Quantifying Temperatures in the Early Solar Nebula and on Parent Bodies Using Cation Ordering in Spinel from CAIs in Carbonaceous Chondrites

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Abstract

Understanding the early solar system requires studying early-formed materials. Calcium-Aluminium-Rich Inclusions (CAIs) are the oldest materials in the solar system. Spinel (MgAl$_2$O$_4$) is common in CAIs. Its cation distribution relates to formation, or most recent equilibration, temperature. This can be measured using $^{27}$Al Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectroscopy. Calibration curves can be used to calculate temperature.

Micro X-ray Diffraction identified spinel-containing CAIs in four of seven meteorites tested. $^{27}$Al MAS NMR and $^{27}$Al Triple Quantum (3Q) MAS NMR was acquired at 21.1 Tesla. Temperature estimates were calculated for each CAI. Allende ($\leq$273 K), NWA 2364 and NWA 6991 (~360-707 K) likely represent parent body processing. NWA 6603 (~1173-1675 K) likely represents nebular formation or processing.

This work demonstrates that this technique can be used to estimate nebular and parent body temperatures experienced by CAIs. This will help in understanding solar system formation and early planetary processes.

Keywords

Keywords: Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy (MAS NMR), Calcium-Aluminium-Rich Inclusions (CAIs), Nebular Temperature, Allende, NWA 2364, NWA 6991, NWA 6603, NWA 4502, NWA 7678, Tagish Lake C2
Co-Authorship Statement

This thesis is broken into eight chapters, five of which are manuscripts. This dissertation was written and researched by Victoria Houde. Dr. R. L. Flemming provided guidance, suggestions and revisions as the supervisor of this thesis. Dr. Flemming is second author on Chapters 3, 4, 5, 6, and 7. V. Terskikh is third author on Chapters 3, 4, and 5 for collecting $^{27}$Al MAS NMR data. He also provided assistance in initial processing and interpretation of NMR data. Dr. A. Bouvier is fourth author on Chapter 4 for providing separated samples of NWA 2364 and NWA 6991. She also provided guidance on sample preparation and selection.
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Chapter 1

1 Introduction and Background

This thesis examines the temperature conditions in the early solar nebula. Calcium-Aluminium-Rich Inclusions (CAIs) are the oldest materials in the solar system. Minerals from CAIs can provide insight into nebular conditions. This project specifically seeks to quantify temperature from the early solar nebula. From cation ordering in spinel from CAIs, we can estimate nebular temperatures. The conditions and processes in the early solar nebula are not well understood, but these processes played a role in the shaping of our solar system.

With advances in technology, instruments can reach farther distances into the universe. Understanding conditions and processes in the early solar nebula, such as temperature regimes, will help the search for habitable planetary systems in the universe. This understanding may also help in examining other planet-forming nebulae. Knowing about the formation of our solar system can help us find similar systems to our own. This is significant because the solar system is the only example we have of a life sustaining system. This thesis using cation distribution in spinel from CAIs will provide a new method for estimating the temperature of CAI formation in the solar nebula.

1.1 Problem Statement

Temperature estimates of the early solar nebula have not yet been made by testing nebular materials. Grossman (1972) created a theoretical condensation sequence for CAI creation from nebular gas. Others have completed heating and cooling experiments to create nebular minerals and textures (McSween Jr. 1999, Ivanova 2016). Mathematical modelling has also been used to model temperatures in the solar nebula (Desch et al. 2010). No method currently has been tested to measure temperature from early nebular materials. This study tests a new technique for measuring nebular temperature using meteoritical material. The technique relies on spinel found in CAIs. As the solar nebula no longer exists, direct measurements of the nebula cannot be made. Thus, remnants from the solar
nepula will have to be used. These remnants contain information about their formation and processing in the solar nebula.

CAIs are thought to be the first solids in the solar system, having condensed directly from solar nebula gases (McSween Jr. 1999, Lundstrom et al. 2006, Ivanova 2016). These inclusions are now found in carbonaceous chondrite meteorites (CCs). CCs are considered some of the most primitive meteorites. They are undifferentiated and relatively unaltered since their formation (McSween Jr. 1999, Weisberg et al. 2006, Ivanova 2016). The inclusions in these unaltered CCs are also relatively unaltered. Studying unaltered CAIs will provide insight into the conditions in the solar nebula.

Spinel (MgAl$_2$O$_4$) is commonly found in CAIs (Brearley and Jones 1998, Ivanova 2016, Rubin and Ma 2017). Spinel consists of a cubic closest packed arrangement of oxygen anions (O$^{2-}$). The charge on oxygen is balanced through the substitution of cations. In spinel sensu stricto, the cations are magnesium (Mg$^{2+}$) and aluminium (Al$^{3+}$). The cations are distributed among tetrahedral and octahedral sites between the oxygen anions. The distribution of these cations relates to the formation temperature of the spinel (Navrotsky and Kleppa 1967, Wood et al. 1986, Millard et al. 1992, Maekawa et al. 1997, Princivalle et al. 1999, Redfern et al. 1999, Andreozzi and Princivalle 2002). The distribution is described by the inversion parameter (x), defined in $(\text{Mg}_{1-x}\text{Al}_x)[\text{Al}_{2-x}\text{Mg}_x]\text{O}_4$. This distribution can be measured directly using $^{27}$Al Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectroscopy (Millard et al. 1992). NMR can be used to determine x (Wood et al. 1986, Millard et al. 1992). Studies of synthetic and natural spinel (MgAl$_2$O$_4$) relate temperature to x (Millard et al. 1992, Maekawa et al. 1997, Princivalle et al. 1999).

It is possible to determine the formation temperature of spinel using cation distribution. Spinel in CAIs was formed in the nebula and was subsequently processed in the nebula and on parent bodies. Because the temperature of formation is related to the degree of disorder, represented by the inversion parameter (x), if x can be measured, the temperature of formation can be determined (Navrotsky and Kleppa 1967, Wood et al. 1986, Peterson et al. 1991, Millard et al. 1992, Navrotsky 1994, Maekawa et al. 1997, Princivalle et al. 1999,
Redfern et al. 1999, Andreozzi and Princivalle 2002). By measuring the cation distribution in spinel from CAIs, it is possible to determine temperatures in the solar nebula and during planetary processing.

The purpose of this study is to measure the temperature of formation of spinel from different CAIs. The temperatures will be measured using cation order-disorder. Temperature estimates from the early solar nebula can be determined from this information.

1.2 Background

1.2.1 Calcium-Aluminium-Rich Inclusions

CAIs are the oldest materials in the solar system. They have been dated to 4 567.9 ± 3 Mya (Bouvier and Wadhwa 2010). Most CAIs have complex histories involving many different mineral formation processes (Grossman 1972, Kerridge 1993, McSween Jr. 1999, Shu et al. 2001, Ivanova 2016). These processes can include condensation, evaporation, melting, crystallization, metasomatic alteration, thermal alteration, and accretion processes (Grossman 1972, Kerridge 1993, McSween Jr. 1999, Shu et al. 2001, Ivanova 2016). Condensation from the nebula is expected to follow the theoretical condensation sequence calculated by Grossman (1972). This sequence can be used to constrain the temperatures expected to be calculated from the cation ordering of spinel in CAIs, if nebular temperatures are recorded (Figure 1.1). They are thought to have originally formed in the early stages of the solar system (Grossman 1972, Shu et al. 2001, Ivanova 2016). They form at temperatures above 1300 K and low pressures, between $10^{-6}$ and $10^{-2}$ atm (Grossman 1972, Desch et al. 2010, Henning and Semenov 2013, Ivanova 2016, Rubin and Ma 2017). Studying CAIs will provide information about the early solar system.
1.2.1.1 Formation

The current model of solar system formation suggests that the solar system formed from the gravitational collapse of a cloud of gas and dust (Shu et al. 1996, 2001, Ivanova 2016). A possible trigger for collapse was a nearby supernova (Ivanova 2016). The collapsing cloud coalesced into a rotating disk (Figure 1.2) (Goldreich and Ward 1973, Shu et al. 1996, Henning and Semenov 2013). The center of the disk collected the most mass and created the sun (Shu et al. 1996, 2001, Montmerle et al. 2006, Henning and Semenov 2013). The remaining material in the disk accreted into the planets and other solar system bodies (Goldreich and Ward 1973, Montmerle et al. 2006, Henning and Semenov 2013). This process created comets, asteroids, and planetary satellites (Goldreich and Ward 1973,
Montmerle et al. 2006). Material could also be ejected from the disk (Shu et al. 1996, 2001, Cuzzi et al. 2003, Desch et al. 2010). In the first stages of star formation, temperatures in the circumstellar disk were too high for solids to form (McSween 1999, Montmerle et al. 2006). As the disk cooled, solids began to condense out of the gas (McSween 1999, Henning and Semenov 2013). Closer to the sun, the solids formed are iron-nickel metals and iron-magnesium silicates (Larimer and Anders 1967, McSween 1999). Farther from the sun, where temperatures are lower, more volatile elements condensed (Lewis 1972, Goldreich and Ward 1973, McSween 1999, Henning and Semenov 2013). These include water and water-ammonia ices (Lewis 1972, Goldreich and Ward 1973). These first condensates would settle into the central plane of the nebular disk (Goldreich and Ward 1973, Montmerle et al. 2006).

CAIs are considered to have been the first solids to condense out of the solar nebula (Grossman 1972, Ivanova 2016). They may also represent high temperature processing of

![Figure 1.2. The nebular accretion disk. Temperatures decrease away from the sun. Ices freeze out of the nebula past the snow line, away from the sun. The temperatures closest to the sun can reach upwards of 1500 K. Vertically, the outer edges are hotter (red). The sun’s energy is blocked by the disk, so the inner parts of the disk tend to be colder (blue). Particles freezing or sublimating out of the nebula will settle into the central plane, where planet formation will occur. Modified from Henning and Semenov (2013).]
the first condensates (Kerridge 1993, Shu et al. 1996, 2001). There is some dispute about whether nebular condensation could adequately explain CAIs (Kerridge 1993). Multiple heating events and evaporation are processes used to help explain all observations (Kerridge 1993, McSween 1999, MacPherson 2003, Ivanova 2016). CAIs are comprised of the most refractory minerals (see section 1.2.3.2) (Grossman 1972, Brearley and Jones 1998, Ivanova 2016). CAIs are found in chondrite meteorites. Chondrites are undifferentiated meteorites and contain early solar system materials (Kerridge 1993, McSween 1999). They are considered to be from parent bodies that accreted at about 2.5 AU from the sun (Shu et al. 1996, 2001, McSween 1999).

Most CAIs have a complex history of multiple heating events. They were exposed to very high temperatures for prolonged periods of time. Current models do not show high temperatures at 2.5 AU (Shu et al. 1996, 2001, McSween 1999). This is where the chondrite parent bodies are expected to have accreted. If temperatures at 2.5 AU were not high enough to form CAIs, another mechanism or location of formation is needed. CAIs may have formed at 2.5 AU as a result of transient heating events, or may have formed at another location in the solar system.

A model which posits a different formation location is the X-wind model (Shu et al. 1996, 2001). The following information about the X-wind model comes from Shu et al. (1996) and Shu et al. (2001) unless otherwise stated. The X-wind model posits that CAIs formed at approximately 0.06 AU from the sun. They were then pushed vertically outwards from the proto-star by the X-winds or bipolar-outflow. This formation would have occurred during a turbulent early stage of star formation. The turbulent X-winds can also explain the multiple heating events. Particles picked up by the X-wind could be lifted from the shielding of the disk and exposed to direct sunlight, before falling back into the disk. Observations of young stars show large amounts of X-ray radiation emanating from the stars (Montmerle et al. 2006). Exposure to direct sun light would result in the high temperatures necessary for formation of CAIs. Particles of different sizes would be transported differently by the X-wind. The small particles would be ejected from the disk. The largest particles would fall back into the disk, some of which would end up at 2.5 AU. These particles could then accrete into chondrite parent bodies. This processing by the X-
wind size-sorts the particles. This sorting can explain the small variation in sizes of chondrules and CAIs. Those that fall back into the disk can be lifted by the X-wind multiple times, as long as they remain in the disk. This model is one possible explanation for the formation of CAIs.

Desch et al. (2010), suggests a nebular shock model is more consistent with experimental constraints on timing of particle formation and cooling histories, as well as mineralogy of CAIs and chondrules. One problem the X-wind model attempts to resolve is the “CAI storage” problem (Shu et al. 1996, 2001, Desch et al. 2010). How can CAIs form early in the nebula and remain in the disk long enough to accrete with later formed materials (chondrules and matrix)? Cuzzi et al (2003), show that CAIs could remain in the disk for millions of years in the presence of mild turbulence. Some CAIs can overcome inward drift and move outward in the disk by turbulence, without the need for an X-wind (Cuzzi et al. 2003, Desch et al. 2010). This model can also explain particle size sorting (Cuzzi et al. 2003, Desch et al. 2010). Smaller particles can survive longer in the disk than others (Cuzzi et al. 2003, Desch et al. 2010). They are transported outwards faster and do not fall into the sun as quickly as larger particles (Cuzzi et al. 2003, Desch et al. 2010). This model would be consistent with transient nebular shock melting, with no need for a strong X-wind.

Bipolar outflows are a common star-forming by-product (Montmerle et al. 2006). They may be a result of the star-forming process itself (Montmerle et al. 2006) and may predict the presence of similar planetary disks around many stars. Many exoplanets have been discovered to date. These planets may have formed in a similar way to our own solar system materials.

Nebular temperatures from multiple CAIs may be able to help distinguish between the different formation mechanisms. CAIs produced by an X-wind style model, should have calculated nebular temperatures which are all similar. This similarity would indicate a similar formation location, corresponding to formation close to the sun and then spread out by the X-wind. CAIs produced by shock heating events, should show various nebular formation temperatures, representing different formation locations in the nebula.
CAIs have a complex formation history. After their original formation in the nebula (Grossman 1972, McSween 1999, Ivanova 2016), secondary processing in the nebula or on a parent body could occur (Kerridge 1993, McSween 1999, Ivanova 2016). After accreting at 2.5 AU, CAIs undergo some alteration in their parent bodies. These processes include thermal metamorphism, brecciation, and aqueous alteration. Temperatures derived from studying pristine CAIs will likely be nebular temperatures. However, the temperatures may not reflect original condensation from the nebula. Spinel may record temperatures from later processing in the nebula. Temperatures from more processed CAIs, may reflect parent body processing. These temperatures will inform us about the thermal regime on the parent body during metamorphism.

1.2.1.2 Mineralogy

Information in this section is taken from Ivanonva (2016), Brearley and Jones (1998), MacPherson (2003) and Rubin and Ma (2017) unless otherwise stated.

CAIs are composed of four main primary minerals (formed first in the sequence): spinel, melilite, fassaite, and anorthite. Perovskite is also a common accessory phase. Some CAIs still contain highly refractory primary minerals such as grossite (common in CH chondrites) and hibonite (MacPherson 2003). These highly refractory minerals are thought to be usually lost through subsequent chemical reactions. Common minerals in CAIs are listed in Table 1.1.

**Table 1.1. Common mineral phases in CAIs (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016)**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
<td>MgAl$_2$O$_4$</td>
<td>Primary phase, Fe-rich spinel is secondary</td>
</tr>
<tr>
<td>Melilite (gehelenite – akermanite solid solution)</td>
<td>Ca$_2$Al$_2$SiO$_7$ – Ca$_2$MgSi$_2$O$_7$</td>
<td>Primary phase, Al-rich gehelenite is first to form at high temperatures</td>
</tr>
</tbody>
</table>
CAIs are divided into different types based on grain size and mineralogy (Table 1.2). The fine-grained types are Fluffy Type A (FTA) CAIs and spinel-rich fine-grained inclusions (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). “Fluffy” inclusions are thought to be a result of the agglomeration of smaller particles, causing a loose, irregular shape (MacPherson and Grossman 1984). The coarse-grained types include Compact Type A (CTAs), Type B, and Type C (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). CTAs and FTAs are rich in spinel and melilite (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). Type B’s are rich in melilite, fassaite, spinel, and minor anorthite (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). Type B1s have a melilite rim around a fassaite, anorthite, melilite, and spinel core (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). Type B2s do not have this melilite rim (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). Type Cs are rich in fassaite and anorthite and can contain spinel (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fassaite (Calcic-pyroxene solid solution)</td>
<td>CaMgSi$_2$O$_6$ – CaAl$_2$SiO$_6$ – CaTi$_4$Al$_2$O$_6$ – CaTi$_3$AlSiO$_6$</td>
<td>Primary in Type B, secondary in most CAI types</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl$_2$Si$_2$O$_8$</td>
<td>Primary in Type B, secondary in most CAI types (altered from melilite)</td>
</tr>
<tr>
<td>Perovskite</td>
<td>CaTiO$_3$</td>
<td>Primary</td>
</tr>
<tr>
<td>Grossite</td>
<td>CaAl$_4$O$_7$</td>
<td>Primary, common in CH chondrites</td>
</tr>
<tr>
<td>Hibonite</td>
<td>CaAl$<em>{12}$O$</em>{19}$</td>
<td>Primary</td>
</tr>
</tbody>
</table>
Table 1.2. Types of CAIs and their mineralogy. Types share mineralogy. Grain size is a separate classification. Information taken from Brearley and Jones (1998), MacPherson et al. (2003), MacPherson et al. (2005), Ivanova (2016), and Rubin and Ma (2017).

<table>
<thead>
<tr>
<th>Type</th>
<th>Mineralogy</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fine-Grained</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluffy Type A (FTA)</td>
<td>Rich in spinel and melilite</td>
<td>Found in all types of chondrites except Cls and Enstatite, were not melted</td>
</tr>
<tr>
<td>Spinel Rich</td>
<td>Rich in spinel</td>
<td>Common in reduced CV3s, most CAIs in CMs are spinel- (and hibonite-) rich</td>
</tr>
<tr>
<td><strong>Coarse-Grained</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compact Type A (CTA)</td>
<td>Rich in spinel and melilite</td>
<td>Found in all types of chondrites except Cls and Enstatite, melted FTAs</td>
</tr>
<tr>
<td>Type B</td>
<td>Rich in melilite, spinel, and fassaite, with</td>
<td>Only found in CV3s, anorthite is primary only in this type of CAI</td>
</tr>
<tr>
<td></td>
<td>minor anorthite</td>
<td></td>
</tr>
<tr>
<td>Type C</td>
<td>Rich in fassaite and anorthite; can contain</td>
<td>Rare, composition is farthest from that predicted by the theoretical condensation</td>
</tr>
<tr>
<td></td>
<td>spinel</td>
<td>sequence from Grossman (1972)</td>
</tr>
</tbody>
</table>

Secondary minerals are those that form from replacement reactions with primary minerals (Ivanova 2016). In primitive chondrites secondary minerals are often a result of aqueous alteration on the parent body (Brearley and Jones 1998, Ivanova 2016). Common secondary minerals include anorthite, nepheline, sodalite, hedenbergite, and grossular (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). Anorthite can be primary or secondary (MacPherson 2003, Ivanova 2016).
1.2.1.3 Spinel in CAIs

Spinel is very common in CAIs from CV3 chondrites. Most spinel in CAIs is pure MgAl$_2$O$_4$. There are some examples of more Fe- and Cr-rich varieties. Spinel occurs as small octahedra and can be poikilitic, framboidal, or can occur as palisades. Poikilitic spinel is typically found as an inclusion in melilite and fassaite. Framboids are small (10-100 μm) groupings of spinel that are shaped like raspberries. Framboidal spinel is typically included in fassaite, melilite, or anorthite. Palisades are chains, narrow bands, or continuous ribbons of spinel grains. They appear as arcs or rings in thin section.

1.2.2 Spinel

Spinel is commonly found in all types of CAIs (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016, Rubin and Ma 2017). It has a relatively simple cubic closest packed structure of oxygen anions that can accommodate a number of different cations (Klein and Dutrow 2007) (Figure 1.2). Spinel *sensu lato* has the structure AB$_2$O$_4$. A and B represent the different substituting cations. The ability to substitute many different elements stabilizes the spinel structure over a large range of pressure and temperature conditions, thus making spinel group minerals important in a variety of different environments (Navrotsky and Kleppa 1967, O’Neill and Navrotsky 1983, Millard et al. 1992). The spinel found in CAIs is typically pure MgAl$_2$O$_4$ spinel or spinel *sensu stricto*, where the substituting cations are Mg$^{2+}$ and Al$^{3+}$ (Figure 1.3) (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016).
1.2.2.1 Structure

The spinel structure is a cubic closest packed arrangement of oxygen anions (space group Fd3m) with 1/8 tetrahedral and 1/2 octahedral interstities filled with cations. The distribution of the Mg$^{2+}$ and Al$^{3+}$ cations between these sites can vary according to the formation temperature (Millard et al. 1992, Maekawa et al. 1997, Andreozzi and Princivalle 2002).

