
grains, likely from an Fe-rich hydrothermal fluid as mentioned above. Dobrică et al. (2020b) reported similar chemical zoning in MET 00526 (L3.05), which they classified as Fe-rich olivine overgrowths consistent with secondary processing. In addition to the Fe-Mg zoning of several larger matrix grains, the presolar silicates in this study are notably Fe-rich. Fe-rich presolar silicate grains were reported in previous studies from both carbonaceous and ordinary chondrites (Bose et al., 2010; Floss and Stadermann, 2009a; Nguyen et al., 2007, 2010, 2016; Ong and Floss, 2015; Vollmer et al., 2009; Seifert et al. 2022c, 2023). Observations of crystalline Fe-rich presolar silicates in planetary materials are inconsistent with astronomical observations that suggest abundant Mg-rich silicates in circumstellar environments (Kemper et al., 2004; Molster et al., 2002a, 2002b). Similarly, crystalline Fe-rich silicates are inconsistent with equilibrium thermodynamic model predictions (Ebel and Grossman, 2000; Lodders, 2003). Though Fe-rich amorphous silicates can be formed through nonequilibrium condensation processes (Ferrarotti and Gail, 2001; Gail and Sedlmayr, 1999). The origins of crystalline Fe-rich presolar silicates are largely attributed to nebular or parent body processing, however, in the most pristine chondrites, crystalline Fe-rich presolar silicates could be primary in origin (Bose et al., 2010; Floss and Stadermann, 2009a; Nguyen et al., 2007, 2010, 2016; Ong and Floss, 2015; Vollmer et al., 2009; Seifert et al. 2022c, 2023). In the present study, evidence for hydrothermal processing is observed in the FIB sections containing presolar silicates MET 3a2-24 o1, QUE b1-3 o1, and QUE c4-4 o1 as discussed above and all three grains have crystalline rather than amorphous structures. Therefore, the Fe-rich nature of these three presolar silicate grains is likely the result of secondary hydrothermal alteration on the parent body asteroid.
5.4.4 Microchondrules in QUE 97008

Microchondrules are found in fine-grained chondrule rims and the fine-grained matrix of UOCs and CCs. Several different types of microchondrules were documented in the literature including low-FeO cryptocrystalline microchondrules consisting of low-Ca pyroxene, and high-FeO microchondrules consisting of fayalitic olivine (Krot et al. 1996). Recent work identified two additional types of microchondrules in the MET 00526 and Semarkona UOCs, denoted as porous and nonporous (Dobrică and Brearley, 2016). The porous microchondrules generally contain irregular-shaped pores and consist of glassy silicate material that contains appreciable amounts of Na and Al (Dobrică and Brearley, 2016; Dobrică et al., 2019). Alternatively, the nonporous microchondrules are largely crystalline, with low-Ca pyroxene being the dominant phase, though some small Mg-rich olivine grains were observed within low-Ca pyroxene microchondrules in Semarkona (Dobrică and Brearley, 2016).

Early work suggested multiple mechanisms for microchondrule formation including impact splash formation, nebular droplet disruption, and nebular sorting by size and type (Rubin and Krot, 1996). Krot et al. (1997) proposed that microchondrules could have formed during a flash heating event, where the pyroxene-rich chondrule exteriors and FeO-rich matrix materials melted. However, more recent work suggests that microchondrules formed from materials splattered from completely or partially molten chondrules during stochastic collisions, as evidenced by the compositions of microchondrules and silicate protuberances in association with chondrules (Dobrică and Brearley, 2016). The nonporous microchondrules are compositionally similar to type I chondrules, suggesting they could have formed as a result of splashing of molten
type I chondrule material, while the porous microchondrules could originate from the melting of a fine-grained matrix-like precursor (Dobrică and Brearley, 2016).

To our knowledge, no TEM characterization of microchondrules in QUE 97008 are available in the literature. The microchondrule present in QUE 97008 matrix #2 is consistent with the chemical composition and structure of nonporous microchondrules, as it is largely crystalline and is composed of a low-Ca pyroxene. The nonporous microchondrule retains its spherical shape and has minor evidence of alteration in the form of Fe-rich pyroxene grains. In comparison, the microchondrule in the FIB section containing the presolar silicate QUE c4-4 o1 is significantly altered and is consistent with a porous microchondrule as it is a glassy silicate that contains small pores. However, such pores do no permeate through the thickness of the FIB section, resembling a porous microchondrule reported in Semarkona (Dobrică et al., 2019). The variability of Na content in microchondrules suggests that Na is a mobile element during aqueous alteration processes, where the concentration of Na increases with the degree of aqueous alteration (Dobrică et al., 2019). However, even though the porous microchondrule in this study appears more extensively altered than the nonporous microchondrule, the Na content at its center is ~2.5 wt% less than that measured in the nonporous microchondrule suggesting varied amounts of Na exchange with the altering fluid.