1.2.2.2 Cation Ordering and Temperature of Formation

Disordering in a mineral is a thermodynamic property which results from the minimization of Gibbs Free Energy where $\Delta G_{\text{dis}} = \Delta H_{\text{dis}} - T\Delta S_{\text{dis}}$, where $G_{\text{dis}}$ is the Gibbs free energy of disorder, $H_{\text{dis}}$ is the enthalpy of disorder, T is temperature, and $S_{\text{dis}}$ is the entropy of disorder. One component of entropy is configurational entropy or cation disorder (Navrotsky 1994). Disorder increases with increasing temperature which will lower G. The lower the value of $\Delta G$, the more stable a substance. When T is low, solids are more ordered (have lower entropy) because S contributes to G less at lower T. Therefore, at low T, S can be low without affecting $\Delta G$. At high T, S has a large impact on G, so solids are more disordered (have higher entropy). High S and high T contribute significantly to reducing G.
Disorder is represented by the amount of entropy ($S$) (Navrotsky 1994). In spinel, the entropy of disorder is assumed to be equal to the configurational entropy ($S_{\text{conf}}$) (Navrotsky 1994). $S_{\text{conf}}$ is related to the distribution of cations among the sites (Navrotsky 1994). This distribution or disorder is represented by the inversion parameter, $x$, which is described by $^{[4]}(\text{Mg}_{1-x}\text{Al}_x)^{[6]}[\text{Al}_{2-x}\text{Mg}_x]\text{O}_4$. Where ( ) and [ ] represent tetrahedral and octahedral sites respectively. $x$ describes the amount of Al$^{3+}$ in the tetrahedral site and can have values between zero and one. When $x$ is zero, the spinel is an ordered normal spinel ($\text{(Mg)}[\text{Al}_2]\text{O}_4$) and when $x$ is one, the spinel is an inverse ordered spinel ($\text{(Al)}[\text{Mg},\text{Al}]\text{O}_4$) (Navrotsky 1994). A completely disordered spinel, with a random distribution of cations would have an $x$-value of $\frac{2}{3}$ or $0.66\overline{6}$ (Figure 1.4) (Navrotsky 1994).

1.2.2.3 Previous Cation Ordering Studies

The relationship between cation disorder, $x$, and temperature has been studied previously using synthetic spinel (Peterson et al. 1991, Millard et al. 1992, Redfern et al. 1999, Andreozzi and Princivalle 2002) and natural spinel (Maekawa et al. 1997, Princivalle et al. 1999). The studies utilized a number of different methods for determining the degree of disorder. Some studies measured cation ordering in situ at high temperatures (Peterson et al. 1991, Maekawa et al. 1997, Redfern et al. 1999). Some measured cation ordering in

![Figure 1.4. Configurational entropy of spinel versus disorder ($x$). Showing values of $x = 0$, 0.667, and 1. The entropy does not go to zero when $x = 1$ because Mg and Al can be disordered within the octahedral site (Table 2). (Modified from Navrotsky 1994)](image)
Peterson et al. (1991) used Rietveld Refinement of *in situ* neutron powder diffraction data on synthetic spinel to determine ordering. Their results showed increased ordering (decreased disorder), with decreasing temperature, consistent with theoretical expectations. They found that the cation distribution was in equilibrium above 973 K. A calibration curve was created by plotting $x$ versus temperature from 273 – 1273 K. The data were fit using the model from O’Neill and Navrotsky 1983:

$$\Delta G^o = \alpha + 2\beta x = -R + \ln x^2(1-x)^{-1}(2-x)^{-1}$$

Where $\alpha$ equals $-31 \pm 1$ kJ/mol, $\beta$ equals $-10 \pm 3$ kJ/mol, and $R$ is the gas constant.

Millard et al. (1992) used $^{27}$Al NMR spectroscopy to determine disorder of synthetic spinel. The tetrahedral and octahedral $\text{Al}^{3+}$ have chemical shifts at different frequencies ($\sim$70 ppm and $\sim$10 ppm, respectively) in the NMR spectrum. The tetrahedral $\text{Al}^{3+}$ is a high frequency peak, and the octahedral $\text{Al}^{3+}$ is a low frequency peak (Figure 1.5). Under appropriate collection conditions, the area under the peaks is quantitative. Using the NMR spectrum, $x$ can be calculated from the octahedral to tetrahedral peak area ratio:
\[ x = 2/(1+^{[6]}\text{Al}/^{[4]}\text{Al}). \]

This calculation is based on \(^{[4]}(\text{Mg}_{1-x}\text{Al}_x)\text{Al}_2\text{Mg}_x\text{O}_4\), where \(^{[6]}\text{Al}/^{[4]}\text{Al} = (2-x)/x\). Their results showed increasing disorder with increasing temperature, as was expected.

In quench experiments there was no change in the x-values for synthetic spinel equilibrated above 1000 °C. The x-values did not increase as expected above 1000 °C. This plateau indicates reordering of cations during quenching (Millard et al. 1992). Millard et al. (1992) found a dependence of observed peak area ratio on the pulse width used in NMR experiments and recommended using 0.8 μs as suggested by (Lippmaa et al. 1986), for quantitative \(^{27}\text{Al}\) NMR spectra. This tip angle of 0.8 μs can also be expressed as \(\Pi/34\) relative to the solution \(\Pi/2\) (90°) pulse width (or 13-14 μs) (Millard et al. 1992). Maekawa et al. (1997) also used \(^{27}\text{Al}\) NMR spectroscopy to determine disorder in synthetic spinel. Maekawa et al. (1997) used spinel up to 1600 °C and also saw reordering effects from quenching. Both Millard and Maekawa constructed x versus temperature curves from 700 – 1400 °C and up to 1600 °C respectively. Millard et al. (1992) fit their data using the Navrotsky-Kleppa (1967) thermodynamic model:

\[ \ln K = \ln[x^2(2-x)^{-1}(1-x)^{-1}] = \Delta H_D/RT \]

Where \(\Delta H_D = 28 \pm 1 \text{ kJ/mol}\). They also used O’Neill and Navrotsky 1983’s model:

\[ \Delta H_D = \alpha x + \beta x^2 \]
Where $\alpha = 25 \pm 5$ kJ/mol and $\beta = 5.8 \pm 9.5$ kJ/mol (Millard et al. 1992). Maekawa et al. (1997) used both high temperature *in situ* and quenched data. They fit this data using O’Neill and Navrotsky’s model from 1983:

$$\ln K = -(\alpha + 2\beta x)/RT$$

Where $\alpha = 35 \pm 5$ kJ/mol and $\beta = -32 \pm 5$ kJ/mol (Maekawa et al. 1997).

Princivalle et al. (1999) measured cation ordering in natural spinels using single crystal XRD. Based on the mineral assemblage in the rock, and the known relationships between minerals and formation temperature, temperatures of 650 – 700 °C were expected to be estimated using the cation ordering in spinel. Temperature estimates from structural refinement of XRD data to determine the cation ordering of the spinel were lower than these expected values, likely because of re-ordering of the cations during slow cooling. Princivalle et al. (1999) plotted $B$ versus temperature (°C) from 0 – 1200 °C. Where $B = \text{Al}_{(\text{tet})}/\text{Al}_{(\text{total})} + C4(1-\text{Mg}_{(\text{tet})} - \text{Al}_{(\text{tet})} +C5(2-\text{Al}_{(M)})$. C4 and C5 are fitting coefficients that take into account elemental differences from pure MgAl2O4. The simplified equation $B = [4] \text{Al}/\text{Al}_{\text{total}}$ is sufficient for our purposes, as spinel in CAIs is very close to pure MgAl2O4 (Brearley and Jones 1998). Experimental values were calculated to be from ~400 – 1200 °C. Princivalle et al. (1999)’s linear relationship is represented by

$$T(°C) = 6440 * B.$$

Redfern et al. (1999) used *in situ* neutron diffraction between room temperature and 1600 °C on synthetic spinels. They found that quenching above 1300 °C typically failed to record the disorder from the higher temperature due to re-ordering during cooling. This re-ordering on quenching was attributed to the rapid kinetics of Mg-Al site exchange in spinel. They plotted the inversion parameter, $x$, versus temperature (K) from ~800 – 2000 K. They fit their data to O’Neill and Navrotsky (1983)’s equilibrium model:

$$-RT\ln((x^2/(1-x)(2-x))) = \alpha + 2\beta x$$

Where $\alpha = 32.8 \pm 0.9$ kJ/mol and $\beta = 4.7 \pm 2$ kJ/mol. They also compared stoichiometric and non-stoichiometric spinel. They found that the overall effect of decreasing Mg, was
to increase disorder. This effect was determined by testing the inversion parameter, $x$, for stoichiometric and non-stoichiometric spinel. Both kinds of spinel were tested at the same temperatures. Non-stoichiometric spinel with less Mg ($\text{Mg}_{0.99}\text{Al}_2\text{O}_4$) was more disordered at every temperature than the stoichiometric spinel ($\text{Mg}_1\text{Al}_2\text{O}_4$).

Andreozzi and Princivalle (2002) examined the cation ordering in synthetic $\text{MgAl}_2\text{O}_4$ spinel. They used single crystal XRD and refined on the oxygen atom position parameter ($u$), which is dependent on cation distribution. They plotted $x$ versus $u$ at various equilibration temperatures. The linear relationship is $x = 21.396 - 80.714u$, with different temperatures recorded along the fitted line (Andreozzi and Princivalle 2002).

This project will use $^{27}\text{Al}$ MAS NMR and $^{27}\text{Al}$ 3Q MAS NMR to directly measure the octahedral to tetrahedral $\text{Al}^{3+}$ ratio, and use this to calculate $x$. The calibration curves from the previous studies will then be used to estimate formation temperatures (Table 1.3). Information from the studies will be used to help determine the cooling history of the CAIs from different environments.

**Table 1.3. Summary of literature calibration curves used in this study.**

<table>
<thead>
<tr>
<th>Source</th>
<th>Natural or Synthetic Spinel</th>
<th>High Temperature or Quenched/ Cooled Samples</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peterson et al. 1991</td>
<td>Synthetic</td>
<td>High Temperature ($T$) in situ</td>
<td>$^{[1]}\Delta G^\circ = \alpha + 2\beta x = -RT\ln(x^2(1-x)^3(2-x)^{-1})$&lt;br&gt; ($\alpha = -31 \text{ kJ/mol, } \beta = -10 \text{ kJ/mol}$)</td>
</tr>
<tr>
<td>Millard et al. 1992</td>
<td>Synthetic</td>
<td>Quenched</td>
<td>$^{[1]}\Delta H_D = \alpha x + \beta x^2$&lt;br&gt; ($\alpha = 25 \text{ kJ/mol, } \beta = 5.8 \text{ kJ/mol}$)</td>
</tr>
<tr>
<td>Maekawa et al. 1997</td>
<td>Natural</td>
<td>Both (Quenched and in situ high T)</td>
<td>$^{[1]}\ln K = -(\alpha + 2\beta x)/RT$&lt;br&gt; ($\alpha = 35 \text{ kJ/mol, } \beta = -32 \text{ kJ/mol}$)</td>
</tr>
</tbody>
</table>
1.2.3 NMR Spectroscopy Theory

The following is summarized from information given in Sanders and Hunter (1987), Kirkpatrick (1988), and Harris (1986) unless otherwise indicated.

1.2.3.1 Introduction

NMR spectroscopy is a powerful tool for determining structure and bonding information of a substance in the solid or liquid state. It can help in determining the atomic environment around the NMR-active nucleus of interest. The nucleus can be shielded from the applied magnetic field by the surrounding atoms. Different chemical environments will cause various amounts of shielding. Therefore, the magnitude of the magnetic field experienced by nuclei will vary. The variance is a result of shielding and is referred to as the effective magnetic field. The difference in the effective magnetic field as a result of chemical environment will result in different observed energy frequencies. Thus, these frequencies are called chemical shifts and are measured in ppm relative to the natural resonant frequency of the nucleus. Chemical shift can help determine structural information, such
as different bonding environments (e.g. octahedral versus tetrahedral) and elemental substitution around the active nucleus can be determined in this way (e.g. Al or Si next nearest neighbours in silicates). This information can be used to determine order-disorder.

NMR spectroscopy relies on the principle that in an applied magnetic field, the nucleus of an NMR active atom will produce its own magnetic field. NMR spectroscopy measures the response of this system of magnetic fields to a disturbance, in the form of a pulse of radio frequency energy. This pulse disturbs the system from equilibrium and the measurement is made as the system slowly returns to equilibrium.

1.2.3.2 Nuclear Spin and Nuclear Zeeman Splitting

Nuclear spin is an inherent property defined by the physical spinning of the nuclei. The angular momentum, \( J \), of a nucleus is described as \( J = \hbar [I(I+1)]^{1/2} \), where \( \hbar \) is Planck’s constant divided by 2\( \pi \) and \( I \) is the spin quantum number. The magnetic moment, \( \vec{\mu} \), of a nucleus describes the strength and direction of the magnetic field produced by the spin of the nucleus. \( \vec{\mu} \) is related to the angular momentum, \( J \), by the gyromagnetic ratio, \( \gamma \): \( \vec{\mu} = \gamma J \). \( \gamma \) is a constant for each nuclide. Only nuclides with spins greater than zero are visible by NMR spectroscopy (Table 1.4). Each NMR active nucleus will have a unique resonant frequency (e.g. \(^{27}\text{Al}\) has resonant frequency 234.6 MHz at 21.1 T).

Table 1.4. The combinations of mass number and nuclear charge which produce different spins and determine if a nucleus is NMR active.

<table>
<thead>
<tr>
<th>Mass number</th>
<th>Charge</th>
<th>Spin</th>
<th>Example Isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Even</td>
<td>Even</td>
<td>(^1)Zero</td>
<td>(^{12}\text{C}, (^{16}\text{O})</td>
</tr>
<tr>
<td>Odd</td>
<td>n/a</td>
<td>Half integer spins</td>
<td>(^{1}\text{H}, (^{13}\text{C}, (^{17}\text{O}, (^{27}\text{Al}, (^{29}\text{Si}, (^{31}\text{P})</td>
</tr>
<tr>
<td>Even</td>
<td>Odd</td>
<td>Integer spins</td>
<td>(^{2}\text{H}, (^{14}\text{N})</td>
</tr>
</tbody>
</table>

\(^1\)These nuclei are not NMR active
The spin quantum number, \( I \), can be either integer or half integer value. Each nuclide has different energy levels that correspond to \( I \), such that the number of energy levels = \( 2I+1 \). The number of energy levels is defined by the quantum number, \( m \), which has various values ranging from \( I \) to \(-I\), in consecutive steps of minus 1 (i.e., \( I, I-1, I-2...\) until \(-I\)). These energy levels have equal energy, or are degenerate, when not in a magnetic field (Figure 1.6 and Figure 1.7).

When a magnetic field is applied, these energy states diverge into higher and lower energies, due to Nuclear Zeeman interactions between the nuclear magnetic moment and the applied magnetic field. This divergence is referred to as Nuclear Zeeman splitting. For a simple spin \( \frac{1}{2} \) nucleus, only two different energy states are created. There is a higher energy state \( \left( -\frac{1}{2} \right) \) which is antiparallel to the applied magnetic field and a lower energy state \( \left( \frac{1}{2} \right) \) which is parallel to the applied magnetic field (Figure 1.6). In nuclei with spins greater than \( \frac{1}{2} \), there are more than two energy states \( (2I+1) \) (Figure 1.7). The difference in energy between the different energy levels is represented by \( \Delta E = |\gamma \hbar H| \), where \( H \) is the magnetic field at the nucleus.

Spin = 1/2

![Nuclear Zeeman Splitting](image)

**Figure 1.6.** Nuclear Zeeman splitting of a spin 1/2 nucleus in the presence of an applied magnetic field. This simple case produces only spin +1/2 and spin -1/2 energy levels. With no magnetic field, the energy levels are degenerate and no splitting occurs. Modified from Navrtosky (1994) and Kirkpatrick (1998).
The number of nuclides of the sample within the high and low energy states is roughly equal as described by a Boltzmann distribution: 

\[
\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{\Delta E}{kT}\right).
\]

The population distribution is related to the magnetization produced by the spin of the nuclei (\(\vec{\mu}\)) and the strength of the applied magnetic field. Because there is only a small difference in the populations of the different energy states, this signal would be of very low strength if measured directly. NMR spectroscopy therefore measures the response of the system after it is disturbed from its Boltzmann distribution. Nuclei can only change energy states by

---

**Figure 1.7.** Energy levels of a spin 5/2 nuclei (such as \(^{27}\text{Al}\)). In an applied magnetic field, the nuclear spins undergo Nuclear Zeeman splitting. The first order quadrupolar effects result from interactions between the electric quadrupole moment of the nucleus and electric field gradient of a site. The quadrupole interactions are described using the Quadrupolar Coupling Constant (QCC or CQ) and the asymmetry parameter (\(\eta\)). Modified from Navrotsky (1994) and Kirkpatrick (1988).
absorbing or emitting a photon with frequency $\nu = \frac{\nu}{2\pi} H$. After disturbing the system from equilibrium with a pulse of radio frequency, the energy of the system as it decays back to equilibrium is measured.

Another way to explain this phenomenon is in terms of vectors. Assume that the applied magnetic field has the direction $B_0$. The collective nuclear magnetic moments of the sample will precess around the orientation of the applied magnetic field ($B_0$). This precession occurs at the Larmor frequency or natural resonant frequency of the nucleus and creates a bulk magnetization produced by the Boltzmann distribution of the spins of the nuclei ($M$). $M$ will have the same direction as the applied magnetic field ($B_0$) (Figure 1.8). The system must be disturbed before the NMR measurement can be made. A current is measured in a coil of wire in the NMR spectrometer that is coiled in the same direction as the applied magnetic field ($B_0$). Pulses are used to disturb the system, so the signal can be measured. A pulse is a second magnetic field ($B_1$). This second magnetic field ($B_1$) is produced by radio frequency energy. The second magnetic field ($B_1$) puts torque on the net magnetization ($M$) and causes it to flip about $B_1$. The angle to which the net magnetization ($M$) is moved depends on the duration of the pulse. As the pulse duration which produces a certain tip angle can vary on different instruments, the pulse duration is typically referred to by the effective tip angle.

![Diagram](image)

**Figure 1.8.** a) The magnetization produced by the spin of the nuclei ($M$) in the same direction as $B_0$. b) Induced magnetic field ($B_1$) perpendicular to $B_0$. c) $M$ precessing around $B_0$, caused by the torque of $B_1$ perpendicular to $B_0$. Modified from Sanders and Hunter (1987).
The magnetization caused by the spin (M) then begins to precess in the x, y plane at the effective tip angle (Figure 1.8). The precession around B₀ can be better visualized using a rotating field of reference in the x,y plane. This precession produces an oscillating current which can be measured. The NMR signal is measured as the magnetization produced by the spin of the nuclei (M) relaxes back to equilibrium. Once B₁ is removed, B₀ is the only influence on M. M relaxes back into alignment with B₀. The time it takes to do this is referred to as T₁. Once B₁ is no longer influencing M, these spins become out of phase in the x-y plane. The time it takes for the spins in this plane to decay in this fashion to zero is referred to as T₂ relaxation, which relates to peak broadening (short T₂ = broad peaks).

1.2.3.3 Data

In systems with a nucleus in more than one chemical environment, precession frequencies of each component will be different. These differences can make it difficult to apply a pulse which will create a uniform tip angle for all components. The measurements assume that all signals are in the same place in the system at the time of measurement. However, multi-component systems will have magnetizations that precess faster or slower than the reference frequency. This will cause some signals to be out of phase with the reference frequency. Fortunately, the differences in the frequencies can be reduced if the pulse duration is short, as well as by using high power radio frequencies, making the phase error small.

The data retrieved from NMR spectroscopy are first collected as a Free Induction Decay (FID) pattern in the time domain. This FID is then digitally transformed using Fourier Transformation into an NMR spectrum in the frequency domain.

An FID is a plot of the frequency over time (collected in the time domain). The signal collected in the NMR spectrometer is collected after the influence from the pulse has subsided (Free). It is a signal that has been induced in the coil surrounding the applied magnetic field (Induced). It is collected as the magnetization is decaying back to equilibrium (Decay). As the signal decays, the frequency will remain the same as the amplitude decreases. The signal collected in an FID is typically the difference between the measured frequency and a reference frequency. The FID therefore measures a relative
frequency, rather than an absolute frequency. The FID is digitally altered into an intensity versus frequency plot (displayed in the frequency domain) using Fourier Transformation. Intensity versus frequency plots are displayed in ppm. The difference between the frequency of the measured signal of the sample and the standard (Hz), divided by the frequency of the NMR spectrometer (MHz), produces a plot of frequency in ppm (Hz/MHz) versus intensity. This eliminates differences in measured frequencies produced by the instrument.

1.2.3.4 Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) Spectroscopy

MAS NMR spectroscopy spins the sample in the spectrometer at an angle of 54.7° (the magic angle) to the applied magnetic field. This technique is used to overcome several effects causing peak broadening in NMR of solids, which is not experienced in low viscosity liquids. Nuclei in liquids tend to all experience the same magnetic field strength in a single structural environment due to random orientation in liquid. Broadening in solids is caused by several interactions which affect the strength of the magnetic field experienced by each nucleus. They increase the range of these experienced fields for an atom in a single structural environment. This increased range makes distinct structural environments harder to interpret from the spectra. There are four types of interaction that cause broadening:

1. Dipole-dipole interactions between the individual magnetic dipole moments of different nuclei (for quadrupolar (spin > ½) nuclei only).
2. Chemical shift anisotropy (CSA), which is heterogeneous electronic shielding of individual nuclides in the same environment depending on orientation in the magnetic field.
3. Quadrupole interactions between the electric quadrupole moment and the electric field gradient of a nucleus.
4. J-coupling interactions, which are typically insignificant in inorganic solids.

Mathematically, the dipole-dipole, CSA, and quadrupole interactions contain the term $3 \cos^2 \theta - 1$, where $\theta$ is the angle between the applied magnetic field and the axis of
interaction at the nucleus (i.e. the direction of interaction of any of the four broadening interactions described above). When $\theta = 54.7^\circ$, the shared term becomes zero, and the magnitude of dipole-dipole, CSA, and first order quadrupole interactions is reduced to zero. Using MAS NMR, the sample is mechanically rotated at an angle of $54.7^\circ$ to $B_0$ to “magically” produce narrower peaks and a higher signal to noise ratio.

### 1.2.3.5 Quadrupole Interactions

Quadrupole interactions occur as a result of interactions between the electric quadrupole moment and the electric field gradient (EFG) for spin > $\frac{1}{2}$ nuclei. The quadrupole moment arises as a result of asymmetrical charge distribution on the nucleus. The EFG represents the rate of change of the electric field at the nucleus. It is generated by the electronic environment surrounding the nucleus and the surrounding nuclei. The EFG increases for distorted environments, but is zero in symmetrical environments, such as a perfect octahedron or a perfect tetrahedron. The quadrupole effects cause peak broadening in distorted environments. 1\textsuperscript{st} order quadrupolar interactions are overcome using MAS. Nuclei with a spin quantum number, I, greater than or equal to 1, have 2\textsuperscript{nd} order quadrupolar interactions, which are not mitigated by MAS NMR. The 2\textsuperscript{nd} order quadrupolar interactions cause peak broadening, distortion of peak shape, and chemical shift displacement. The effects of 2\textsuperscript{nd} order quadrupole interactions decrease by the square of the strength of the applied magnetic field. Data on samples which produce 2\textsuperscript{nd} order quadrupole interactions are therefore typically collected on the highest available field strength NMR spectrometer. The Quadrupolar Coupling Constant (QCC or CQ) and the asymmetry parameter ($\eta$) are used to describe the quadrupole effects. QCC represents the magnitude of the electric field gradient and $\eta$ represents any variation from a symmetrical electric field gradient. $\eta$ affects peak shapes (Figure 1.9).
Two-Dimensional NMR

NMR spectra over two dimensions can provide more information about the structure of a sample than simple one-dimensional spectra. It is done by collecting a series of spectra, each with a different time variable. This time variable depends on the experiment being run. For example, a common time variable to change is the evolution time of the second order quadrupole spins. This is the time between pulses in a multiple pulse experiment. These pulse sequences are usually more complex than those used in one-dimensional experiments. They include two time variables, $t_1$ and $t_2$. $t_1$ is part of the pulse sequence. It can also be called spin-lattice relaxation time. It is related to relaxation in the z-direction. This direction is the same as the applied magnetic field. It allows time to re-establish a Gaussian distribution after perturbation, or a specific type of pulse. The $t_1$ time variable is the one that is varied during a two-dimensional pulse sequence. It is the time delay after the first pulse before the spins of the different nuclei to go back into phase. This allows

Figure 1.9. Difference in line shape of a MAS quadrupolar peak with an asymmetry parameter ($\eta$) equal to 0 and 1. $\eta = 0$ represents axial symmetry (Kentgens 1997). All other shape parameters are kept equal.
the anisotropic effects to be averaged. \( t_2 \) is the detection period. It is the time when a spectrum is measured. Fourier transformation is done over these two time variables to produce a 2-D spectrum.

Multiple Quantum (MQ) MAS is a useful 2-D NMR technique which can separate isotropic and anisotropic interactions. Internal anisotropic interactions are those which can cause peak broadening in solids: dipole-dipole, CSA, and quadrupolar. 2\(^{nd}\) order quadrupolar interactions, which are not mitigated by MAS, can be averaged using MQ NMR. Averaging an anisotropic interaction makes it an isotropic interaction, as is seen in NMR of solutions. Triple Quantum (3Q) MAS NMR used in this study produces a spectrum of MAS NMR (F2) versus the isotropic interactions (F1) (Figure 1.10). Along the isotropic axis of the spectrum, the anisotropic effects are removed. These effects produce broadening. The spectrum has better resolution without them. The pulse sequence is designed to remove them by averaging anisotropic interactions. Averaging is done by using different evolution times between pulses. This controls the direction of the magnetic fields, which can be cancelled by interference. The isotropic dimension is a combination of isotropic chemical shift and a shift produced by second order quadrupole interactions. The relationship between the MAS NMR and isotropic dimensions is linear and falls on a 1:1 diagonal.
Aluminium-27 as an NMR Active Nucleus

$^{27}$Al is an NMR active nucleus that is useful in mineralogical and geological studies. It is often studied in aluminosilicates, where $^{27}$Al NMR can provide information about Al-Si disorder (Flemming et al. 2015). In oxides, it can provide information about Al-Mg disorder (Wood et al. 1986). $^{27}$Al has a spin quantum number of $I = 5/2$ making it quadrupolar. It has a nearly 100% natural abundance compared to other Al isotopes, which makes it easy to observe. $^{27}$Al in different coordination environments have chemical shifts that are well separated in NMR spectra, and their chemical shifts are well constrained (Table 1.5). On the negative side, it is less sensitive than $^{29}$Si MAS NMR, and $^{27}$Al MAS NMR peak position is relatively insensitive to cation substitution at next nearest neighbour.
cation sites. Because $^{27}$Al is quadrupolar, it has additional peak broadening, but it is sensitive to site distortion.

**Table 1.5. Expected MAS NMR chemical shift of $^{27}$Al in different coordinated environments for aluminates and aluminosilicates (Kirkpatrick 1988, Stebbins 1995).**

<table>
<thead>
<tr>
<th>Description</th>
<th>Shift (ppm)</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral (4-coordinated) Al</td>
<td>50 – 80</td>
<td>Spinel, nepheline, anorthite</td>
</tr>
<tr>
<td>Octahedral (6-coordinated) Al</td>
<td>-10 – 15</td>
<td>Spinel, corundum, vesuvianite</td>
</tr>
<tr>
<td>5-coordinated Al</td>
<td>35 – 40</td>
<td>Andalusite, vesuvianite</td>
</tr>
</tbody>
</table>

### 1.2.4 Meteorite Classification

The following information is taken from McSween (1999) and Brearley and Jones (1998) unless otherwise stated.

Meteorites fall into three main categories. These are further divided into groups or clans. The three main categories are iron, stony-iron, and stony. Iron meteorites consist of mostly Fe-Ni metal alloys. They are thought to represent the cores of differentiated parent bodies. Stony-iron meteorites are approximately an equal mixture of Fe-Ni alloys and silicate minerals. They include pallasites and mesosiderites. One theory is that stony-iron meteorites represent the core-mantle boundary of differentiated parent bodies. Stony meteorites are mostly silicate and oxide minerals with some metal grains. They include chondrites and achondrites. Stony meteorites represent undifferentiated parent bodies or the crust of differentiated parent bodies. Differentiated bodies have become segregated into a crust, mantle, and core.

Achondrites would have originally consisted of chondritic material. They have since undergone igneous melting and crystallization on their parent body. Achondrites come from large asteroids or Kuiper belt objects such as Vesta. They can also be from planetary bodies or satellites such as Mars or the Moon. Chondrites are accreted early solar system
materials. Their parent bodies were never large or hot enough to result in igneous processing.

### 1.2.4.1 Chondrites

Chondrites consist of a “mish-mash” of early solar system materials. They are comprised of refractory inclusions, chondrules, metal, and matrix. Refractory inclusions include CAIs and are thought to have formed via condensation (Grossman 1972). Chondrules are thought to have formed as molten droplets in the solar nebula, melted by transient heating events (Connelly et al. 2012). Metals are FeNi alloys. Matrix material is mostly nebular dust. Chondrites have not undergone much alteration since their formation. Thus, they contain information about the conditions and processes in the early solar nebula (Kerridge 1993).

Chondrites are divided into groups, which are organized into clans. Groups are compositionally similar. It is considered likely groups are from the same parent body. Clans are sets of groups that have similar properties. Clans are considered to have formed at the same place in the solar system before accretion. Clans include Ordinary, Carbonaceous, Enstatite, Rumuruti, and Kakangari. Ordinary chondrites (OCs) are the most abundant. Carbonaceous chondrites (CCs) were thought to contain the most carbon. They also contain CAIs. Enstatite chondrites (ECs) are rich in the mineral enstatite (MgSiO$_3$). Rumuruti and Kakangari chondrites are considered separate clans, but each only contains one group.

The CCs have the most similar composition to the sun of all chondrites. Groups in the CCs include CI, CO, CV, CM, CR, CH, CB, CK, CB, and ungrouped Cs. Groups are named after the fall or find location of the type specimen. For example, CV is named for Vigarano, Italy.

### 1.2.4.2 Formation

Chondrite parent bodies are asteroids, typically found in the asteroid belt between Mars and Jupiter. Chondrite parent bodies likely formed by accretion like other solar system bodies. The first materials settled into the center of the disk (Goldreich and Ward 1973,
Montmerle et al. 2006, Henning and Semenov 2013). Gravitational instability then drove the accretion of the small particles into larger ones. Accretion may also be attributed to properties of the particles, such as a “stickiness” (Safronov and Ruskol 1994). Goldreich and Ward (1973), argue that accretion would be faster using gravitational instability. They argue that particle stickiness was not needed to drive accretion. In their model, these first large accreted bodies would cluster together in groups. The components of these clusters would combine into larger planetesimals. Then planet-sized objects would accrete, though not likely because of gravitational instability. In this model, planetesimals can occur in two stages. They can be the first large accreted bodies or the larger combined clusters. The chondrite parent body is likely one these generations of planetesimals.

Impact events eject material from planetesimals. The ejected material becomes chondrite meteorites once on Earth. The generally accepted formation model of chondrites includes condensation, accretion, and ejection. CAIs and chondrules condense from or are formed in the nebula. These early solids accrete to form larger and larger parent bodies. Alteration of primary condensates can occur in the nebula or on the parent body after accretion.

1.2.4.3 C-Type Asteroid: Carbonaceous Chondrite Parent Body

Chondrites are linked to candidate parent body asteroids through spectral similarities. C-Type asteroids are considered to be the CC parent body. C-type asteroids have very low albedos, making them very dark. Being so dark can make spectral measurements difficult because of a lack of reflected light. C-type asteroids are very abundant in the asteroids belt. Spectral measurements in the infrared (IR) spectrum show bands associated with hydrated minerals. These spectral features are interpreted as hydrated phyllosilicates. They could be interpreted as some iron phyllosilicates, and possibly some organic matter. Carbonaceous chondrite meteorites commonly have evidence of aqueous alteration. Aqueous alteration is consistent with C-type asteroids. The presence of phyllosilicates indicates some amount of aqueous activity.

1.2.4.4 Thermal History

Ordinary chondrites have the most well-constrained parent body thermal history. From studies of OCs, highly metamorphosed meteorites experienced 750-950 °C. More pristine
meteorites experienced temperatures of 400-600 °C. Cooling rates for these parent bodies are considered to be around tens of degrees Celsius per million years.

Carbonaceous chondrite parent body thermal histories are less constrained. Aqueous alteration on the parent body is estimated to have occurred at low temperatures, around 100 °C. Models by Travis and Schubert (2005) showed peak temperatures between 90 and 180 °C. These were models of aqueous alteration at around 4 AU (Travis and Schubert 2005). $^{26}$Al decay can be a heat source for planetesimal heating after accretion (Grimm and McSween Jr. 1989, Travis and Schubert 2005). Similar modelling done by Grimm and McSween Jr. (1989) assumed temperatures of up to 350 °C. Travis and Schubert (2005) showed that heterogeneous aqueous alteration on the parent body is possible. Ice accreted with the parent body is expected to have acted as a buffer to short term heating (Grimm and McSween Jr. 1989). When the ice had melted, temperatures in the parent body would have risen. Rising temperatures may explain differences in metamorphic alteration among CCs. This ice buffer may also explain alteration seen in certain inclusions in Allende and Vigarano CV3 (Johnson et al. 1990). Some Dark Lithic Inclusions (DIs) show evidence of aqueous alteration followed by thermal dehydration (Johnson et al. 1990, Kojima and Tomeoka 1996). The melting ice would provide water for aqueous alteration. Once the ice was melted, the heating would lead to thermal metamorphism.

1.2.4.5 Classifying Meteorites

Meteorites are classified based on constituents and mineralogy, which determine chemical group or clan. Meteorites are also classified base on petrologic type, shock stage, and degree of weathering.

1.2.4.5.1 Petrologic Type

The following petrologic type information is taken from Weisberg et al. (2006) unless otherwise stated.
The petrologic type of a meteorite describes how much it has equilibrated and recrystallized. These effects are commonly attributed to thermal metamorphism. In addition, chemical reactions involving water, produce aqueous alteration on the parent body. The scale is mostly used for chondrite meteorites as achondrites are completely recrystallized. The types range from 1-6 and represent differing levels of alteration (Figure 1.11). Type 3 chondrites are thought to represent the most pristine material available. Type 3s have undergone little, if any, aqueous or thermal alteration. Types 3.1 to 6 have increasing degrees of thermal alteration and recrystallization. Types 2 to 1 represent increasing degrees of aqueous alteration. The meteorites in this study are all Type 3 chondrites, indicating they have undergone little to no parent body alteration.

### Petrologic type

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Most pristine</td>
</tr>
<tr>
<td>2</td>
<td>Increasing aqueous alteration</td>
</tr>
<tr>
<td>3</td>
<td>Increasing thermal metamorphism</td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Most thermally metamorphosed</td>
</tr>
</tbody>
</table>

**Figure 1.11.** Petrologic type scale, where 3 is pristine, 1 is the most aqueously altered, and 6 is the most thermally metamorphosed.

1.2.4.5.2 Shock Stage

The following shock information is taken from Stöffler et al. (1991) and Stöffler et al. (2018), unless otherwise indicated.

Shock stage relates to the amount of pressure a meteorite has experienced during impact events. Shock may result from one or more impacts. Shock effects can vary within a meteorite on cm-scales. Shock also affects different minerals to different degrees. Therefore, there are different shock classifications for different types of rocks. Chondrite shock stages increase from C-S1 to C-S7 according to Stöffler et al. (2018). Shock stage is usually determined using optical microscopy, but can be studied using other methods, such as μXRD (Flemming 2007, Izawa et al. 2011, Pickersgill et al. 2015). The meteorites used
in this study are typically of low shock stage. It can be inferred that they may have experienced pressure from less than 4 up to 5 GPa (Stöffler et al. 1991, 2018). They have not melted during impact events nor have they been recrystallized because of shock metamorphism.

1.2.4.5.3 Weathering Grade

The following information about weathering is taken from Wlotza et al. (1993) unless otherwise indicated.

Weathering of a meteorite occurs on Earth. Knowing the degree of weathering can be useful for interpretation of chemical and isotopic data. Weathering can also indicate how long a meteorite had been on Earth before it was found. Weathering affects metals first, then troilite, then silicates. Wlotza et al. (1993), created a weathering scale for ordinary chondrites (Table 1.6). The scale can be used on other chondrite types. The scale is based on weathering effects observed in polished thin sections. The weathering stages range from W0 to W6. W0 is the least weathered and typically describes meteorites that are observed to fall (falls) and recovered immediately. W0 is defined as having no visible oxidation of metal or sulfides. W1 shows minor oxide rims around metal and troilite. Some falls can be W1. W2 shows moderate oxidation of metal, around 20 to 60% of metal being affected. W3 has heavy oxidation of metal and troilite. 60-95% of metal and troilite is replaced with oxidized phases. W4 has complete, >95%, oxidation of metal and troilite. W5 shows mafic silicates beginning to alter, mainly in cracks. Metal and troilite are already replaced in the previous stages. W6 has major replacement of silicates with clay minerals and oxides.

Table 1.6. Weathering stages and the effects seen on metals and sulphides, and silicates.

<table>
<thead>
<tr>
<th>Weathering Stage</th>
<th>Metals and Sulphides</th>
<th>Silicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>W0 (falls)</td>
<td>No visible alteration</td>
<td>No alteration</td>
</tr>
<tr>
<td>W1</td>
<td>Minor oxide rims, troilite present</td>
<td>No alteration</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weathering Stage</th>
<th>Metals and Sulphides</th>
<th>Silicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>W2</td>
<td>Moderate oxidation of metal and troilite (20-60 % alteration)</td>
<td>No alteration</td>
</tr>
<tr>
<td>W3</td>
<td>Heavy oxidation of metal and troilite (60-95 % alteration)</td>
<td>No alteration</td>
</tr>
<tr>
<td>W4</td>
<td>Complete oxidation of metal and troilite (&gt;95 % alteration)</td>
<td>Mafic silicates in cracks beginning to alter</td>
</tr>
<tr>
<td>W5</td>
<td>Complete oxidation of metal and troilite (&gt;95 % alteration)</td>
<td>Major replacement of silicates with clay minerals and oxides</td>
</tr>
</tbody>
</table>

### 1.2.5 Sample Choices

Samples were chosen based on presence of CAIs and petrologic type. Samples were known to have some CAIs, some very large (cm-scale). Samples of petrologic type 3 were chosen. Type 3 meteorites represent the most pristine meteorites. They are the most likely to retain nebular temperatures. One sample, Allende, was chosen despite it having undergone some thermal alteration. This choice was made to ensure measurement of parent body temperature regimes. The samples chosen are all primitive CV3 carbonaceous chondrites. NWA 2364, NWA 6991, NWA 6603, NWA 7678, and NWA 4502 are thought to have undergone little to no thermal metamorphism on a parent body. Allende is also a CV3 carbonaceous chondrite, however, Allende shows evidence of thermal metamorphism. NWA 2364, NWA 6991, NWA 4502, NWA 6603, and NWA 7678 samples are expected to have recorded temperatures close to nebular temperatures. Allende is expected to show lower temperatures consistent with parent body processing.

### 1.2.6 Rationale for Research Approach

μXRD can be used in situ and is therefore non-destructive. This method for identifying spinel is useful as this project uses meteorites, which are rare and valuable materials. The
ability to survey these meteorite samples in situ and non-destructively is important in preserving as much meteoritic material as possible.

Though NMR requires the sample to be powdered, that powder is recoverable after the sample has been examined using NMR. MAS NMR was used to reduce peak broadening in the solid samples. $^{27}$Al MAS NMR shows distinct chemical shifts for tetrahedral and octahedral $\text{Al}^{3+}$. $^{27}$Al MAS NMR is therefore very well suited to directly measure the cation ordering in spinel. $^{27}$Al 3Q MAS NMR is useful in distinguishing the peak locations (chemical shifts) of each Al-bearing phase in the CAIs. As it is better to retain as much CAI material as possible, the ability to separate NMR signals from different phases is important, so dissolution of unwanted phases is unnecessary.
1.3 References


Chapter 2

2 Materials and Methods

Cation-ordering in spinel sampled from CAIs in meteorites was measured using NMR spectroscopy. Samples were procured from a number of people and institutions (described in Section 2.6). This chapter will describe the methods used to find, extract, and analyze spinel from CAIs. Preparation of samples varied, and the preparation of each sample will be described in detail.

2.1 Micro X-ray Diffraction

X-ray diffraction (XRD) is used to determine the crystal structure of materials. In this study the focus of XRD was the identification of minerals. A mineral is defined by an ordered internal atomic arrangement of atoms along with a chemical formula. This atomic arrangement can be determined using XRD. X-rays directed at the samples are of known wavelength and these diffract off lattice planes of atoms in the mineral. Diffraction only occurs when Bragg’s Law of diffraction is satisfied: \( n\lambda = 2dsin\theta \); where \( \lambda \) is the wavelength of the incident radiation (CoK\( \alpha \) = 1.78897 Å), \( n \) is assumed to be 1, and \( d \) is the perpendicular distance between lattice planes. The theta value(s) is/are determined by the geometry of the instrument (Figure 2.1).