5.4.5 Stellar and Thermodynamic Origins

The O-isotopic compositions of O-rich presolar grains are reproducible with nucleosynthetic models of stellar evolution (Choi et al., 1998; Nguyen and Messenger, 2014; Nittler et al., 1997; Nittler et al., 2008). Comparison of the isotopic compositions of presolar grains
with such models can provide information on the type, mass, and metallicity of the progenitor star from which the presolar grains originate (Boothroyd and Sackmann, 1999; Boothroyd et al., 1994; Leitner and Hoppe, 2019a; Lugaro et al., 2017; Nittler et al., 1997, 2008; Nollett et al., 2003).

In addition to the information gained from the isotopic compositions of O-rich presolar grains, the structure and chemical composition of such grains provides a snapshot of the thermodynamic landscape under which they formed. The crystal structures and chemical compositions of presolar grains can be compared with thermodynamic model predictions available in the literature to infer the pressure and temperature conditions under which they formed (Nguyen et al., 2007, 2010, 2016; Seifert et al., 2022; Vollmer et al., 2007, 2009, 2013; Zega et al., 2011, 2014a, 2015, 2020). Equilibrium thermodynamic models predict at what temperature mineral phases will condense from a gas, typically defined as solar composition, given an assumed set of total pressures. Such models also exist for dust condensation specific to supernovae environments. Comparison of presolar grain data with thermodynamic model predictions can therefore provide first-order constraints on the pressure and temperature conditions under which these grains form in their host environments.

5.4.5.1 RGB/AGB Origins

Comparison of the O-isotopic composition of MET 3a2-24 o1 with nucleosynthetic model predictions indicates origins in an AGB star of approximately 1.5 M☉ (Boothroyd and Sackmann, 1999; Boothroyd et al., 1994). The O-isotopic compositions of QUE b1-3 o1 and QUE c4-4 o1 are consistent with origins in the circumstellar envelopes of AGB/RGB stars of approximately 1.5 M☉ and 1.2 M☉, respectively, with a close-to-solar metallicities (Boothroyd and Sackmann, 1999;
Boothroyd et al., 1994). The stoichiometric olivine and orthopyroxene compositions and crystalline structures of MET 3a2-24 o1 and QUE c4-4 o1, respectively, are consistent with equilibrium condensation. Similarly, the chemistry and microstructure of QUE b1-3 o1 is consistent with materials sequentially condensing from a gas of solar composition, with the Ca-rich olivine “core” condensing first, followed by the surrounding Fe-Mg-rich olivine “shell”. Equilibrium thermodynamic models predict the olivine solid solution to condense from a gas of solar composition at 1444 K and 1240 K, assuming total pressures of $10^{-3}$ and $10^{-6}$ bar, respectively (Ebel and Grossman, 2000). The orthopyroxene solid solution is predicted to condense via equilibrium processes at 1366 K and 1190 K, assuming total pressures of $10^{-3}$ and $10^{-6}$ bar, respectively (Ebel and Grossman, 2000). We note, however, that Fe-rich compositions of MET 3a2-24 o1, QUE b1-3 o1, and QUE c4-4 o1 are likely the result of secondary processing, rather than being primary in origin. It is therefore likely that MET 3a2-24 o1, QUE b1-3 o1, and QUE c4-4 o1 condensed via equilibrium processes before being hydrothermally altered on its parent body asteroid.

Recent Mg-isotopic studies have suggested that some Group 1 and Group 2 presolar grains could instead originate in supernovae or in the stellar winds of red/blue supergiants (Hoppe et al., 2021; Leitner and Hoppe, 2019b; Verdier-Paoletti et al., 2019). We do not have Mg-isotopic data for any grains in this study to confirm possible supernova origins for MET 3a2-24 o1, QUE b1-3 o1, and QUE c4-4 o1. Regardless, equilibrium models of dust condensation in the ejecta of supernovae predict the olivine and orthopyroxene solid solutions to condense between 1063 and 1575 K and between 1090 and 1548 K in 15-25 M☉ supernovae, respectively (Fedkin et al., 2010). If QUE b1-3 o1 were to have supernova origins, the Ca-rich olivine core and Fe-Mg-rich olivine
shell likely condensed sequentially. Following parent body accretion, MET 3a2-24 o1, QUE b1-3 o1, and QUE c4-4 o1 likely obtained their high Fe-content as a result of secondary processing.

5.4.5.2 Supernova Origins

MET 3a2-12 o1 consists of both amorphous and polycrystalline olivine, making it difficult to constrain its thermodynamic origins. The O-isotopic composition of MET 3a2-12 o1 is consistent with origins in the ejecta of a type-II core-collapse supernova. While we were not able to obtain EDS data on this grain, we note that the combined amorphous and polycrystalline assemblage suggests a nonequilibrium formation history. Such origins are consistent with previous work on polycrystalline and amorphous presolar silicate that suggest either a nonequilibrium or multistep condensation process (Holzapfel et al., 2009; Nguyen et al., 2010; Seifert et al., 2022; Zega et al., 2020). Nonequilibrium models of dust condensation in the ejecta of supernovae are available in the literature and predict olivine to condense at a range of temperatures. For example, Nozawa et al. (2003) predicted the phases that condense in the ejecta of both unmixed supernova ejecta and mixed supernova ejecta, suggesting that Mg-silicates like olivine condense between 1400 and 1500 K. Alternatively, Todini & Ferrara (2001) predict Mg-silicates at lower temperatures, around 1100 K.

That MET 3a2-12 o1 contains both amorphous and polycrystalline structures suggests that the original presolar grain could have also been partially altered following its formation. As a result of secondary processing, originally amorphous grains could transition to polycrystalline assemblages. As noted by Nguyen et al. (2016), amorphous grains with nonstoichiometric compositions could result in the formation of a polycrystalline assemblage. While we were not
able to obtain EDS data on this grain, precluding determination of its stoichiometry, a partial transition from amorphous to polycrystalline olivine due to secondary alteration processes cannot be ruled out.

5.4.6 Presolar Grains in Ordinary Chondrites

Detailed, in situ TEM analyses of presolar grains preserved in ordinary chondrites are limited, with only one other study to date focused on such an effort (Singerling et al., 2022). That study found crystalline and stoichiometric oxide and SiC grains, along with several silicates with weakly nanocrystalline structures and nonstoichiometric compositions. Such results are consistent with previous TEM studies of presolar grains from carbonaceous chondrites and interplanetary dust particles. In contrast, the silicate grains in this study differ from previous work in that they are all crystalline to some degree, with three well-crystallized grains and one grain that contains both amorphous and polycrystalline material. Similar to the results reported in Singerling et al. (2022), the presolar silicates reported here also contain Fe-rich compositions that are generally not predicted through equilibrium thermodynamic models. Previous TEM characterization of presolar silicate grains in carbonaceous chondrites have documented Fe-rich silicates, some of which are thought to be primary in origin, and others thought to be the result of secondary processing (Floss and Stadermann, 2012; Seifert et al., 2022). However, the crystalline structures and nearly stoichiometric compositions of MET 3a2-24 o1, QUE b1-3 o1, and QUE c4-4 o1 reported on here make non-equilibrium origins unlikely and suggest that the Fe-rich compositions observed are the result of secondary processing. Though both MET 00526 and QUE 97008 are L3.05 UOCs indicating minimal secondary alteration, clear evidence of processing is present in FIB sections.
from both chondrites in this study. As noted above for the matrix of both UOCs in this study, we did not observe phyllosilicates, but do observe abundant Fe-rich silicates and Ni-rich sulfides. Three presolar silicates in this study have Fe-rich compositions, two of which also have adjacent Ni-rich sulfides indicative of aqueous alteration. We therefore suggest that the Fe-rich compositions observed in the presolar silicates in this study are the result of secondary hydrothermal alteration that resulted in Fe-diffusion into presolar silicates and matrix grains alike.