MicroXRD (\( \mu \)XRD) was done on a Bruker D8 Discover Microdiffractometer in Dr. Roberta Flemming’s Lab in the Department of Earth Sciences at Western University, London, Ontario, Canada. The diffractometer uses a Co X-ray source (CoK\( \alpha \) \( \lambda \) = 1.7889 Å), a 60 mm Cobalt Gobel mirror, and a 300-micron nominal beam diameter (Figure 2.2). The microdiffractometer has a Vantec-500 two-dimensional detector, which uses General Area Detector Diffraction System (GADDS) software. The beam diameter will change as a function of take-off angle according to simple trigonometry. The source angle relative to the sample is called \( \theta_1 \) and the detector angle relative to the sample is \( \theta_2 \). \( \theta_1 \) plus \( \theta_2 \) is the
observed 2θ angle in the center of the diffraction pattern (Figure 2.1). Radiation was generated at 35 kV and 40 mA.

Using μXRD, the samples can be tested in situ with a small (300 μm) beam diameter. Having theta-theta geometry, the sample remains horizontal while the source and detector are rotated clockwise around the sample, mounted on an XYZ stage. The stage is drive-able in X, Y, and Z-directions to center the sample and provide the capability of running more than one sample at a time. The stage has 10 cm of working space in the Y-direction. This space allows the user to line up multiple samples in the Y-direction and test them all in the same run. The drive-able stage has a positional accuracy of 12.5 μm (Flemming 2007). Using μXRD, any sample can be placed on the stage: a single crystal, a powder, a rock containing several minerals, meteorites, etc. The 2D detector provides information about the grain size and strain of the samples. Samples of small grain sizes such as powders will produce complete cones of diffraction, giving spotty rings to solid rings on decreasing

\[ \theta_1 + \theta_2 = 2\theta \]

Figure 2.1. Left: Schematic diagram of microdifractometer showing X-ray source (beam) and collimator (1, incident X-ray beam), detector (2, diffracted X-ray beam), and stage (3). The diagram shows how 2θ is calculated based on the geometry of the diffractometer. Right: Schematic of a GADDS frame image showing 2θ is the center of the detector. The range of the scan goes from 2θ ± the radius of the detector (r). The value of 2θ remains constant during each frame, as the source and detector are moving at the same rate clockwise around the stage.
grain size. In these types of samples, all possible lattice planes will be detected. In the case of a single crystal, it is possible that not all lattice planes will be detected as they may not all be visible to the X-rays in their *in situ* orientation. These omissions can be mitigated by using the Omega scan method, where the source and detector both rotate clockwise around the sample within a limited range of angles, mimicking sample rotation. This allows other lattice planes to satisfy Bragg’s law as more orientations are moved through.

Data were collected using omega scan mode (see exact parameters in sample sub sections). Omega scan is a type of scan that emulates rotating the sample. The rotation is accomplished by moving the X-ray source (beam) and detector around the sample. The beam and detector rotate clockwise at the same rate. The beam moves up, while the detector moves down. Both move through the same amount of space. This distance is measured in degrees and is represented by the omega symbol (ω). The diffraction pattern ranges from this angle plus or minus the radius of the detector (25 degrees 2θ at a 12 cm distance) (Figure 2.1). Parameters for μXRD in this project describe two frames collected by the omega scan function. For a 50° 2θ detector to collect from 10-110° 2θ, one must collect two frames of data with some overlapping degrees of 2θ. This is done by changing θ₁ and θ₂ over two runs on the same target location. This produces two different values of 2θ, one higher and one lower, which creates the high and low 2θ frames (Table 2.1). The frames can be stitched together to give a larger range of 2θ values than one frame. Values of 2θ can be varied between experiments depending on the d-spacings of the expected minerals. θ₁ and θ₂ are the starting angles for
the source and detector, respectively. \( \omega \) is the number of degrees through which the beam and detector will move. The time is the total collection time for the frame.

**Table 2.1. Example set up of a two-frame run on the \( \mu XRD \).** Theta values are ones that are commonly used for data collection with the set up in Flemming’s Lab. Range is calculated using \( 2\theta \pm 25^\circ \), where \( 25^\circ \) is the radius of the Vantec 500 detector used at the 12 cm distance used in the set up in this lab.

<table>
<thead>
<tr>
<th>Frame</th>
<th>( \theta_1 )</th>
<th>( \theta_2 )</th>
<th>( 2\theta )</th>
<th>Range ((2\theta \pm 25^\circ))</th>
<th>Total range of stitched frames</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.5</td>
<td>20.5</td>
<td>34.5</td>
<td>9.5 to 59.5</td>
<td>9.5 to 105</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>40</td>
<td>80</td>
<td>55 to 105</td>
<td></td>
</tr>
</tbody>
</table>

XRD analyses were done using the DIFFRAC.SUITE EVA (EVA) software (Bruker-AXS 2010-2016, 2016 release) and the International Centre for Diffraction Data (ICDD) database. EVA enables the integration of imported GADDS detector images to produce conventional intensity versus \( 2\theta \) diffractograms. The phases can then be identified by matching to known sample diffraction patterns from the ICDD database. The composition of the mineral on the selected ICDD card is not necessarily the same as the composition in the mineral. There is a correlation between the composition and structure or unit cell of a mineral, however, XRD does not measure chemical composition.

\( \mu XRD \) was used to identify CAIs containing spinel in meteorite samples and to identify other phases present in the samples before NMR spectroscopy. CAIs were identified by their mineralogy. CAI mineralogy is very different from matrix on chondrule mineralogy. CAIs contain spinel, fassaite, gehlenite (melilite), and other phases. Matrix and chondrules are rich in olivine and pyroxene, not seen in CAIs. The minerals are identified structurally using XRD. The mineralogy of CAIs varies based on type of CAI. Identification of these phases enabled the collection of the correct standards for NMR spectroscopy. Phases identified using \( \mu XRD \) include spinel, fassaite, gehlenite, grossular, and anorthite; though not all were present in every sample. Samples from this project included powders, slabs/slices, and pieces of meteorites.
2.2 Heavy Liquids Density Separation

Heavy Liquids Density Separation (HLDS) is used to separate components of a powdered mixture. Liquids of different densities are used to create fractions of the original material that are of specific densities. The material to be separated is placed in a centrifuge or microcentrifuge tube with one or more liquids of known density. The vial is centrifuged to thoroughly mix the materials and the liquids. As the sample settles post-mixing, the liquids will form layers. The sample to be separated will settle into the layers corresponding to their density. In this project, the sample sizes (<1 g) required the use of a microcentrifuge. The heavy liquid of importance is methylene iodide with a density of 3.2 g/cm³. The fraction used was the fraction of greater than 3.2 g/cm³ density. The separations were done only on NWA 2364 and NWA 6991 by Dr. Audrey Bouvier (Bouvier and Wadhwa 2010, Bouvier and Boyet 2016).

2.3 Micro Computed Tomography

Micro Computed Tomography (μCT) scans allow high resolution 3-D imaging of a sample. The scans provide structural and density information. μCT is a small-scale version of CT scans used for medical imaging. It is a non-destructive technique. X-rays are focused on the sample and a detector collects the X-ray images. The imaging is done at various angles by rotating the sample or the X-ray source. Virtual slices of the sample are created in a computer from the X-ray images, which can be scrolled through on a 3-D model of the sample.

Scans of NWA 4502 collected at Dr. David Holdsworth’s Lab in Robarts Imaging at Western University by Dr. Joseph Umoh for Dr. Melissa Strait. Scans were used to help determine cut locations for the sample by locating large inclusions. μCT scans were done on a GE eXplore speCZT. Collection parameters used were defined by McCausland et al. (2010) and Charles et al. (2018). Collection energies ranged from 80 – 110 kV. Scans were 900 separate images over one full 360° rotation. The X-ray source rotates a full 360° around the sample mount. Detector is a CdZnTe array surrounding the sample. Scan files were viewed and manipulated using MicroView software.
2.4 Wire Saw

The wire saw located in the Department of Earth Sciences at Western University was used to cut samples to search for CAIs. Two cuts were made on NWA 4502. The cuts were made dry, with a 0.180 mm thick wire. The cut location was lubricated with blowing air. The sample is clamped and surrounded by foil to protect the sample and collect off cut material. The wire makes its cut by bowing and attempting to return to straight. The system holding the wire moves down as the bow straightens to keep the wire bowed. A sensor on the system determines the angle of the wire and the system uses this information to determine when to move down as the wire straightens.

2.5 Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy

As detailed in Chapter 1, NMR spectroscopy probes the atomic structure of and bonding in materials. NMR can differentiate between the different atomic environments around an element. This differentiation is accomplished by placing the sample in a strong magnetic field (21.1T) achieved using a super conducting magnet. There, atoms in different environments will be exposed to different apparent magnetic fields. The system is disturbed by a pulse and the response is measured. The resulting spectra show the different chemical environments of the active nucleus as different chemical shifts.
Al MAS NMR spectroscopy was done on a Bruker Avance II 21.1T (900 MHz) NMR spectrometer located at the National Research Center in Ottawa, Ontario, Canada, with the help of Dr. Victor Terskikh (Figure 2.3). $^{27}$Al MAS NMR was used to determine the environment around Al atoms in the spinel. The technique enables the determination of the relative amounts of tetrahedral and octahedral Al, which enables calculation of the spinel inversion parameter, $x$. Samples were run with the same parameters to ensure they were comparable to one another. One-dimensional $^{27}$Al MAS NMR spectra (Figure 2.4 top) were collected at a spinning frequency of 31.25 kHz, with a pulse width of 0.5 μs which produced a tip angle of $30^\circ$ ($\pi/6$) to the solid. Spectral width was 100 kHz for the MAS NMR spectra. Multiple scans were acquired with a relaxation delay of 5 seconds. Parameters were tested before collection. They were tested to ensure quantitative data by testing various delay times. Two-dimensional $^{27}$Al triple quantum (3Q) MAS NMR spectra (Figure 2.4 bottom) were collected at a spinning frequency of 31.25 kHz. They were rotor-synchronized in the F1 dimension ($^{27}$Al MAS NMR dimension). Two dimensional $^{27}$Al 3Q MAS NMR spectra were collected using a standard 3-pulse experiment. The experiment used a zero quantum filter (Amoureux et al. 1996). Spectral width for roto-synchronized samples was 100 kHz in the MAS NMR (F1) dimension and 31.25 kHz in the isotropic (F2) dimension. NWA 6603 was not rotor-synchronized in F1 due to broad resonances. The spectral width for NWA 6603 was 100 kHz in the MAS NMR (F1) spectra and 125 kHz in the isotropic (F2) dimension. In all 3Q MAS NMR experiments, the $P_1$ excitation pulse was 2.6 μs. The $P_2$ conversion pulse was 0.9 μs. The $P_3$ 90-degree soft selective pulse was 10 μs. Number of scans and t1 increments varied (Table 2.2). Each t1 time increment lasted 32 μs.
For NWA 6603 the number of scans collected was 6400. The total collection time was four days 20 hours. For NWA 6991 and NWA 2364 the number of scans collected was 1800. The total collection time was two days and 16 hours. For Allende 3529 the number of scans collected was 960 with a relaxation delay of 2 seconds. Total collection time was one day. Allende TS62b had 2160 transients collected over 72 t1 increments, with a relaxation delay of 2 seconds. $^{27}$Al NMR spectroscopy chemical shift reference was 0.5 mol of AlCl$_3$(aq) at 0 ppm.

NMR analyses were done using Topspin and DMfit. Topspin was used at the High Field NMR facility in Ottawa, Ontario, Canada for the initial Fourier Transformation processing of the collected Free Induction Decays (FIDs). DMFit was used on the transformed spectra (Massiot et al. 2002). $^{27}$Al MAS NMR fits were modelled using quadrupolar parameters, and the models were integrated to determine the area under the peaks, which is quantitative in the one-dimensional $^{27}$Al MAS NMR spectra under the previously described acquisition parameters. Two-dimensional $^{27}$Al 3Q MAS NMR spectra were acquired by performing a triple quantum experiment.

Table 2.2. Number of scans and t1 increments for each CAI sample examined with $^{27}$Al 3Q MAS NMR spectroscopy

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total t1 increments collected (td1)</th>
<th>Number of Transients per t1 increment (ns)</th>
<th>Relaxation Delay (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende 3529</td>
<td>24</td>
<td>960</td>
<td>2</td>
</tr>
<tr>
<td>Allende TS62b</td>
<td>72</td>
<td>2160</td>
<td>2</td>
</tr>
<tr>
<td>NWA 2364</td>
<td>64</td>
<td>1800</td>
<td>2</td>
</tr>
<tr>
<td>NWA 6991</td>
<td>64</td>
<td>1800</td>
<td>2</td>
</tr>
<tr>
<td>NWA 6603</td>
<td>64</td>
<td>6400</td>
<td>1</td>
</tr>
</tbody>
</table>
3Q MAS NMR used in this study produces a spectrum of MAS NMR versus the isotropic interactions (Figure 2.4). In the isotropic dimension of the spectrum, the anisotropic effects are removed. These effects produce broadening; thus, the resulting spectrum has better resolution. The pulse sequence is designed to remove the effects by averaging anisotropic interactions. Averaging is done by using different evolution times between pulses. This controls the direction of the magnetic fields, which can be cancelled by interference. The isotropic dimension is a combination of isotropic chemical shift and a shift produced by second order quadrupole interactions (Kentgens 1997, Flemming et al. 2015). The relationship between these is linear and falls on a 1:1 diagonal. Spectra were displayed and stacked in DMFit to determine peak locations for the different phases (Figure 2.4).
Figure 2.4. Top: MAS NMR spectrum of NWA 2364 Bottom: Two-dimensional NMR spectrum of NWA 2364. F2 axis is the MAS NMR dimension and F1 axis is isotropic dimension, 1:1 diagonal displayed.
2.6 Sample Preparation

Six meteorite samples were used: Allende, NWA 2364, NWA 6991, NWA 4502, NWA 6603, and NWA 7678. Each sample was prepared for NMR spectroscopy by a different set of methods.

Meteorite information is taken from the Meteoritical Bulletin unless otherwise indicated.

2.6.1 Allende

Allende fell in 1969 in Mexico. It was a fall, which means its fall was observed. The fireball was seen in Northern Mexico and the Southwestern United States, travelling south to north. The meteorite shower covered over 50 square km of area. The fallen meteorite was found in the village of Pueblito de Allende, Chihuahua, Mexico, after which it was named. Two tonnes of materials were collected. Allende has been classified as a CV3 by Dr. E King (NASA), Dr. B Masin and Dr. R Clark (Smithsonian).

Allende samples used in this project were procured from Dr. Tim McCoy at the Smithsonian Institution, Washington, D.C., USA (USNM 3529), originally for use in a fassaite crystal structure project by Monika Haring at UWO in 2011-2012. Additional material was procured from Dr. Carl Agee at the Institute of Meteoritics (IOM) at the University of New Mexico (UNM) Albuquerque, New Mexico, USA.
2.6.1.1 Allende 3529

Allende 3529 was loaned by Dr. Tim McCoy and the Smithsonian Institute (USNM), Washington DC, USA. The sample was a whole CAI that was crushed to a coarse powder. The NMR data for this sample were collected by Haring et al. 2012. Hand separation under ethanol was done of this sample. However, because of the small sample size, there was not enough material in the separated fraction to collect NMR spectra. μXRD data were collected on Allende 3529 powder (Figure 2.5) for phase identification. Collection was done on the Bruker D8 Discover Microdiffractometer (Table 2.3).

Table 2.3. Table showing the parameters used to collect the XRD data for Allende 3529.

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 2017</td>
<td>14.5</td>
<td>21</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Frame 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Frame 2</td>
<td>33.5</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>May 2016*</td>
<td>14.5</td>
<td>40</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Frame 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Frame 2</td>
<td>33.5</td>
<td>40</td>
<td>18</td>
</tr>
</tbody>
</table>

[A new detector was installed after the first run. Data collected with the new detector were consistent with the previous data]
Allende 3529 is a whole CAI that was crushed for NMR spectroscopy with no separation of phases. The sample preparation was done in 2012 (Haring 2013).

2.6.1.2 Allende TS62b

Allende TS62b was loaned by Dr. Steve Simon (now at the IOM) and Dr. Lawrence Grossman from the University of Chicago, Chicago, Illinois, USA. The sample had been hand-picked from a thin section of a large Allende CAI, to attempt to isolate the fassaite (Figure 2.6). This sample was used as one of the NMR standards, discussed later. Table 2.4 lists XRD parameters.

![Figure 2.6. Allende TS62b thin section, the thin section has been carbon coated.](image)

Table 2.4 Table showing the parameters used to collect the XRD data for Allende TS62b.

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 2014</td>
<td>15</td>
<td>25.5</td>
<td>15</td>
<td>45</td>
</tr>
<tr>
<td>Frame 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frame 2</td>
<td>38.5</td>
<td>40</td>
<td>15</td>
<td>75</td>
</tr>
</tbody>
</table>

2.6.1.3 Allende Cr 3.17 and Allende Cr 3.7c

Allende Cr 3.17 and Allende Cr 3.7c (Allende Cr samples) were loaned by Dr. Carl Agee at the University of New Mexico in Albuquerque, New Mexico, USA (Figure 2.7 and Figure 2.8). The samples were fragments from multiple cycles of freeze-thaw disaggregation done in 2011. The samples were thought to be CAIs. They consisted of a number of fragments in petri dishes. Fragments appeared black on the outside, with some having a bright white interior. The bright white interior was thought to be the CAIs. Samples were broken open to reveal a fresh white face. Samples were mounted on thin sections using Crystal Bond. The mounted samples were then tested using μXRD (Table 2.5).
Figure 2.7. Allende Cr samples, left Allende Cr3.7c and right Allende Cr3.17.

Figure 2.8. Samples of Allende Cr3.7c CAIs.
Table 2.5. Parameters used to collect μXRD data for Allende Cr samples

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 2016</td>
<td>14.5</td>
<td>22</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Frame 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frame 2</td>
<td>35.5</td>
<td>40</td>
<td>18</td>
<td>25</td>
</tr>
</tbody>
</table>

2.6.2 Tagish Lake C2

The Tagish Lake meteorite fell on January 18, 2000 in Canada. It was a fall. The fireball was seen in the Yukon Territory and northern British Columbia. The strewn field was on Tagish Lake in BC. Collection was done by a team from Western University and the University of Calgary. Ten kilograms of the meteorite was collected. Tagish Lake was classified as an ungrouped C2 carbonaceous chondrite. Classification was done by M. Zolensky at the Johnson Space Center, and M. Grady of the Natural History Museum. Tagish Lake C2 is described as matrix rich, with a few small chondrules and other inclusions, including CAIs. The matrix is mostly phyllosilicates, sulphides, and magnetite. Fe, Ca, and Mg carbonates are all common. The shock stage is C-S1 and the weathering stage is W0 (fall).

Four Tagish Lake C2 samples from the meteorite collection at Western University were examined. The samples were HG 48a, HG 48b, PM 032, and MM01 26c. HG48a and HG48b are small samples of inclusion-rich Tagish Lake. The samples are approximately 1 cm sized. MM01 26c is a large sample of inclusion-rich Tagish Lake, about 2 cm x 1 cm in size. MM01 26c contains an unusual clast. The clast colour is similar to the matrix, but appears more physically compact and consolidated. The clast also contains fewer inclusions than the matrix. PM 032 is a large inclusion rich sample of Tagish Lake. It is roughly 3 cm x 2 cm in size. The matrix of all four samples is fine-grained black to dark-grey in colour. Visually the inclusions appear similar. They are white to grey colour and of various shapes and sizes. Tagish Lake samples are very friable. These samples were all mounted using tinfoil to prevent contamination. The samples were examined by μXRD on the Bruker D8 Discover Microdiffractometer with 60 mm Colbalt Gobel mirror and a 300
μm beam diameter. Parameters for each sample are summarized in Table 2.6, Table 2.7, and Table 2.8.

Figure 2.9. Tagish Lake Samples HG48a, HG 48b, and MM01 26c.

Figure 2.10. Tagish Lake PM 032.
Table 2.6. μXRD parameters for HG 48a and HG 48b

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
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<tr>
<td>February and March 2017</td>
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<td>21</td>
<td>10</td>
<td>45</td>
</tr>
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<td></td>
</tr>
<tr>
<td>Frame 2</td>
<td>33.5</td>
<td>40</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 2.7. μXRD parameters for MM01 26c

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>April 2017</td>
<td>14.5</td>
<td>21</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Frame 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frame 2</td>
<td>33.5</td>
<td>40</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 2.8. μXRD parameters for PM 032. Sample is bumpy, so higher angles were chosen to avoid X-rays being blocked by bumps. Spot 1 and 4 were run for shorter times (20 and 30 minutes for the first and second frame respectively).