The results of this study indicate that presolar grains in MET 00526 and QUE 97008 are similar to those reported in other ordinary chondrites and contain a similar diversity in structure and chemistry compared to presolar grains in carbonaceous chondrites. Similarities in the structure and chemistry of presolar grains among chondrite groups suggests that despite originating from distinct reservoirs, the ordinary and carbonaceous chondrites inherited similar types of dust from diverse stellar origins.

5.5 Conclusions

We report on the TEM characterization of presolar grains and the matrices of two UOCs, MET 00526 and QUE 97008. Though both UOCs are petrologic type 3.05, evidence for alteration processes are observed in the FIB sections in this study. The primary alteration phase observed in both UOC matrices is Fe-rich olivine grains that likely resulted from hydrothermal alteration processes on their parent asteroids. Two microchondrules with evidence of alteration are also observed in the matrix of QUE 97008. The presolar grains in this study include four presolar silicates, all of which are crystalline to some degree. Three of the silicates are single crystals with Fe-rich compositions and have O-isotopic compositions consistent with origins in low-mass
AGB/RGB stars. The remaining silicate has an O-isotopic composition consistent with origins in the ejecta of a type-II supernova. The presolar silicates are Fe-rich, suggesting secondary processing following accretion on the parent body asteroid. To date, the presolar grains analyzed in UOCs have similar structures and chemistries to presolar grains in the carbonaceous chondrites, suggesting that both chondrite groups were seeded with similar types of dust. Given that so few grains from UOCs have been studied in situ for their detailed structure and chemistry, future work is still crucial to understanding how the presolar grain populations in UOCs compare to those in other planetary materials.

5.6 Acknowledgements

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CHAPTER 6. SUMMARY, IMPLICATIONS, AND FUTURE WORK

In this dissertation, presolar grains were analyzed using a coordinated analytical approach including NanoSIMS, FIB-SEM, and TEM. Such an approach allowed for isotopic analysis and detailed structural and chemical characterization on the same grain. The focus of this dissertation is presolar silicate grains, which are very small (submicron), therefore requiring the use of TEM to gain detailed nanometer scale information on the structure (SAED, HRTEM) and chemistry (EDS) of such grains. This dissertation is separated into three main components to address knowledge gaps in presolar grain research, each of which will be summarized below.

The first component of this work (Chapter 3) is focused on the detailed analysis of six presolar silicate grains preserved in one of the most pristine CO carbonaceous chondrites DOM 08006. This work was mainly focused on the analysis of presolar silicate grains from SNe to better understand the types of solids that form in these environments and how they compare to grains from other stellar origins. The first identification of a likely presolar Fe-sulfide embedded in a SN silicate grain was reported and the results of this work indicate that despite differences in CSEs of RGB/AGB stars and the ejecta of SNe, these distinct environments can form dust with comparable structures and compositions. In addition to the analysis of SN silicates, two AGB grains were also analyzed in this work. Most notable is a chemically zoned olivine grain that contains a Fe-rich rim, suggestive of secondary alteration. DOM 08006 is a CO3.0 chondrite and therefore, this rim is likely an indication of nebular processing of a clump of dust that was later accreted onto the DOM parent body asteroid.
The second component of this work is focused on the analysis of four presolar silicate grains in the uniquely altered MIL 07687 chondrite that contains regions of relatively altered and unaltered materials. This research focused on the analysis of grains from both matrix lithologies to understand the effects of secondary processing on presolar silicates and the mechanisms by which such alteration occurs. The dominant alteration phase in the FIB sections in this study is ferrihydrite, a poorly crystalline to amorphous Fe-oxide mineral that likely formed through the dissolution of matrix materials, resulting in free Fe$^{2+}$ that experienced oxidation and hydrolysis to form ferrihydrite. Fe that was not incorporated into ferrihydrite was mobile through the matrix, resulting in three of the four presolar grains in this work containing Fe-rich rims. However, such alteration was not extensive enough to replace primary presolar grain phases with secondary alteration phases. To get an idea of the likelihood of O-isotopic equilibration of the presolar silicate with the surrounding matrix, we estimated to timescale of O-diffusion, with some assumptions, and arrived at timescales exceeding the age of the solar system. Therefore, though presolar grains were affected by secondary alteration processes in this work, such alteration was not extensive enough to result in extensive isotopic exchange between the presolar silicates and the surrounding matrix. This work demonstrates that presolar silicate grains can withstand mild aqueous alteration while retaining at least some of their isotopically anomalous compositions.

The final component of this work is focused on analyzing presolar grains and the matrices of the unequilibrated ordinary chondrites (UOCs) MET 00526 and QUE 97008. The UOCs and carbonaceous chondrite are thought to originate from distinct reservoirs in the inner and outer solar system, respectively (Kruijer et al., 2019; Nanne et al., 2019). To date, only one other in situ TEM study focused on analyzing presolar grains in the UOCs is available in the literature (Singerling et
and so the work here focuses on increasing statistics on such grains and comparing them to presolar grains in other chondrite groups and IDPs. The matrices of these two UOCs contain a range of structure and chemistries, from relatively pristine amorphous silicates to heavily altered matrix, where the dominant alteration phase is Fe-rich olivine. These Fe-rich olivine grains are consistent with formation through hydrothermal processing where they likely replaced primary amorphous silicate phases or precipitated from an SiO-rich fluid. The presolar grains in this work differ from previous studies in that they are all crystalline, with four well-crystallized grains and one grain that contains both amorphous and polycrystalline material. The presolar silicates in this work are largely Fe-rich, crystalline, and have stoichiometric compositions, suggesting that their Fe-rich nature is the result of secondary processing. This work also reports the first TEM analysis of microchondrules in QUE 97008.

Presolar silicate grains make up a significant fraction of the material that is among the building blocks of the solar system. The work detailed in this dissertation not only increases statistics on these important building blocks, but contributes to understanding how such grains formed around their host stars, survived solar system formation, were preserved in asteroids, and how they are affected by secondary alteration processes in the solar nebula and on the parent body asteroid. However, based on a survey of literature to date, less than 10% of presolar silicates that have been identified have been studied for their detailed structure and chemistry. Therefore, more studies focused on the detailed analysis of presolar silicate grains are necessary in order to achieve a more complete understanding of their origins. Such detailed analyses are possible through the advanced electron microscopy techniques used to complete the work in this dissertation, including FIB-SEM for site-specific sample preparation and TEM for atomic-scale characterization of
presolar grains. These detailed analyses of presolar grains have the ability to drive future thermodynamic and nucleosynthetic modeling efforts to further constrain the origins of these grains.