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 2016</td>
<td>21</td>
<td>22</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Frame 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frame 2</td>
<td>40</td>
<td>40</td>
<td>13.5</td>
<td>45</td>
</tr>
</tbody>
</table>

2.6.3 NWA 2364 and NWA 6991

Northwest Africa (NWA) 2364 was found in 2004 at an unknown location in Northwest Africa. It was a find, which means its fall was not observed. Recovered mass was 1493 g from 18 pieces. NWA 2364 is a CV3 chondrite, classified by Ted Bunch at Northern Arizona University. It has a shock stage of 2 and a weathering grade of 4. This weathering
grade is higher and means most or all the metallic iron and primary sulphides have been replaced by oxides. It had been noted to have an Allende-like matrix.

NWA 6991 was found in 2010 at an unknown location in Northwest Africa. It was a find. Recovered mass was 487 g from a single stone. NWA 6991 is classified as a CV3 chondrite, by Lawrence Garvie at Arizona State University. It has a low shock stage and a low weathering grade. Petrography is described by Lawrence Garvie as chondrules poor in iron oxide, set in a fine-grained matrix.

The NWA 2364 and NWA 6991 samples used in this project were provided by Dr. Audrey Bouvier and are on loan from Dr. Garvie at Arizona State University, Phoenix, Arizona, USA and Dr. Ebel at the American Museum of Natural History, New York, New York, USA, respectively. Both samples are coarse powders of individual CAIs from these meteorites, “The Crucible” CAI from NWA 2364 (Figure 2.11) and CAI B4 from NWA 6991 (Figure 2.12). The samples we received had been separated using heavy liquids density separation by Bouvier et al. 2016. The fraction we received was the methylene iodide fraction, >3.2 g/cm³.

NWA 2364 (5 mg) has undergone no further separation. NWA 6991 (13.7 mg) was hand separated under ethanol into two fractions, a light coloured (white, 12.7 mg) and a dark

![Figure 2.11. NWA 2364 powder. Images taken on microdiffractometer, left is zoomed in, right is zoomed out for context.](image-url)
coloured (black, ~8.6 mg) fraction. This separation was done to further isolate spinel from the other CAI phases. μXRD was collected on NWA 2364 and NWA 6991 (Table 2.9).

![Image](image1.png)

**Figure 2.12. NWA 6991 powder.** Images taken on microdiffractometer, left is zoomed in, right is zoomed out for context. Image was taken prior to hand separation of sample.

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
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</thead>
<tbody>
<tr>
<td>August 2017</td>
<td>14.5</td>
<td>20.5</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>Frame 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frame 2</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>

**Table 2.9 Parameters used to collect μXRD data for NWA 2364 and NWA 6991**

2.6.4 NWA 4502

NWA 4502 was found in December 2005 in Algeria. It was not an observed fall. Recovered mass was 100 kg from many pieces of dark stones. NWA 4502 was classified as a CV3 chondrite by M. S. Sapah and A. N. Krot. It has a shock stage of 2 and a weathering grade of 1. Petrography done by Ted Bunch and J Wittke at Northern Arizona University, describes well defined chondrules and refractory inclusions in a slightly weathered matrix. Type A and Type C CAIs and Ameboid Olivine Aggregates (AOAs)
are common. The estimated modal volume percentages are chondrules at 48%, CAIs and AOAs at 14%, and Matrix 38%.

NWA 4502 samples are on loan from Dr. Kim Tait at the Royal Ontario Museum, Toronto, Ontario, Canada (NWA 4502 ROM) and from Dr. Melissa Strait at Alma College, Alma, Michigan, USA (NWA 4502) (Figure 2.13 and Figure 2.14). Micro Computed Tomography scans of the NWA 4502 sample were collected at Western University. The CT scans were provided by Dr. Melissa Strait and aided in the selection of locations to cut the sample using a wire saw. The sample has also been artificially shocked in a previous study, leading to numerous cracks throughout the sample. The instantaneous shock is unlikely to have altered the cation ordering, given that the shock did not produce any melt. μXRD data were collected on the sample (Table 2.10) and do not show any evidence of

Figure 2.13. NWA 4502 ROM sample from Dr. Kim Tait.

Figure 2.14. NWA 4502 sample from Dr. Melissa Strait, prior to cutting.
melting or highly shocked phases. The shock experiments are completed on small time scales of seconds. It is unlikely that any heat produced from the shock would remain long enough to significantly affect cation ordering, which takes minutes to reach equilibrium (Andreozzi and Princivalle 2002).

Table 2.10. Parameters used for collecting $\mu$XRD data for NWA 4502

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<tr>
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2.6.5 NWA 6603 and NWA 7678

NWA 6603 was found in 2006 at an unknown location in Northwestern Africa. It was a find. Recovered mass was 481 g in a single piece. NWA 6603 is a CV3 chondrite, classified by K. Metzler, Institute for Planetology, University of Münster. It has a shock stage of C-S1 and a weathering grade of W2. It was described as having chondrules and CAIs in a dark matrix. It has magnetite because of weathering. It is part of the oxidized CV3 subgroup.

NWA 7678 was found in 2012 in Morocco. It was a find. Recovered mass was 4.24 kg in 182 pieces. NWA 7678 is a CV3 chondrite, classified by Dr. Carl Agee at the University of New Mexico. It was described as having most of the iron oxidized by weathering and having abundant troilite. Thus, it is likely a weathering grade of W3 or W4. It also likely has a low shock stage like most CV3s (Brearley and Jones 1998).

Two NWA 6603 samples (1-92 and 16-7) were purchased online from the Meteorite Market (Figure 2.15). Both samples are slices with at least one large white inclusion and several smaller white inclusions. One slice of NWA 7678 was purchased online from the Meteorite Exchange (Figure 2.16). The sample has one large white inclusion and some
smaller white inclusions. The samples were examined using μXRD (Table 2.1). Spinel-bearing CAIs were identified visually and by μXRD structural analysis. Visually, bright white and irregularly shaped inclusions were chosen for examination by μXRD. The μXRD results confirmed the presence or absence of spinel and other CAI phases.

A CAI was picked out of the sample (NWA 6603 1-92) using dental picks. Picking was done under ethanol. A magnet was used to remove any magnetite from the picked material. NWA 6603 1-92 was chosen because the CAI was large and located at the edge of the slice.

Figure 2.15. NWA 6603 samples, the small slab NWA 6603 1-92 is on the left, the large NWA 6602 16-7 is on the right. The large CAI shown on the left image (lower right) was extracted for NMR. (Photo of NWA 6603 1-92 was taken by Eric Twelker of the Meteorite market, and used with his permission.)
The location provided a good surface for picking out the CAI without much matrix contamination.

Table 2.11. µXRD parameters used for NWA 6603 and NWA 7678

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Figure 2.16. NWA 7678 slice. (This photo was taken by Eric Twelker of the Meteorite Market and used with his permission.)
2.6.6  NMR Standards

Standards for use in identifying phases in NMR spectra were chosen using data from \( \mu \)XRD. Standards were from different sources and prepared by various methods as detailed here (see Appendix B for XRD and NMR characterization of standards).

2.6.6.1  Fassaite Standard

The fassaite standard used was fassaite from the Allende meteorite as extracted by Simon and Grossman (see section 2.7.1.2 for details). The standard NMR data were collected by Monika Haring in 2011/2012 for her thesis (Haring et al. 2012, Haring 2013). Results showed that meteoritic fassaite was more ordered and distorted than Earth fassaite (Haring et al. 2012, Haring 2013). These differences are one reason we chose to use Allende fassaite as our standard as our application was also meteoritic. Because the Allende TS62b fassaite is not pure fassaite, a second standard was used for fassaite: synthetic \( \text{Di}_{75}\text{CaT}_{25} \) (RM 009D). This standard only has one-dimensional \( ^{27}\text{Al} \) MAS NMR data. It is a synthetic solid solution of diopside (\( \text{CaMgSi}_2\text{O}_6 \)) and Ca-Tschermak clinopyroxene (\( \text{CaAlAlSiO}_6 \)) (Flemming and Pawsey 2008). This composition is a fair approximation of fassaite, which is an aluminous diopside. The one-dimensional data for this standard were used to separate fassaite peaks from contamination in the Allende TS62b fassaite standard.
2.6.6.2 Spinel Standard

Two spinel standards were used during this project: a synthetic spinel and a natural spinel. The synthetic spinel was synthesized by Melissa Quinlan for Dr. Roberta Flemming at Queens University in 2000. It is known to be pure MgAl$_2$O$_4$. The natural spinel standard is DANA collection #4305 from Myanmar (Figure 2.17), donated by Greg Hutton in 2016. The natural standard is pink in colour. The sample was ground by hand in an agate mortar and pestle for 30-40 minutes. μXRD shows the powdered sample is structurally similar to pure MgAl$_2$O$_4$.

2.6.6.3 Grossular Standard

Two grossular standards were collected. One is a natural sample, the other a synthetic sample. The natural grossular standard was chosen from the DANA collection at Western University (DANA #3209 from Chihuahua, Mexico) and is light green in colour (Figure 2.18). The sample was ground by hand using an agate mortar and pestle for one hour. μXRD of the powdered sample shows it is structurally similar to grossular containing Fe and/or Ti; it matched with ICDD card PDF 75-1681 with formula (Ca$_{2.87}$Fe$^{2+}_{0.13}$)(Al$_{1.61}$Ti$_{0.07}$Fe$^{3+}_{0.28}$)Si$_3$O$_{12}$. The synthetic grossular was synthesized by Roberta Millard in 1997. A small amount of sample powder remains from experiments done in 1999. The sample is Ca$_3$Al$_2$Si$_3$O$_{12}$.
grossular, synthesized from a glass of that composition at 6 GPa and 1200 °C for 8 hours. μXRD confirmed the grossular structure.

2.6.6.4 Gehlenite

The gehlenite standard is a natural sample chosen from the DANA collection at Western University (DANA #3461 from Crestmore, California) (Figure 2.19). The sample was examined as part of Sarah McFadden’s undergraduate thesis project in 2016. This project examined melilite, end members gehlenite and akermanite, and showed the chosen gehlenite was closest to pure end member gehlenite. The sample was ground by hand using an agate mortar and pestle for about 40 minutes. The sample is a poly-minerallic rock from which crystals were picked. μXRD showed it also contained monticellite and calcite, and some grossular was found in the rock (see Appendix B).

2.7 Samples Summary

The following tables summarize the sample information (Table 2.12) and the methods used on each sample (Table 2.13).

Table 2.12. Summary of sample information – who/where sample is from, location of meteorite fall or find and reasons for selecting the meteorite

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<th>Sample Name</th>
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<th>Location</th>
<th>Selection</th>
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<td>Loaned by Dr. Tim McCoy, USNM, Washington, DC</td>
<td>Allende, Mexico</td>
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</tr>
<tr>
<td>Sample Name</td>
<td>From</td>
<td>Location</td>
<td>Selection</td>
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<td>----------------------------------------------------------------------</td>
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<td>Allende Cr Samples</td>
<td>Loaned by Dr. Carl Agee, UNM, New Mexico</td>
<td>Allende, Mexico</td>
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<td>Allende ts62b</td>
<td>Loaned by Dr. Steve Simon (IOM) and Dr. Lawrence Grossman (U of Chicago)</td>
<td>Allende, Mexico</td>
<td>CV3, CAIs, some thermal alteration, Fassaite used as NMR standard</td>
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Table 2.13. Methods and techniques used on each sample.

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*NWA 6991 and NWA 2364 were given to us as separated CAI samples – the CAIs were extracted, but not during this project.*

*(1)* Heavy Liquids Density Separations were done by Bouvier and Boyet 2016 and Bouvier and Wadhwa 2010.
2.8 References


Haring, M.M. 2013. Crystal structure and Al/Si cation ordering in “Fassaite”: A combined single crystal, $^{27}$Al and $^{29}$Si NMR study. The University of Western Ontario.


Chapter 3

3 Nebular Temperatures Using Cation Ordering from a CAI from NWA 6603 CV3 by $^{27}$Al Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy

3.1 Executive Summary

Two samples of NWA 6603 were examined in situ with µXRD in search of spinel-containing CAIs. Two CAIs were found, one in each sample. The CAI in NWA 6603 1-92 was chosen for extraction because of its large (~0.5 cm) size and ideal location (edge of the cut piece). After successful extraction, $^{27}$Al MAS NMR was collected to measure the cation ordering in the spinel (~MgAl$_2$O$_4$). Literature calibration curves were used with cation ordering information to calculate nebular temperature estimates of 1173 to 1675 K. These temperatures bracket those expected in the early nebula and they are higher than expected for processing in planetary bodies. These temperatures likely represent nebular formation or nebular processing temperatures, from subsequent high temperature nebular heating events.

3.2 Introduction

To understand how the solar system formed we have to look at materials that formed early in the solar system. Calcium-Aluminium-Rich Inclusions (CAIs) are the oldest materials in the solar system (Grossman 1972, Brearley and Jones 1998, McSween Jr. 1999, Ivanova 2016). They have been dated to 4, 567.9 ± 0.3 My (Bouvier and Wadhwa 2010). CAIs can provide a window into the conditions during the early solar system.

CAIs consist of four main minerals: spinel, fassaite, gehlenite (melonite), and anorthite (Grossman 1972, Brearley and Jones 1998, Ivanova 2016). They are divided into types based on mineralogy and grain size (Brearley and Jones 1998, Ivanova 2016). Different types are considered to have undergone different amounts of processing (McSween 1977, Ivanova 2016). Coarse-grained CAIs are considered altered from their original formation in the nebula (McSween 1977, Bullock et al. 2014, Johnson et al. 2017). “Fluffy”, fine-grained Type As are considered closest to nebular condensates (McSween 1977, Ivanova ...
Coarse-grained CAIs can be Type A, B, or C, based on mineralogy (Ivanova 2016). Type A CAIs are rich in gehlenite and spinel (Brearley and Jones 1998, Ivanova 2016, Rubin and Ma 2017). Type B CAIs are rich in gehlenite, fassaite, and spinel, with some anorthite (Brearley and Jones 1998, Ivanova 2016, Rubin and Ma 2017). They are considered to be recrystallized from a melt (Brearley and Jones 1998, Ivanova 2016, Rubin and Ma 2017). Type C CAIs are rare; they are rich in fassaite and anorthite (Brearley and Jones 1998, Ivanova 2016, Rubin and Ma 2017).

CAIs are found as inclusions in chondrite meteorites. CAIs in CV3 type carbonaceous chondrites (CCs) are some of the largest (Brearley and Jones 1998, Ivanova 2016). CV CCs display a range of degrees of alteration (Brearley and Jones 1998). CV3s are petrologic Type 3. This type is the most pristine, with little thermal or aqueous alteration (Weisberg et al. 2006). These types of CCs should record early solar system processes, and the high temperature record should be relatively unaltered (Kerridge 1993, McSween Jr. 1999, Ivanova 2016).

CAIs are considered to be condensates from the early solar nebula (Grossman 1972). They may also undergo subsequent processing (Kerridge 1993, McSween Jr. 1999). This processing could happen in the nebula or on the parent body (Kerridge 1993, Brearley and Jones 1998, Bolser et al. 2016). After the CAIs condense, they accrete with other early solar system materials (Goldreich and Ward 1973, Montmerle et al. 2006). These materials accrete into planetesimals or parent bodies (Goldreich and Ward 1973, Montmerle et al. 2006). On these planetesimals the CAIs can be subjected to thermal metamorphism and/or aqueous alteration (Weisberg et al. 2006).
Spinel (MgAl$_2$O$_4$) is commonly found in CAIs (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016, Rubin and Ma 2017). It has a cubic closest packed structure of oxygen anions (Figure 3.1) (Klein and Dutrow 2007). There are tetrahedral and octahedral sites between the oxygen anions (Klein and Dutrow 2007).

In a *sensu stricto* Mg$^{2+}$ and Al$^{3+}$ cations substitute into these sites (Navrotsky 1994, Klein and Dutrow 2007). In an ordered normal spinel, the tetrahedral sites are populated only by Mg$^{2+}$. The Al$^{3+}$ goes into the octahedral sites (Navrotsky and Kleppa 1967, O’Neill and Navrotsky 1983, Navrotsky 1994, Klein and Dutrow 2007). In a hypothetical, inverse ordered spinel, these are reversed (Navrotsky 1994). The Al$^{3+}$ would occupy all the tetrahedral sites. The Mg$^{2+}$, of which there is less, goes into the octahedral sites. Al$^{3+}$ fills the remaining octahedral sites. A disordered spinel is anything in between normal ordered and inverse ordered (Navrotsky and Kleppa 1967, O’Neill and Navrotsky 1983, Navrotsky 1994). The disorder is represented by the inversion parameter, $x$. $x$ is the amount of Al$^{3+}$ in the tetrahedral site, as in $[\text{Mg}_{1-x}\text{Al}_x\text{]}^{6}\text{[Al}_{2-x}\text{Mg}_x\text{]}\text{O}_4$ (Navrotsky and Kleppa 1967, O’Neill and Navrotsky 1983, Millard et al. 1992, Navrotsky 1994). In an ordered normal spinel $x = 0$. In an inverse ordered spinel $x = 1$. Anything from $0 < x > 1$ is a disordered spinel.

**Figure 3.1.** Ball and stick structure of spinel. The octahedral site cation is blue, and the tetrahedral site cation is black. Oxygen anions are represented by white circles. Modified from Morimoto et al 1969.
$^{27}$Al Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectroscopy can be used to directly measure $x$ (Wood et al. 1986, Millard et al. 1992). $^{27}$Al MAS NMR spectroscopy monitors the environment around Al in the spinel (Kirkpatrick 1988). It can distinguish between octahedral and tetrahedral spinel (Figure 3.2) (Kirkpatrick 1988, Millard et al. 1992). The ratio between tetrahedral and octahedral Al can be used to calculate $x$, where $x = 2/(1+[6]Al/[4]Al)$ (Wood et al. 1986, Millard et al. 1992).

This study will examine inclusions in NWA 6603 CV3. The goal is to determine a formation temperature for the spinel in a CAI. After finding a sufficiently large CAI, the CAI will be extracted. $^{27}$Al MAS NMR spectroscopy will be used to measure the cation ordering in spinel in the CAI. The cation ordering will be used to estimate formation temperature of the spinel. The temperature estimates will be made using calibration curves from the literature (Navrotsky and Kleppa 1967, O’Neill and Navrotsky 1983, Peterson et al. 1991, Millard et al. 1992, Maekawa et al. 1997, Princivalle et al. 1999, Redfern et al. 1999, Andreozzi and Princivalle 2002).

**Figure 3.2.** One-dimensional $^{27}$Al MAS NMR spectroscopy spectrum for a spinel standard. The octahedral and tetrahedral site peaks are distinct. Spinel is from Western University’s DANA collection #4305.
3.3 Methods

3.3.1 Sample Preparation

Two NWA 6603 samples (1-92 and 16-7) were purchased online from Eric Twelker at the Meteorite Market (Figure 3.3). The slices contain at least one large white inclusion and several smaller white inclusions. They were examined in situ using μXRD (Table 3.1). Spinel-bearing CAIs were identified visually and by μXRD structural analysis. Visually, bright white and irregularly shaped inclusions were chosen for examination by μXRD. The μXRD results confirmed the presence or absence of spinel and other CAI phases.

Figure 3.3. NWA 6603 samples, the small slab NWA 6603 1-92 (1.92 g) is on the left, the large NWA 6603 16-7 (16.7 g) is on the right. The white inclusions shown by arrows, were the main targets for μXRD.
3.3.2 Extraction

Extraction of the large CAI was completed using stainless steel dental picks. The CAI was scraped out of the matrix. Extraction was done under ethanol to prevent loss of material. Matrix material was hand-picked out of the scraped CAI powder. A neodymium magnet was used to remove magnetite from the powder. The powder was transferred to a sample vial by washing with ethanol. The sample was then dried in a low temperature (<100 °C) drying oven for a half hour.

3.3.3 Micro X-ray Diffraction

Phase identification of the minerals in the sample was done using micro X-ray diffraction (μXRD) (Flemming 2007). A Bruker D8 Discover Microdiffractometer having Co X-ray source (Co kα = 1.78897 Å) with a 60 mm Gobel mirror, and a 300 μm nominal beam diameter was used. The diffractometer is based on theta-theta geometry. The source moves through θ1 and the detector moves by θ2 (Flemming 2007) (Figure 3.4). This geometry can emulate sample rotation, while keeping the sample stationary (Flemming 2007). μXRD identifies the structure of a mineral based on the lattice planes of the mineral. The data is collected as a General Area Detector Diffraction System (GADDS) image by the Vantec-500 detector. The GADDS image can be integrated along 2θ. 2θ is the sum of the angles between the source and the sample and between the detector and the sample (Figure 3.4). The resulting diffractogram was analyzed using DIFFRAC.SUITE EVA software (Bruker AXS 2010-2016, 2016 release). The software matches the diffraction pattern to those in the International Centre for Diffraction Data (ICDD) database. The source and detector were rotated around the sample in an omega scan. The beam and detector rotate

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Table 3.1. μXRD parameters for NWA 6603 1-92 and NWA 6603 16-7
simultaneously clockwise around the sample through an angle (ω). This motion imitates rotating the sample.