However, constraining the origins of presolar grains in this dissertation and the work of others is limited by the availability of thermodynamic models. As mentioned in Chapter 2, equilibrium thermodynamic models come with several assumptions and limitations. Models available in the literature assume a closed system and only include a small subset of mineral phases that are observed in meteoritic samples. Additionally, models that consider nonequilibrium condensation are nearly non-existent in the literature. The detailed characterization of presolar grains have demonstrated that current thermodynamic models are not sufficient to explain the diversity in structure and chemistry observed to date. Circumstellar environments and the ejecta of supernovae are certainly dynamical environments that include transport and mixing of solids and gas and therefore should be treated as an open system. Additionally, a wider range of mineral species and solid solutions need to be considered in order to represent accurately the presolar grain record. Therefore, further development of thermodynamic models is necessary to constrain the origins of microstructures and crystal chemistries observed in presolar grains and meteorites as a whole.
**Figure S1:** NanoSIMS and FIB-SEM grain alignment and Pt fiducial marker placement for DOM-49 and DOM-50. To confirm the grain alignment from the ImageAlign software, the SE FIB-SEM image was made semi-transparent, scaled appropriately, and overlaid onto the SE NanoSIMS image. The SE NanoSIMS and FIB-SEM images were then overlaid onto the O-isotope maps to confirm that the grain alignments match the isotope anomaly. The same procedure was used for all subsequent grains. a-b) NanoSIMS $\delta^{18}O$ and $\delta^{17}O$ maps with DOM-49 and DOM-50 indicated by arrows. Legend at right of image in units of per mil ($\%$). c) Semi-transparent $\delta^{18}O$ and $\delta^{17}O$ maps showing the location of anomalous grains with overlay of the corresponding SE NanoSIMS image. d) NanoSIMS $\delta^{18}O$ and $\delta^{17}O$ maps with semi-transparent overlay of the SE FIB-SEM image confirming the correct alignment of DOM-49 and DOM-50. e) SE image with aligned anomalous regions DOM-49 and DOM-50 labeled and outlined in red. Dotted yellow line indicates FIB transect. f) SE image of Pt fiducial markers with DOM-49 and DOM-50 grain fiducials indicated.
by red arrows. Distances between fiducial markers labeled. g) SE image of protective C capping layer before FIB trenching and liftout. h) HAADF STEM image of FIB section containing DOM-49 and DOM-50. Distances between markers labeled and grain fiducials indicated by red arrows.
Figure S2: NanoSIMS and FIB-SEM grain alignment and Pt fiducial marker placement for DOM-22. A) NanoSIMS δ¹⁸O map of DOM-22, with legend at right of image in units of per mil (‰). B) δ¹⁸O map showing the location of the anomalous grain with semi-transparent overlay of the corresponding SE NanoSIMS image. c) NanoSIMS δ¹⁸O map with semi-transparent overlay of the SE FIB-SEM image confirming the correct alignment of DOM-22. D) SE FIB-SEM image with anomalous region outlined in red, dotted yellow line indicates FIB transect. e) SE image of Pt fiducial markers with the DOM-22 grain fiducial indicated by red arrow. Distances between fiducial markers labeled. F) SE image of protective C capping layer before FIB trenching and liftout. G) HAADF STEM image of the FIB section containing DOM-22 with distances between markers labeled and grain fiducial indicated by red arrow.
Figure S3: NanoSIMS and FIB-SEM grain alignment and Pt fiducial marker placement for DOM-35. A) NanoSIMS $\delta^{18}O$ map of DOM-35, with legend at right of image in units of per mil ($\permil$). B) $\delta^{18}O$ map showing the location of the anomalous grain with semi-transparent overlay of the corresponding SE NanoSIMS image. c) NanoSIMS $\delta^{18}O$ map with semi-transparent overlay of the SE FIB-SEM image confirming the correct alignment of DOM-35. D) SE FIB-SEM image with anomalous region outlined in blue, dotted yellow line indicates FIB transect. e) SE image of Pt fiducial markers with the DOM-35 grain fiducial indicated by red arrow. Distances between fiducial markers labeled. F) SE image of protective C capping layer before FIB trenching and liftout. G) HAADF STEM image of FIB section containing DOM-35 with distances between markers labeled and grain fiducial indicated by red arrow.
**Figure S4:** NanoSIMS and FIB-SEM grain alignment and Pt fiducial marker placement for DOM-39. 
A-b) NanoSIMS $\delta^{17}$O and $\delta^{18}$O maps of DOM-39, with legend at right of image in units of per mil ($\%$). 
C) $\delta^{18}$O map showing the location of the anomalous grain with semi-transparent overlay of the corresponding SE NanoSIMS image. 
D) NanoSIMS $\delta^{18}$O map with semi-transparent overlay of the SE FIB-SEM image confirming the correct alignment of DOM-39. 
E) SE image with aligned anomalous region outlined in red, dotted yellow line indicates FIB transect. 
F) SE image of Pt fiducial markers with the DOM-39 grain fiducial indicated by red arrow. Distances between fiducial markers labeled. 
G) SE image of protective C capping layer before FIB trenching and liftout. 
H) HAADF STEM image of the FIB section containing DOM-39 with distances between markers labeled and grain fiducial indicated by red arrow.
Figure S5: EDS data from the footprint region of DOM-39. (a) HAADF image of the footprint region in DOM-39 with rim indicated by arrows. (b) TEM image of oriented iron sulfide crystal at a 5.7° tilt about the sample rod axis (t_x) and 2.7° tilt normal to it (t_y). (c-h) False color EDS maps of footprint region in DOM-39 for Fe, O, Mg, Si, S, and Ni, respectively. (i-k) SAED patterns obtained from regions labeled (i), (j), and (k) in TEM image.
Figure S1: NanoSIMS $\delta^{18}$O and $\delta^{17}$O isotopic maps for the four presolar grains in MIL 07687 reported here. Legend at right of images in units of per mil ($\%$). Delta notation denotes the deviation of an isotopic ratio of an element R from a standard [$\delta R = ((R_{\text{measured}}/R_{\text{standard}}) - 1) \times 1000$], where R is the ratio of the heavy to light isotope. All maps are 10$\mu$m field of view.
APPENDIX C- LIST OF PUBLICATIONS

C.1 JOURNAL PUBLICATIONS


C.2 CONFERENCE ABSTRACTS


Supernova Orthopyroxene Grain in the CO Chondrite Dominion Range 08006. LPSC LI, abstract #2471.


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