3.3.4 $^{27}$Al Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) Spectroscopy

$^{27}$Al MAS NMR was done on a Bruker Avance II 21.1 T 900 MHz (Al at 234.6 MHz) NMR spectrometer. NMR spectroscopy was done at the Ultrahigh Field NMR facility for solids at the National Research Center in Ottawa, Canada. Samples were loaded in a 2.5 mm H/X MAS Bruker probe. Because of the small amount of sample, a Kel-f insert was used to center the material in the probe. $^{27}$Al MAS NMR and two-dimensional 3Q MAS NMR were collected (Figure 3.5). $^{27}$Al MAS NMR spectra were run at a frequency of 31.25 kHz, with a pulse width of 0.5 μs which tipped the field 30 degrees ($\pi/6$) to the solid. The relaxation delay between scans was 5 seconds. Relative intensities of the tetrahedral and octahedral peaks were monitored at various relaxation delays to ensure the data was quantitative. Two-dimensional $^{27}$Al 3Q MAS NMR spectra were collected at 31.25 kHz.
Along the isotropic axis of the spectrum, the anisotropic effects, which cause broadening, are removed. The pulse sequence is designed to remove them by averaging anisotropic interactions. $^{27}$Al 3Q MAS NMR spectra were collected using a standard 3-pulse experiment. The experiment used a zero quantum filter (Amoureux et al. 1996). NWA 6603 was not rotor-synchronized in F1 due to broad resonances. The P1 excitation pulse was 2.6 $\mu$s. The P2 conversion pulse was 0.9 $\mu$s. The P3 90-degree soft selective pulse was 10 $\mu$s. Each t1 time increment lasted 32 $\mu$s. 64 t1 increments were collected, with 6400 transient scans per t1 increment, and a relaxation delay of 1 second. Total collection time was 4 days and 20 hours.

DMfit software (Massiot et al. 2002) was used to analyze the $^{27}$Al MAS NMR and the $^{27}$Al 3Q MAS NMR spectra. The $^{27}$Al MAS NMR spectrum, under the aforementioned experimental conditions, is quantitative. The software was used to fit the spectrum by creating a model of the whole spectrum, using individual peaks. These individual modelled peaks were then integrated, using the same software. Integration gives the area under the peaks. These areas were then used to calculate the inversion parameter x. The 3Q MAS NMR spectra of the sample and the standards were used to help determine peak locations of the different phases present.

Slices of the MAS NMR (F2) dimension of the 3Q MAS NMR spectra helped provide constraints on peak shape and position of phases. Slices through the main gehlenite peak and the tetrahedral spinel peak were taken. These slices helped fit the gehlenite and spinel tetrahedral peaks. Stebbins (1995) was also used to provide constraints on peak shape and location. Stebbins (1995) shows $^{27}$Al NMR chemical shifts ($\delta_{iso}$), quadrupolar coupling

**Figure 3.5. Schematic showing the location of the sample with respect to the magnetic field ($B_0$).**

In a MAS NMR experiment, the sample is rotated at 54.7 ° to $B_0$. 

\[ \theta = 54.7 \, ^\circ \]
constants (QCC or C_Q), and asymmetry (etaQ or η) values for various compounds (Table 3.2).

Table 3.2. Summary of information for NMR peak constraints taken from Stebbins (1995). No 27Al NMR data were included in Stebbins (1995) for the other phases (fassaite and gehlenite).

<table>
<thead>
<tr>
<th>Peak</th>
<th>[1]Chemical Shift (δ_{iso}) (ppm)</th>
<th>QCC or C_Q (KHz)</th>
<th>etaQ or η</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel Tetrahedral</td>
<td>~72 (MAS position)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spinel Octahedral</td>
<td>~ 11</td>
<td>3680</td>
<td>0</td>
</tr>
<tr>
<td>Grossular Octahedral</td>
<td></td>
<td>3610</td>
<td>0</td>
</tr>
</tbody>
</table>

[1]δ_{iso} can be different from the observed chemical shift in MAS NMR of solids because of quadrupolar interactions, in high field strengths (>14 T) this shift is minimized.

3.3.5 Calibration Curves

Temperature estimates were made using calibration curves from previous studies. The studies examined cation ordering in spinel in relation to temperature. Studies were completed on both synthetic and natural spinel. Different techniques looked at the cation ordering in situ at high temperatures or after quenching or cooling of samples. A summary of the models determined by each previous study used in this study is below (Table 3.3).
### Table 3.3. Summary of literature calibration curves used in this study.

<table>
<thead>
<tr>
<th>Source</th>
<th>Natural or Synthetic Spinel</th>
<th>High Temperature or Quenched/Cooled Samples</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peterson et al. 1991</td>
<td>Synthetic</td>
<td>High Temperature in situ</td>
<td>$^{[1]} \Delta G^o = \alpha + 2\beta x = -RT\ln(x^2(1-x)^{-1}(2-x)^{-1})$ ($\alpha = -31 \pm 1 \text{ kJ/mol}, \beta = -10 \pm 3 \text{ kJ/mol}$)</td>
</tr>
<tr>
<td>Millard et al. 1992</td>
<td>Synthetic</td>
<td>Quenched</td>
<td>$^{[1][2]} H_D = \alpha x + \beta x^2$ ($\alpha = 25 \pm 5 \text{ kJ/mol}, \beta = 5.8 \pm 9.5 \text{ kJ/mol}$)</td>
</tr>
<tr>
<td>Maekawa et al. 1997</td>
<td>Natural</td>
<td>Both (Quenched and in situ high temperature)</td>
<td>$^{[1][2]} \ln K = -(\alpha + 2\beta x)/RT$ ($\alpha = 35 \pm 5 \text{ kJ/mol}, \beta = -32 \pm 5 \text{ kJ/mol}$)</td>
</tr>
<tr>
<td>Redfern et al. 1999</td>
<td>Synthetic</td>
<td>Room temperature and high temperature</td>
<td>$^{[1]} RT\ln(x^2/((1-x)(2-x))) = \alpha + 2\beta x$ ($\alpha = 32.8 \pm 0.9 \text{ kJ/mol}, \beta = 4.7 \pm 2 \text{ kJ/mol}$)</td>
</tr>
<tr>
<td>Andreozzi and Princivalle 2002</td>
<td>Synthetic</td>
<td>Quenched</td>
<td>$^{[4]} x = 21.396 - 80.714u$</td>
</tr>
</tbody>
</table>

$^{[1]}$ These models are based on O’Neill and Navrotsky 1983 model.

$^{[2]}$ This model is also based on the Navrotsky and Kleppa 1967 model.

$^{[3]}$ Princivalle et al. 1999 uses B value instead of x-value, where $B = [^4] Al/Al_{total}$ for pure MgAl$_2$O$_4$ spinel.

$^{[4]}$ This model uses the oxygen position parameter (u). The model calculates inversion parameter (x) vs u for various temperatures, showing a linear relation. This model is used to estimate both an oxygen positional parameter (u) and a temperature.
3.4 Results

3.4.1 μXRD

Examination of inclusions in the two pieces of NWA 6603 showed some CAI minerals. Two large CAIs, one from each piece, were found (Figures 3.6 and Figure 3.7). The larger

![Image of μXRD results](image)

Figure 3.6. μXRD of the large inclusion in NWA 6603 1-92 (small slab). This target on the sample was extracted for NMR spectroscopy. Red: Gehlenite ((Ca\(_{1.96}\)Na\(_{0.05}\))(Mg\(_{0.24}\)Al\(_{0.64}\)Fe\(_{0.12}\))(Si\(_{1.39}\)Al\(_{0.61}\)O\(_7\)), PDF 72-2128); Green: Spinel (Mg(Al\(_{0.91}\)Fe\(_{0.09}\))O\(_4\), PDF 02-1075); Blue: Fassaite (Ca\(_{1.00}\)Mg\(_{0.39}\)Ti\(_{0.35}\)Ti\(_{0.13}\)Al\(_{0.13}\)(Al\(_{0.74}\)Si\(_{1.26}\))O\(_6\), PDF 71-1541); Pink: Grossular (Ca\(_3\)Al\(_2\)Si\(_3\)O\(_{12}\), PDF 03-0826).
of the two CAIs was chosen because of its size and location (Figure 3.6). This CAI was on the edge of the sample, making extraction easier. About 6 mg of sample was extracted.

Figure 3.7. μXRD of the large inclusion in NWA 6603 16-7 (large slab). Red: Gehlenite \(((\text{Ca}_{1.96}\text{Na}_{0.05})(\text{Mg}_{0.24}\text{Al}_{0.64}\text{Fe}_{0.12})(\text{Si}_{1.39}\text{Al}_{0.61}\text{O}_7)), \text{PDF 72-2128}\); Green: Spinel \((\text{MgAl}_2\text{O}_4), \text{PDF 03-0901}\); Blue: Fassaite \((\text{Ca}_{1.00}\text{Mg}_{0.39}\text{Ti}_{0.35}\text{Ti}_{0.13}\text{Al}_{0.13}(\text{Al}_{0.74}\text{Si}_{1.26})\text{O}_6), \text{PDF 71-1541}\); Pink: Grossular \((\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3), \text{PDF 03-0827}\).
3.4.2 $^{27}$Al MAS NMR Spectroscopy

$^{27}$Al 3Q MAS NMR and $^{27}$Al MAS NMR were collected on the NWA 6603 (1-92) CAI. $^{27}$Al 3Q MAS NMR of the sample, stacked with the $^{27}$Al 3Q MAS NMR of the sample overlain by standards, show the approximate location of tetrahedral and octahedral spinel peaks (Figure 3.8). A slice through the $^{27}$Al 3Q MAS NMR spectrum at the expected location of the spinel tetrahedral peak was used to help determine the location of the phases in the $^{27}$Al MAS NMR spectrum at the tetrahedral site (Figure 3.9). The fit parameters for the peaks modelled in the slice are reported in Table 3.4. The standards were collected under the same conditions as the sample spectrum. The spinel (MEQ 003) and grossular (RM 003A) standards used here are the synthetic versions of these standards. The fassaite (Allende TS62b) and gehlenite (DANA #3461) standards are natural standards and are not pure samples. Gehlenite does not have octahedral Al, but our standard has some contamination. Fassaite does have octahedral Al. A second standard, synthetic Di$_{75}$CaTs$_{25}$ was used. It is a solid solution of diopside (CaMgSi$_2$O$_6$) and Ca-Tschermak clinopyroxene (CaAl$_2$AlSiO$_6$) (Flemming et al. 2015). Fassaite is an aluminous-diopside so that composition is a good approximation. The one-dimensional $^{27}$Al MAS NMR of Di$_{75}$CaTs$_{25}$ shows that the synthetic fassaite octahedral peak does not overlap the spinel octahedral peak (Figure 3.10). In a fully ordered normal spinel, Al occupies only octahedral sites. Any disorder in the spinel will be represented by Al in the tetrahedral site.
Figure 3.8. Top: Two-dimensional $^{27}$Al 3Q MAS NMR spectra for NWA 6603 (1-92). Bottom: The same spectra from NWA 6603 (1-92), with NMR standards overlain. Synthetic spinel standard (MEQ 003) is green, natural fassaite standard (Allende TS62b) is purple, natural gehlenite standard (DANA #3461) is red, synthetic grossular standard (RM 003A) is light blue. From these spectra, the sample contains gehlenite, spinel, grossular, and possibly some fassaite. Arrows show the location of spinel peak. There is intensity in the sample spectrum at the spinel peak location, indicating the spinel is disordered.
Figure 3.9. The slice through the $^{27}$Al 3Q MAS NMR spectrum at the spinel peak location. a) shows the slice location and b) is zoomed in on the slice location and shows the slice location, synthetic spinel (MEQ 003) standard, and is overlain by the spectrum of the slice. c) shows an approximate fit of the slice (light blue). Gehlenite (red) is a low intensity broad peak as seen in the 3Q MAS spectrum at the slice location. Fassaite (blue) begins to have intensity at ~60 ppm until ~70 ppm at the slice location. Spinel (green) occupies the intensity between the low intensity gehlenite (~80 ppm) and the beginning of the fassaite peak (~70 ppm).
Table 3.4. Fit parameters for the slice of NWA 6603 1-92 CAI $^{27}$Al 3Q MAS NMR spectrum

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Position (ppm)</th>
<th>Em (Hz)</th>
<th>CQ (KHz)</th>
<th>$\eta$Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gehlenite</td>
<td>Q mas 1/2</td>
<td>241.99</td>
<td>75.40</td>
<td>10715.14</td>
<td>8352.35</td>
<td>0.8</td>
</tr>
<tr>
<td>Spinel</td>
<td>Q mas 1/2</td>
<td>174.39</td>
<td>72.19</td>
<td>1141.94</td>
<td>4224.12</td>
<td>0</td>
</tr>
<tr>
<td>Fassaite</td>
<td>Q mas 1/2</td>
<td>319.94</td>
<td>66.65</td>
<td>1334.26</td>
<td>3228.65</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 3.10. NWA 6603 $^{27}$Al MAS NMR (black) overlain by the synthetic spinel (MEQ 003) standard (green), the synthetic Di$_{75}$CaTs$_{25}$ (RM 009D) standard (blue), the synthetic grossular (RM 003A) standard (grey) and the natural gehlenite (DANA #3461) standard (red). The gehlenite octahedral peak is contamination from the natural sample. Gehlenite has a strong overlap with the spinel in MAS NMR, therefore two-dimensional NMR is critical for discerning peak locations. The Di$_{75}$CaTs$_{25}$ (RM 009D) standard shows there isn’t a lot of overlap between octahedral fassaite and octahedral spinel. Spinning side bands are indicated by blue triangles.
The $^{27}\text{Al}$ MAS NMR spectrum was fit to a combination of phases identified by μXRD (Figure 3.11). Spectra of standards for each phase were used as starting points for fit parameters. Table 3.5 gives the fit parameters for each fitted peak. The integrated area of the modelled fit gives areas under the peak for each phase. The two peaks of interest are the spinel peaks, which are used to calculate $x$, where $x = 2/(1+[^{6}\text{Al}]/[^{4}\text{Al}])$ (Millard et al. 1992) and $B$, where $B =[^{4}\text{Al}]/\text{Al}_{\text{total}}$ (Table 3.6) (Princivalle et al. 1999).

Figure 3.11. DMfit of $^{27}\text{Al}$ MAS NMR spectrum of NWA 6603 (1-92) CAI (black). Both tetrahedral and octahedral sites are fit using phases and peak locations identified by μXRD and $^{27}\text{Al}$ 3Q MAS NMR spectra. The model of the entire fit is light blue. At the tetrahedral site, gehlenite is the red peak, spinel is the light green peak, and fassaite is the blue peak. At the octahedral site, spinel is the green peak, fassaite is the dark blue peak, and grossular is the pink peak. Spinning side bands are indicated by blue triangles.
Table 3.5. Table of peak fitting parameters for DMfit $^{27}$Al MAS NMR spectrum of NWA 6603 using starting phases shown in Figure 3.10.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Position</th>
<th>Em (Hz)</th>
<th>CQ (KHz)</th>
<th>etaQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>spinel tetrahedral</td>
<td>Q mas 1/2</td>
<td>29.4</td>
<td>76.35</td>
<td>913.12</td>
<td>4978.51</td>
<td>1</td>
</tr>
<tr>
<td>gehlenite tetrahedral</td>
<td>Q mas 1/2</td>
<td>121.5</td>
<td>84.05</td>
<td>1428.60</td>
<td>8352.09</td>
<td>0.8</td>
</tr>
<tr>
<td>fassaite tetrahedral</td>
<td>Q mas 1/2</td>
<td>203.66</td>
<td>71.49</td>
<td>2276.34</td>
<td>5444.31</td>
<td>0</td>
</tr>
<tr>
<td>spinel octahedral</td>
<td>Q mas 1/2</td>
<td>366.71</td>
<td>14.66</td>
<td>1821.48</td>
<td>3681.44</td>
<td>0</td>
</tr>
<tr>
<td>grossular octahedral</td>
<td>Q mas 1/2</td>
<td>16.69</td>
<td>-2.41</td>
<td>650.94</td>
<td>3565.68</td>
<td>0</td>
</tr>
<tr>
<td>fassaite octahedral</td>
<td>Q mas 1/2</td>
<td>46.23</td>
<td>2.9</td>
<td>4613.47</td>
<td>7750.66</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.6. Results of integration of the fitted $^{27}$Al MAS NMR spectrum model for NWA 6603, calculated x-value, and calculated B-value for Princivalle et al. (1999)

<table>
<thead>
<tr>
<th>Integration of Tetrahedral Spinel</th>
<th>Integration of Octahedral Spinel</th>
<th>Inversion Parameter, x</th>
<th>B-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>10390.47</td>
<td>58271.63</td>
<td>0.3027</td>
<td>0.1513</td>
</tr>
</tbody>
</table>
3.4.3 Temperature Estimates

x-values and B-values calculated from integration of the fitting of the $^{27}\text{Al}$ MAS NMR spectrum are used to calculate temperature estimates, which are summarized in Table 3.7. These temperatures could be formation temperature or most recent equilibration temperature of the CAI. The temperatures are calculated using calibration curves from the literature (Table 3.3). The calibration curves are rearranged to solve for temperature in Kelvin using the R-value $3.814 \times 10^{-3}$ kJ/K/mol. Errors are calculated using the errors provided in the literature and/or by fitting the one-dimensional spectra to a higher and lower baseline. This fitting will give a range of integration values which will account for fitting errors. In the cases where no error was reported in the literature, only the fitting error was used. Temperature estimates from all models used range from 735-1675 K (error range 330-1936). Each model yielded a different temperature range: Peterson et al. (1991) yielded 1173 K (error range 1040-1349 K), Millard et al. (1992) yielded 1340 K (error range 835-1936 K), Maekawa et al. (1997) yielded 735 K (error range 330-1126 K), Princivalle et al. (1999) yielded 1248 K (error range 1248-1285), and Redfern et al. (1999) yielded 1675 K (error range 1576-1853 K). The plot of x versus u from Andreozzi and Princivalle et al. (2002), was used to estimate a u parameter and a temperature of ~1473 K (Figure 3.12). Calculated temperature estimates for NWA 6603 from mathematical models, are plotted in Figure 3.13.

### Table 3.7. calculated temperature estimates for NWA 6603 from multiple calibration curves from the literature.

<table>
<thead>
<tr>
<th>Source</th>
<th>Model</th>
<th>$\alpha$ and $\beta$ (kJ/mol)</th>
<th>$T$ (K)</th>
<th>Error Range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peterson et al. 1991</td>
<td>$^{[1]} \Delta G^\circ = \alpha + 2\beta x = -RT\ln(x^2(1-x)-1(2-x)-1)$</td>
<td>$\alpha = -31 \pm 1$ $\beta = -10 \pm 3$</td>
<td>1173</td>
<td>1040-1349</td>
</tr>
<tr>
<td>Source</td>
<td>Model</td>
<td>$\alpha$ and $\beta$ (kJ/mol)</td>
<td>$T$ (K)</td>
<td>Error Range (K)</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------------------------------------------</td>
<td>-------------------------------</td>
<td>---------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Millard et al. 1992</td>
<td>$[1][2] \Delta HD = \alpha x + \beta x^2$</td>
<td>$\alpha = 35 \pm 5$</td>
<td>1340</td>
<td>835-1936</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta = -32 \pm 5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maekawa et al. 1997</td>
<td>$[1] \ln K = -(\alpha + 2\beta x)/RT$</td>
<td>$\alpha = 25 \pm 5$</td>
<td>735</td>
<td>330-1126</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta = 5.8 \pm 9.5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>($\sim1250$ from graph (Figure 3.13))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Princivalle et al. 1999</td>
<td>$[3] T(K) = (6440 * B) + 273.15$</td>
<td></td>
<td>1248</td>
<td>1248-1285</td>
</tr>
<tr>
<td>Redfern et al. 1999</td>
<td>$[1].RT\ln(x2/((1-x)(2-x))) = \alpha + 2\beta x$</td>
<td>$\alpha = 32.8 \pm 0.9$</td>
<td>1675</td>
<td>1576-1853</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta = 4.7 \pm 2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Andreozzi and Princivalle 2002</td>
<td>$[4] x = 21.396 - 80.714u$</td>
<td>$u=0.2604$</td>
<td>$&gt;1373$</td>
<td>($\sim1473$)</td>
</tr>
<tr>
<td></td>
<td>(Figure 3.12)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[1] These models are based on O’Neill and Navrotsky 1983 model.

[2] This model is also based on the Navrotsky and Kleppa 1967 model.


[4] This model uses the oxygen position parameter (u). The model calculates inversion parameter (x) versus u for various temperatures, showing a linear relation. The linear relation in Figure 3.12 between x and u is being used to estimate a u parameter as well as a temperature.
Figure 3.12. Graph of oxygen positional parameter versus x-value for different temperatures. The value of $u = 0.2613$ was estimated using the calculated x-value of 0.3027. This graph shows the calculated temperature for $x = 0.3027$ is greater than 1100 °C (1373.15 K) at approximately 1200 °C (1473 K). Modified from Andreozzi and Princivalle (2002).
3.5 Discussion

The calculated temperatures are consistent with nebular condensation temperatures. The temperature could be initial condensation or early re-processing when the nebula was still very hot (>1400 K). Peterson et al. (1991), Millard et al. (1992), Redfern et al. (1999), Princivalle et al. (1999), and Andreozzi and Princivalle (2002) give estimates above 1000 K, from 1173 to 1675 K. Temperatures during CAI formation are expected to be upwards of 1400 K. The higher temperature estimates bracket 1400 K. The lowest estimate is 735 K (error puts this between 330 and 1126 K). These estimates result from Maekawa et al. (1997)’s equation of their model. Using the graph of temperature vs x-value in their paper provides a different estimate (Figure 3.13). This estimate is much closer to the estimates from other models at ~1523 K (error range ~1200 to 1350 K). For this discussion, the interpretation from the graph of Maekawa et al. (1997), will be used, as it agrees more closely with the estimates from the other models used.
Based on the “fluffy”, irregularly shaped appearance, fine-grained mineralogy, and dominance of melilite (gehlenite) phase, the CAI from NWA 6603 (1-92) is likely a Fluffy Type A CAI. This type of CAI is considered closest to nebular condensates, in that it is thought to have not been melted since it formed in the nebula. This view is consistent with the temperatures calculated here.

Figure 3.14. Graph of temperature (°C) versus inversion parameter, x from Maekawa et al. (1997). Open circles are $^{27}$Al MAS NMR data from in situ high temperature measurements. Solid circles are $^{27}$Al MAS NMR data from quenched samples. The line is fit with O’Neill and Navrotsky’s model from 1983: $\ln K = -(a + 2\beta x)/RT$, where $a = 35(5)$ kJ/mol and $\beta = -32(5)$ kJ/mol.

The temperature according to the graph from an x-value of ~0.3 is around 1250 °C (1523 K). This temperature differs from the one calculated via the equation of their model, which gives ~735 K. Modified from Maekawa et al 1997.

These temperatures are much higher than those in carbonaceous chondrite parent body models. The carbonaceous chondrite parent body has undergone low temperature metasomatism (25 – 350 °C or 298 – 623 K) (Grimm and McSween Jr. 1989, McSween Jr. 1999, Travis and Schubert 2005). It is unlikely that this high temperature record of near nebular temperatures was acquired during parent body processing.
Impact events during ejection and delivery of the meteorite, occur on very short time-scales (seconds) (Gucsik 2009). These short time scales are unlikely to have been long enough for the sample to reach equilibrium and cause significant reordering. At 900 °C, it takes the cation ordering reaction 4 minutes to reach equilibrium, and 700 minutes at 700 °C (Andreozzi and Princivalle 2002). NWA 6603 also has a low shock stage, suggesting pressures not greater than 5 GPa (Stöffler et al. 1991, 2018). The low pressure is not enough to cause significant, if any, shock metamorphism (Gucsik 2009). Entry through Earth’s atmosphere also causes heating. However, the heat is concentrated on the outside of the meteorite, creating a fusion crust (McSween Jr. 1999). The short time scales of impacts, the low pressures related to the shock history of the sample, and the inability for entry heating to penetrate the fusion crust, indicate that cation reordering is unlikely to be a result of ejection and delivery of the meteorite to Earth. Once on Earth, re-ordering is unlikely to occur spontaneously as the cation re-ordering reaction requires an activation energy of 197 ± 22 kJ/mol (Andreozzi and Princivalle 2002).

The high temperatures are indicative of nebular temperatures. The recorded temperatures are around the maximum temperatures reached in quench experiments of cation ordering in synthetic spinel (approximately 1000 °C or 1273 K) (Millard et al. 1992). These temperatures, greater than the quench experiment maximum, could be due to error in the fit of the $^{27}$Al MAS NMR spectrum or error from the models. As well, pressure-temperature conditions in the nebula, different from laboratory conditions, may limit cation re-ordering on cooling.

It is possible to measure nebular temperatures in spinel from CAIs. Isolating the spinel completely would also provide more accuracy. The best ways to do this isolation require dissolution of the other phases. Because CAIs are small and rare glimpses into the nebula, a method which does not destroy most of the material would be preferred.

### 3.6 Conclusions

A CAI was successfully extracted from NWA 6603 (1-92). $^{27}$Al MAS NMR and $^{27}$Al 3Q MAS NMR spectroscopy were collected on the bulk CAI. Temperatures calculated from the $^{27}$Al MAS NMR spectrum were close to expected nebular temperatures. Nebular
temperature estimates range from 1300-1500 K (Grossman 1972, Henning and Semenov 2013, Ivanova 2016). The measured temperatures ranged from 1173-1675 K. These temperatures are too high for carbonaceous chondrite parent body processing (98-623 K) (Grimm and McSween Jr. 1989, McSween Jr. 1999, Travis and Schubert 2005). The temperature is likely nebular. The cation ordering of spinel in a CAI from NWA 6603 recorded nebular condensation or nebular processing temperatures. Better constraints on NMR peak shape and size will produce better fits and more accurate temperature calculations.

In the future, the CAI identified in NWA 6603 (16-7) should be extracted and examined by $^{27}$Al MAS NMR spectroscopy. As it also appears to be a Fluffy Type A CAI. This could provide a replicate result. Measurement of the temperature recorded in that CAI will contribute to the understanding of the thermal history, both of NWA 6603 and carbonaceous chondrites.

For the first time, this project successfully measured high temperatures, within the expected nebular temperature range, recorded in a CAI using cation ordering in spinel in the bulk CAI. This preserves the entire sample. Looking at cation ordering in other minerals in CAIs can provide an independent test of temperature information about their formation in the nebula.

### 3.7 Acknowledgements

Eric Twelker of the Meteorite Market provided the 6603 samples. I thank Monika Haring for collecting NMR data of the Allende fassaite standard provided by Simon and Grossman. I thank Sarah McFadden for characterizing the natural gehlenite standard and Dr. Roberta Flemming and Marissa Quinlan, who synthesized the synthetic grossular and spinel standards. The DANA collection at Western University provided the natural samples of gehlenite, spinel, and grossular. I thank Dr. Audrey Bouvier for providing guidance during the project.

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3.8 References


Chapter 4
4 NMR Spectroscopy of CAIs from NWA 2364 and NWA 6991

4.1 Executive Summary
Two CAIs, one each from NWA 2364 and NWA 6991, were examined using µXRD and $^{27}$Al MAS NMR spectroscopy. µXRD was used to confirm the presence of spinel ($\text{MgAl}_2\text{O}_4$). $^{27}$Al MAS NMR was used to measure cation ordering in the spinel. Cation ordering was used with literature calibration curves to estimate the temperature of formation, or most recent equilibration temperature of the spinel. NWA 6991 yielded temperatures of 360 to 606 K and NWA 2364 yielded 521 to 707 K. These temperatures are lower than expected for nebular condensation temperatures, so likely represent an equilibration temperature from parent body processing.

4.2 Introduction
Calcium-Aluminium-Rich Inclusions (CAIs) are the oldest materials in the solar system (Grossman 1972, MacPherson 2003, Bouvier and Wadhwa 2010, Ivanova 2016). CAIs are thought to be the first solids to condense out of the solar nebula (Grossman 1972). They consist of refractory minerals predicted in the theoretical condensation sequence (Grossman 1972), however, they have a complex history of multiple heating events (Kerridge 1993, McSween Jr. 1999, MacPherson 2003). Unravelling information about the formation and subsequent alteration of CAIs can provide insight into the early solar system and the accretion of solar system bodies (Kerridge 1993, McSween Jr. 1999, Ivanova 2016). CAIs consist of four main minerals: spinel, fassaite, melilitie, and anorthite (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). CAIs are divided into types based on dominant mineralogy and grain size (McSween 1977, Brearley and Jones 1998, Ivanova 2016). Type A CAIs are rich in spinel and melilitie. Type B CAIs are rich in melilitie, fassaite, spinel, and anorthite. Type C CAIs are rich in fassaite and anorthite and contain spinel (MacPherson 2003). Fine-grained CAIs include Fluffy Type A CAIs, which are considered closest to nebular condensates (Brearley and Jones 1998, MacPherson et al. 2005). Coarse-grained CAIs can be either Compact Type A, Type B, or Type C. Coarse-
grained CAIs are generally considered altered since their original formation in the nebula (McSween 1977, Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). They are considered to have undergone partial melting in the nebula after their initial condensation (Friedrich et al. 2005, Bullock et al. 2014, Ivanova 2016).

CAIs are found today as inclusions in certain chondrite meteorites, including Carbonaceous Chondrites (CCs), studied here. Chondrites are a class of meteorite which contain early solar system materials (Kerridge 1993, Brearley and Jones 1998, McSween Jr. 1999). They have not undergone much parent body alteration (Brearley and Jones 1998, McSween Jr. 1999, Weisberg et al. 2006). CAIs are common in (CCs), and tend to be quite large in CV3 chondrites, a clan of CCs (Brearley and Jones 1998, McSween Jr. 1999, Ivanova 2016). CV CCs show a wide range of degrees of alteration (Brearley and Jones 1998). CV3 chondrites are petrologic Type 3, indicating very little secondary alteration (Weisberg et al. 2006). There is evidence showing variation in alteration on the CV3 parent bodies (McSween 1977, Brearley and Jones 1998). As a result, CV3 CAIs could record nebular processing or parent body processing.

Spinel (MgAl$_2$O$_4$), commonly found in CAIs, has a cubic closest packed structure of oxygen anions (Klein and Dutrow 2007, Ivanova 2016). The spaces between the oxygen form tetrahedral and octahedral sites (Figure 4.1). Mg$^{2+}$ and Al$^{3+}$ substitute into these voids to offset the negative charge on the oxygen atoms. Mg$^{2+}$ typically fills the tetrahedral sites (Navrotsky 1994, Klein and Dutrow 2007). Al$^{3+}$ fills the octahedral sites (Figure 4.1) (Navrotsky 1994, Klein and Dutrow 2007). These cations can be distributed between the sites in different ways (Navrotsky 1994). The distribution of these cations in the sites is related to the temperature at which the spinel formed, or to the most recent equilibration.

$^{27}\text{Al}$ Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy can directly measure the cation ordering of spinel (Wood et al. 1986, Kirkpatrick 1988, Millard et al. 1992). $^{27}\text{Al}$ MAS NMR can determine the environment around the $\text{Al}$ atoms in the sample (Kirkpatrick 1988). With this information, the ratio of octahedral to tetrahedral can be obtained (Figure 4.2). This ratio can be used to calculate $x$ where $x = 2/(1+[^{[6]}\text{Al}/[^{[4]}\text{Al}])$ (Wood et al. 1986, Millard et al. 1992). $x$ can be related to formation temperature of spinel. Previous studies of spinel have created calibration curves for this purpose (Peterson et al. 1991, Millard et al. 1992, Maekawa et al. 1997, Princivalle et al. 1999, Redfern et al. 1999, Andreozzi and Princivalle 2002). The studies looked at natural and synthetic spinel. Measurements were taken at high temperatures or from quenched samples.

**Figure 4.2.** One-dimensional $^{27}\text{Al}$ MAS NMR spectroscopy spectrum for a spinel standard. The octahedral and tetrahedral site peaks are distinct. Spinel is from Western University’s DANA collection #4305.
Two samples are examined here, NWA 2364 and NWA 6991. NWA 2364 shows some evidence of aqueous alteration. The CAI from NWA 2364, “The Crucible”, is a large Type B CAI which encloses some of the host matrix. The CAI shows evidence of partial melting (Friedrich et al. 2005). Friedrich et al. 2005, postulated that this was from parent body deformation events. The CAI from NWA 6991, “B4”, shows some evidence of partial melting (Bullock et al. 2014). It is a coarse-grained Type A CAI. B4 has been dated to 4567.9 ± 03 My (Bouvier and Wadhwa 2010). Despite some alteration in the parent body, the NWA 2364 and NWA 6991 CAIs may represent nebular temperatures. These temperatures could be nebular condensation or nebular processing. The recorded temperature would depend on the amount of processing the CAI had undergone. The cation ordering reaction in spinel ($\text{MgAl}_2\text{O}_4$) requires an activation energy of 197 ± 22 kJ/mol (Andreozzi and Princivalle 2002). If there was high temperature processing on the parent body to exceed the activation energy, the temperatures recorded would be parent body temperatures.

$^{27}\text{Al}$ MAS NMR spectroscopy will be used to examine the cation ordering in spinel from these CAIs. The CAIs from NWA 2364 and NWA 6991 should give temperatures during formation in the solar nebula.

4.3 Methods

4.3.1 Sample Preparation

Two CAIs from two CV3 CCs, NWA 2364 and NWA 6991, were examined. “The Crucible” CAI from NWA 2364 is on loan from Dr. Denton Ebel at the American Natural History Museum, New York, New York, USA. It is 0.5 mg of powder that had previously been separated, by heavy liquids density separation (Bouvier and Wadhwa 2010, Bouvier and Boyet 2016). The NWA 6991 CAI is on loan from Dr. Lawrence Garvie at Arizona State University, Pheonix, Arizona, USA. The sample is 13.7 mg of powder that also had previously been separated using Heavy Liquids Density Separation (Bouvier and Boyet 2016). The NWA 6991 CAI was then hand separated under ethanol into a “black” and “white” fraction. Separation was done to try to isolate spinel. Both samples have previously been separated using Heavy Liquids Density Separation. They were separated
by microcentrifuge using Methylene Iodide (Density = 3.2 g/cm$^3$). The methylene iodide fraction (>3.2 g/cm$^3$) was used.

4.3.2 Micro X-ray Diffraction

Initial phase identification of the samples was done using micro X-ray diffraction ($\mu$XRD) on a Bruker D8 Discover Microdiffractometer having a Co X-ray source (Co $k\alpha = 1.78897$ Å), with a 60 mm Gobel mirror, and a 300 μm nominal beam diameter was used (Figure 4.3). The diffractometer uses a theta-theta geometry, where the source moves through $\theta_1$ and the detector through $\theta_2$, mimicking rotation of the stationary sample (Flemming 2007). $\mu$XRD identifies the structure of a mineral based on the lattice planes of the mineral. The data are collected as a General Area Detector Diffraction System (GADDS) image by the Vantec 500 detector. The GADDS image can be integrated along 2θ for conventional phase identification. 2θ is the sum of the angles between the beam and the sample and between the detector and the sample (Figure 4.3). The resulting diffractogram was analyzed using Diffrac.SUITE EVA software (Bruker AXS 2010-2016, 2016 release). The software matches the diffraction pattern to those in the International Centre for Diffraction Data (ICDD) database. The source and detector were rotated around the sample in an omega scan (Table 4.1). They rotate clockwise around the sample at the same rate, imitating rotation of the sample. The movement is done over a set number of degrees ($\omega$).
Table 4.1. μXRD parameters for both NWA 2364 and NWA 6991, data collected in August of 2017 at Western University for both samples

<table>
<thead>
<tr>
<th>Date</th>
<th>θ₁ (degrees)</th>
<th>θ₂ (degrees)</th>
<th>ω (degrees)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 2017 Frame 1</td>
<td>14.5</td>
<td>20.5</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>Frame 2</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>

### 4.3.3 $^{27}$Al MAS NMR Spectroscopy

$^{27}$Al MAS NMR was done on a Bruker Avance II 21.1 T 900 MHz (Al at 234.6 MHz) NMR spectrometer. NMR spectroscopy was done at the Ultrahigh Field NMR facility for solids at the National Research Council in Ottawa, Canada. For more details about the technique see Chapter 1 section 1.2.2 and Chapter 2 section 2.5. Samples were loaded in a 2.5 mm H/X MAS Bruker probe. Because of the small amount of sample a Kel-f insert was used to center the material in the probe. One-dimensional MAS NMR and two-dimensional 3Q MAS NMR were collected. $^{27}$Al MAS NMR spectra were run at a spinning frequency of 31.25 kHz, with a pulse width of 0.5 μs which tipped the field 30 degrees ($\pi/6$) to the solid. The delay between scans was 5 seconds. Relative intensities of the tetrahedral and octahedral peaks were monitored at various delays, ensuring the data were quantitative. $^{27}$Al 3Q MAS NMR spectra were collected at a spinning frequency of 31.25 kHz. They were rotor-synchronized in the indirect F1 dimension (isotropic). In the isotropic axis dimension of the spectrum, the anisotropic effects are removed by the pulse sequence. The spectra were collected using a standard 3-pulse experiment, using a zero quantum filter (Amoureux et al. 1996). The P1 excitation pulse was 2.6 μs, the P2 conversion pulse was 0.9 μs and the P3 90-degree soft selective pulse was 10 μs. Each t1 time increment lasted 32 μs. For both NWA 6991 and NWA 2364, 1800 transient scans were collected during each t1 increment. 64 t1 increments were collected, with a relaxation time of 2 seconds between increments. Total collection time for each was two days and 16 hours.
The $^{27}$Al MAS NMR spectrum was fit and the $^{27}$Al 3Q MAS NMR spectra were displayed with DMFit (Massiot et al. 2002). $^{27}$Al MAS NMR spectra is quantitative under the previously described experimental conditions. The software was used to fit the one-dimensional $^{27}$Al MAS NMR spectrum by creating a model of the whole spectrum, using individual peaks. The software can integrate the individual peaks to calculate the area under the peak. These areas were then used to calculate the inversion parameter $x$.

The 3Q MAS NMR spectra of the sample and the standards were used to help determine peak locations of the different phases present. Slices of the MAS NMR (F2) dimension of the 3Q MAS NMR spectra helped provide constraints on peak shape and position of phases. Slices through the main gehlenite peak and the tetrahedral spinel peak were taken. These slices helped fit the gehlenite and spinel tetrahedral peaks. NMR slices were taken through the octahedral peak in 3Q MAS NMR. The slices were overlaid with spinel and grossular standards. This overlay helped separate the spinel and grossular peaks in the octahedral site. Stebbins (1995) was also used to provide constraints on peak shape and location. Stebbins (1995) shows $^{27}$Al NMR chemical shifts ($\delta_{iso}$), quadrupolar coupling constants (QCC or $C_Q$), and asymmetry (etaQ or $\eta$) values for various compounds (Table 4.2).

**Table 4.2. Summary of information for NMR peak constraints taken from Stebbins (1995).** $^{27}$Al NMR data were not included in Stebbins (1995) for the other phases (fassaite and gehlenite).

<table>
<thead>
<tr>
<th>Peak</th>
<th>$^{[1]}$Chemical Shift ($\delta_{iso}$) (ppm)</th>
<th>QCC or $C_Q$ (KHz)</th>
<th>etaQ or $\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel Tetrahedral</td>
<td>~72 (MAS position)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spinel Octahedral</td>
<td>~ 11</td>
<td>3680</td>
<td>0</td>
</tr>
<tr>
<td>Grossular Octahedral</td>
<td>3610</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

$^{[1]}$ $\delta_{iso}$ can be different from the observed chemical shift in MAS NMR of solids because of quadrupolar interactions, at high field strengths (>14 T) this shift is minimized (Stebbins 1995). Our spectra were acquired at 21.1 T, so the shifts should be minimized.
4.3.4 Calibration Curves

Temperature estimates were made using calibration curves from previous studies. The studies examined cation ordering in spinel in relation to temperature. Studies were completed on both synthetic and natural spinel. Different techniques looked at the cation ordering *in situ* at high temperatures or after quenching or cooling of samples. A summary of the models determined by each previous study used in this study is in Table 4.3.
Table 4.3. Summary of literature calibration curves used in this study.

<table>
<thead>
<tr>
<th>Source</th>
<th>Natural or Synthetic Spinel</th>
<th>High Temperature or Quenched/ Cooled Samples</th>
<th>Model</th>
</tr>
</thead>
</table>
| Peterson et al. 1991 | Synthetic                   | High Temperature *in situ*                  | $^{[1]}\Delta G^\circ = \alpha + 2\beta x = -RT\ln(x^2(1-x)^{-\frac{3}{2}}(2-x)^{-1})$  
  $(\alpha = -31 \pm 1 \text{ kJ/mol}, \beta = -10 \pm 3 \text{ kJ/mol})$ |
| Millard et al. 1992 | Synthetic                   | Quenched                                    | $^{[1][2]}H_D = \alpha x + \beta x^2$  
  $(\alpha = 25 \pm 5 \text{ kJ/mol}, \beta = 5.8 \pm 9.5\text{ kJ/mol})$ |
| Maekawa et al. 1997 | Natural                     | Both (Quenched and in situ high temperature) | $^{[1][2]}\ln K = -(\alpha + 2\beta x)/RT$  
  $(\alpha = 35 \pm 5 \text{ kJ/mol}, \beta = -32 \pm 5 \text{ kJ/mol})$ |
| Princivalle et al. 1999 | Natural                    | Cooled                                      | $^{[3]}T(\text{°C}) = 6440 \times B$  
  $(B = ^{[4]}\text{Al/Al_{total}})$ |
| Redfern et al. 1999 | Synthetic                   | Room temperature and high temperature        | $^{[1]}-RT\ln(x^2/((1-x)(2-x))) = \alpha + 2\beta x$  
  $(\alpha = 32.8 \pm 0.9 \text{ kJ/mol}, \beta = 4.7 \pm 2\text{ kJ/mol})$ |
| Andreozzi and Princivalle 2002 | Synthetic | Quenched | $^{[4]}x = 21.396 – 80.714u$ |

$^{[1]}$These models are based on O’Neill and Navrotsky 1983 model.  
$^{[2]}$This model is also based on the Navrotsky and Kleppa 1967 model.  
$^{[3]}$Princivalle et al 1999 uses B value instead of x-value, where B = $^{[4]}\text{Al/Al_{total}}$ for pure MgAl$_2$O$_4$ spinel.  
$^{[4]}$This model uses the oxygen position parameter (u). The model calculates inversion parameter (x) versus u for various temperatures, showing a linear relation. This model is used to estimate the u parameter and a temperature.
4.4 Results

4.4.1 XRD

Phase identification using XRD, most importantly for this work, showed the presence of spinel in the sample. Fassaite, anorthite, melilite, and grossular were also identified (Figure 4.4 and 4.5). All phases present contain Al which will produce a visible signal by $^{27}$Al.

Figure 4.4. µXRD of NWA 6991 “B4” CAI powder, used for identification of phases to be used as NMR standards and to confirm the presence of spinel. Spinel is fine-grained (rings in GADDS image), other phases are coarse-grained (spots in GADDS image)

Blue: Fassaite ($\text{[Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059}})(\text{Si}_{1.728}\text{Al}_{0.272})\text{O}_{6}$, PDF 83-2083);
Pink: Grossular ($\text{Al}_{2}\text{Ca}_{3}(\text{SiO}_{4})_{3}$, PDF 02-0944); Red: Gehlenite ($\text{Ca}_{2}\text{Al}(\text{Al, Si})_{2}\text{O}_{7}$, PDF 25-0123); Green: Spinel ($\text{MgAl}_{2}\text{O}_{4}$, PDF 03-0901).
NMR, so standards for each of these minerals were chosen and data for each standard were collected on the NMR.

![Image](image-url)

**Figure 4.5.** μXRD of NWA 2364 “The Crucible” CAI powder, used for identification of phases to be used as NMR standards and to confirm the presence of spinel. Spinel corresponds to the homogenous Debye rings in the GADDS image, indicating the spinel is fine-grained (<5 μm), which would not be separable by hand-picking.

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083); Pink: Grossular (Al$_2$Ca$_3$(SiO$_4$)$_3$, PDF 02-0944); Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$, PDF 09-0216); Green: Spinel (MgAl$_2$O$_4$, PDF 05-0672).
4.4.2 NMR

$^{27}$Al 3Q MAS NMR and $^{27}$Al MAS NMR were collected on NWA 6991 (white fraction) and NWA 2364. $^{27}$Al MAS NMR was collected on NWA 6991 (black fraction). $^{27}$Al MAS NMR and $^{27}$Al 3Q MAS NMR of the standards were collected under the same conditions. The fassaite (Allende TS62b) and gehlenite (DANA #3461) standards are natural standards and are not pure samples. Gehlenite does not have octahedral Al, but our standard has some. Fassaite does have octahedral Al. A second standard, synthetic Di$_{75}$CaTs$_{25}$ was used. It is a solid solution mixture of diopside (CaMgSi$_2$O$_6$) and Ca-Tschermak clinopyroxene (CaAlAlSiO$_6$) (Flemming et al. 2015). Fassaite is an aluminous-diopside so that mixture is a good approximation of it. The $^{27}$Al MAS NMR of Di$_{75}$CaTs$_{25}$ (RM 009A) shows the fassaite octahedral peak does not overlap the spinel octahedral peak (Figure 4.6). In looking at spinel, the octahedral peak is larger as, in an ordered normal spinel, Al occupies only octahedral sites. Any disorder in the spinel will be represented by Al in the tetrahedral site. Standards were used to give starting parameters for the $^{27}$Al MAS NMR fitting.
4.4.2.1 NWA 6991

NWA 6991 was hand separated into two fractions: NWA 6991 (white fraction) and NWA 6991 (black fraction). $^{27}\text{Al}$ MAS NMR spectroscopy was collected on both separates.

4.4.2.1.1 NWA 6991 (white fraction)

The $^{27}\text{Al}$ 3Q MAS NMR of NWA 6991 (white fraction), stacked with the two-dimensional $^{27}\text{Al}$ 3Q MAS NMR of all the standards, shows the relative and absolute peak locations of all phases and the approximate location of the spinel tetrahedral and octahedral peaks (Figure 4.7). This peak location information is used to help with fitting the one-dimensional $^{27}\text{Al}$ MAS NMR spectra. $^{27}\text{Al}$ 3Q MAS NMR was not acquired for NWA 6991 (black). A slice through the $^{27}\text{Al}$ 3Q MAS NMR spectrum produced a one-dimensional representation of the peak locations.
dimensional spectrum at the location of the spinel peak (Figure 4.8). The slice helped with fitting the tetrahedral Al peak, which has overlapping phases. The spinel peak fitted in the slice had an amplitude of 362.99, a position of 73.74 ppm, quadrupolar couple constant (CQ) of 6505.15 kHz, a broadening parameter (Em) of 5416.44 Hz, and an axial symmetry parameter (η) of 0.
Figure 4.7. Top: $^{27}$Al 3Q MAS NMR spectrum for NWA 6991 (white fraction). Bottom: The same spectrum from NWA 6991 (white fraction), with NMR standards overlaid. Spinel standard is green (synthetic MEQ 003), fassaite standard is blue (natural Allende TS62b), gehlenite standard is red (natural, DANA #3461), grossular standard is grey (synthetic RM 003). From these spectra, it is clear that the sample contains gehlenite, spinel, grossular, and possibly some fassaite. Arrows indicate the position of the tetrahedral spinel peak. There is intensity at the tetrahedral spinel peak, indicating the spinel is disordered.
Al MAS NMR spectrum of NWA 6991 (white fraction) was fit with multiple phases, which were identified by μXRD (Figure 4.9). Table 4.4 gives the fit parameters for each fitted peak. The integrated area of the modelled fit gives areas under each of the modelled peaks. The two peaks of interest are the spinel peaks, which are used to calculate $x$, where $x = 2/[1+^{6}\text{Al}^{4}\text{Al}]$ (Millard et al. 1992) and $B$, where $B = ^{4}\text{Al}/\text{Al}_{\text{total}}$ (Table 4.5) (Princivalle et al. 1999).

Figure 4.8. The slice through the $^{27}\text{Al}$ 3Q MAS NMR spectrum at the spinel peak location. a) shows the slice location and b) is zoomed in on the slice location and shows the slice location, synthetic spinel (MEQ 003) standard, and is overlain by the spectrum of the slice (green). c) shows an approximate fit of the slice, where the green peak is spinel.

$^{27}\text{Al}$ MAS NMR spectrum of NWA 6991 (white fraction) was fit with multiple phases, which were identified by μXRD (Figure 4.9). Table 4.4 gives the fit parameters for each fitted peak. The integrated area of the modelled fit gives areas under each of the modelled peaks. The two peaks of interest are the spinel peaks, which are used to calculate $x$, where $x = 2/[1+^{6}\text{Al}^{4}\text{Al}]$ (Millard et al. 1992) and $B$, where $B = ^{4}\text{Al}/\text{Al}_{\text{total}}$ (Table 4.5) (Princivalle et al. 1999).
Table 4.4. Table of peak fitting parameters for DMfit $^{27}\text{Al}$ MAS NMR fit of NWA 6991 (white fraction)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amp</th>
<th>Position (ppm)</th>
<th>Em (Hz)</th>
<th>CQ (KHz)</th>
<th>etaQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>spinel tetrahedral</td>
<td>Q mas 1/2</td>
<td>68.35</td>
<td>72.91</td>
<td>474.65</td>
<td>2486.05</td>
<td>0</td>
</tr>
<tr>
<td>gehlenite tetrahedral</td>
<td>Q mas 1/2</td>
<td>189.97</td>
<td>75.61</td>
<td>3492.42</td>
<td>6743.17</td>
<td>0</td>
</tr>
<tr>
<td>Peak</td>
<td>Type</td>
<td>Amp</td>
<td>Position (ppm)</td>
<td>Em (Hz)</td>
<td>CQ (KHz)</td>
<td>etaQ</td>
</tr>
<tr>
<td>------------------</td>
<td>------------</td>
<td>-------</td>
<td>----------------</td>
<td>----------</td>
<td>----------</td>
<td>------</td>
</tr>
<tr>
<td>fassaite tetrahedral</td>
<td>Q mas 1/2</td>
<td>7.53</td>
<td>71.47</td>
<td>1028.40</td>
<td>6358.65</td>
<td>0</td>
</tr>
<tr>
<td>spinel octahedral</td>
<td>Q mas 1/2</td>
<td>1466.05</td>
<td>15.23</td>
<td>1031.74</td>
<td>4477.27</td>
<td>0</td>
</tr>
<tr>
<td>fassaite octahedral</td>
<td>Q mas 1/2</td>
<td>9.04</td>
<td>6.76</td>
<td>519.18</td>
<td>6368.80</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 4.5. Results of integration of the fitted $^{27}$Al MAS NMR spectra model of NWA 6991 (white fraction), calculated x-value, and calculated B-value for Prinville et al. 1999

<table>
<thead>
<tr>
<th>Integration of Tetrahedral Spinel</th>
<th>Integration of Octahedral Spinel</th>
<th>Inversion Parameter, x</th>
<th>B-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>5488.75</td>
<td>403542.73</td>
<td>0.0268</td>
<td>0.0134</td>
</tr>
</tbody>
</table>
4.4.2.1.2    NWA 6991 (black fraction)

No $^{27}\text{Al}$ 3Q MAS NMR was collected on NWA 6991 (black fraction). Using the spectrum from NWA 6991 (white fraction), $^{27}\text{Al}$ MAS NMR spectrum of NWA 6991 (black fraction) can be fitted with the modelled peaks. The fit will be less constrained than the NWA 6991 (white fraction), because of the lack of a two-dimensional NMR spectrum. $^{27}\text{Al}$ MAS NMR spectrum of NWA 6991 (black fraction) was fit using multiple phases identified by μXRD (Figure 4.10). Table 4.6 gives the fit parameters for each fitted peak. The integrated area of the modelled fit gives areas under each peak. The two peaks of interest are the spinel peaks, which are used to calculate $x$, where $x = 2/(1+[6^{\text{Al}}/^{4}\text{Al}])$ and $B$, where $B = [^{4}\text{Al}]/^{\text{Al}_{\text{total}}}$ (Table 4.7) (Millard et al. 1992, Princivalle et al. 1999).

![Figure 4.10. DMfit to $^{27}\text{Al}$ MAS NMR spectrum of NWA 6991 (black fraction). Both tetrahedral and octahedral sites are fit using phases and peak locations identified by μXRD and two-dimensional $^{27}\text{Al}$ 3Q MAS NMR spectra from NWA 6991 (white fraction). In the tetrahedral peak gehlenite is the broad red peak, spinel is the narrow green peak, and fassaite is the small broad dark blue peak. In the octahedral site spinel is the large and narrow dark green peak. Fassaite and grossular share the small blue peak as they fall on top of each other and the peak is very low relative intensity. Blue triangles indicate spinning side bands.](image-url)
Table 4.6. Table of peak fitting parameters for one-dimensional $^{27}$Al MAS NMR fit of NWA 6991 (black fraction)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amp</th>
<th>Position (ppm)</th>
<th>Em (Hz)</th>
<th>CQ (KHz)</th>
<th>eta Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>spinel tetrahedral</td>
<td>Q mas 1/2</td>
<td>70.45</td>
<td>73.21</td>
<td>871.15</td>
<td>3368.00</td>
<td>0</td>
</tr>
<tr>
<td>gehlenite tetrahedral</td>
<td>Q mas 1/2</td>
<td>35.63</td>
<td>78.63</td>
<td>2916.34</td>
<td>9581.79</td>
<td>0.1</td>
</tr>
<tr>
<td>fassaite tetrahedral</td>
<td>Q mas 1/2</td>
<td>98.16</td>
<td>65.47</td>
<td>3974.63</td>
<td>7194.05</td>
<td>0</td>
</tr>
<tr>
<td>spinel octahedral</td>
<td>Q mas 1/2</td>
<td>3966.01</td>
<td>13.80</td>
<td>1099.72</td>
<td>2931.17</td>
<td>0</td>
</tr>
<tr>
<td>fassaite octahedral</td>
<td>Q mas 1/2</td>
<td>22.78</td>
<td>111.93</td>
<td>1057.82</td>
<td>9090.90</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 4.7. Results of integration of the fitted one-dimensional $^{27}$Al MAS NMR spectra model of NWA 6991 (black fraction), calculated x-value, and calculated B-value for Prinvicalle et al. 1999.

<table>
<thead>
<tr>
<th>Integration of Tetrahedral Spinel</th>
<th>Integration of Octahedral Spinel</th>
<th>Inversion Parameter, x</th>
<th>B-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>10383.87</td>
<td>404258.33</td>
<td>0.0501</td>
<td>0.0250</td>
</tr>
</tbody>
</table>

**4.4.2.2 NWA 2364**

$^{27}$Al 3Q MAS NMR of NWA 2364 The Crucible” is shown in Figure 4.11 (top). The same two-dimensional spectrum of NWA 2364 is stacked with all standards in Figure 4.11 (bottom). This stack shows the relative locations of the peaks for the different phases present. This information is used to help fit the $^{27}$Al MAS NMR spectrum. From the standard overlays, it is clear that grossular is not a phase that overlaps spinel in either the tetrahedral or octahedral sites.
Figure 4.11. Top: $^{27}$Al 3Q MAS NMR spectrum for NWA 2364. Bottom: The same spectrum from NWA 2364, with NMR standards overlay. Synthetic spinel standard is green (synthetic MEQ 003), natural fassaite standard is blue (Allende TS62b), natural gehlenite standard is red (DANA #3461), synthetic grossular standard is grey (RM 003A). From these spectra, the sample contains fassaite, spinel, grossular, and some gehlenite. There is intensity at the tetrahedral spinel site indicating the spinel is disordered. Arrows indicate the location of the tetrahedral spinel peak.
A slice through the 3Q MAS NMR at the expected peak location of the tetrahedral spinel, produced a one-dimensional spectrum of the MAS NMR dimension at the slice location (Figure 4.12). The resulting spectrum was used to help determine the peak location of the spinel where it overlaps with gehlenite. The fit of the spinel peak in the slice spectrum had an amplitude of 249.19, a position of 71.76 ppm, a broadening parameter (Em) of 3868.89 Hz, a quadrupole coupling constant of 8692.87 kHz, and an asymmetry parameter (η) of 0.

Figure 4.12. The slice through the $^{27}$Al 3Q MAS NMR spectrum of NWA 2364 at the spinel peak location. a) shows the slice location and b) is zoomed in on the slice location and shows the slice location, synthetic spinel (MEQ 003) standard, and is overlain by the spectrum of the slice (green). c) shows an approximate fit of the slice, where the green peak is spinel.
The fit of the $^{27}$Al MAS NMR spectrum for NWA 2364 (Figure 4.13) was fit using a number of phases, identified by μXRD. Table 4.8 gives the fit parameters for each fitted peak. The integrated area fit gives areas under each peak. The two peaks of interest are the spinel peaks, which are used to calculate $x$, where $x = 2/(1 + ^{[6]}\text{Al}/^{[4]}\text{Al})$ and $B$, where $B = ^{[6]}\text{Al}/\text{Al}_{\text{total}}$ (Table 4.9). These values were used in conjunction with the calibration curves to produce temperature estimates (Table 4.10).

![Figure 4.13. DMfit of $^{27}$Al MAS NMR spectrum of NWA 2364. Both tetrahedral and octahedral sites are fit using phases and peak locations identified by μXRD and two-dimensional $^{27}$Al 3Q MAS NMR spectra. In the tetrahedral peak gehlenite is the broad red peak, spinel is the narrow green peak, and fassaite is the broad dark blue peak. In the octahedral site spinel is the large and narrow dark green peak. Fassaite and grossular share the small blue peak as they fall on top of each other and the peak is small. Blue triangles indicate spinning side bands.](image-url)
Table 4.8. Table of peak fitting parameters for one-dimensional $^{27}$Al MAS NMR fit of NWA 2364

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amp</th>
<th>Position (ppm)</th>
<th>Em (Hz)</th>
<th>CQ (KHz)</th>
<th>etaQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel Tetrahedral</td>
<td>Q mas 1/2</td>
<td>46.75</td>
<td>74.75</td>
<td>1406.58</td>
<td>4240.93</td>
<td>0</td>
</tr>
<tr>
<td>Gehlenite Tetrahedral</td>
<td>Q mas 1/2</td>
<td>37.68</td>
<td>74.27</td>
<td>790.09</td>
<td>8761.70</td>
<td>0.9</td>
</tr>
<tr>
<td>Fassaite Tetrahedral</td>
<td>Q mas 1/2</td>
<td>55.56</td>
<td>58.85</td>
<td>3105.80</td>
<td>6946</td>
<td>0.51</td>
</tr>
<tr>
<td>Spinel Octahedral</td>
<td>Q mas 1/2</td>
<td>1604.51</td>
<td>14.52</td>
<td>1399.29</td>
<td>3696.66</td>
<td>0</td>
</tr>
<tr>
<td>Fassaite (and Grossular)</td>
<td>Octahedral</td>
<td>45.00</td>
<td>3.78</td>
<td>974.00</td>
<td>6896.35</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 4.9. Results of integration of the fitted one-dimensional $^{27}$Al MAS NMR spectra model of NWA 2364 “The Crucible” CAI, calculated x-value, and calculated B-value from Prinville et al. 1999

<table>
<thead>
<tr>
<th>Integration of Tetrahedral Spinel</th>
<th>Integration of Octahedral Spinel</th>
<th>Inversion Parameter, x</th>
<th>B-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>10898.54</td>
<td>272434.7</td>
<td>0.0770</td>
<td>0.0385</td>
</tr>
</tbody>
</table>

4.5 Temperature Estimations

Using the x-values and B-values calculated in the previous section, temperature estimates can be made. These estimates will represent either formation or most recent equilibration temperature of the spinel in these CAIs. Temperature estimates are made using calibration
curves from the literature (Table 4.3). The calibration curves are rearranged to solve for temperature in Kelvin. The R-value used is \( 8.314 \times 10^{-3} \text{kJ/K/mol} \). Errors are calculated using the errors provided in the literature and/or by fitting the one-dimensional spectra to a higher and lower baseline. This fitting will give a range of integration values which will account for fitting errors. In the cases where no error was reported in the literature, only the fitting error was used.

4.5.1 NWA 6991

The inversion parameter calculated for NWA 6991 (white fraction) was 0.0268. The B-value was calculated at 0.0385. The inversion parameter calculated for NWA 6991 (black fraction) was 0.0501. The B-value was calculated at 0.0250. These values were substituted into the appropriate calibration curves to produce a temperature estimate (Table 4.10). NWA 6991 (white) had a calculated temperature range of 360 to 507 K (error range 300 to 594 K). Peterson et al. (1991) yielded 464 K (444 to 488 K), Maekawa et al. (1997) yielded 507 K (425 to 594 K), Millard et al. (1992) yielded 386 K (300 to 476 K), Redfern et al. (1999) yielded 504 K (485 to 526 K), and Princivalle et al. (1999) yielded 360 K (357 to 364 K). The model of x versus u from Andreozzi and Princivalle (2002) was used to estimate a u parameter from the calculated x parameter. No temperature was estimated here as the points of x versus u fall off the chart at the low end.

NWA 6991 (black) had a calculated temperature range of 434 to 607 K (error range 357 to 688 K). Peterson et al. (1991) yielded 546 K (523 to 579 K), Maekawa et al. (1997) yielded 579 K (479 to 688 K), Millard et al. (1992) yielded 466 K (357 to 586 K), Redfern et al. (1999) yielded 606 K (586 to 637 K), and Princivalle et al. (1999) yielded 434 K (434 to 443 K). The model of x versus u from Andreozzi and Princivalle (2002) was used to estimate a u parameter from the calculated x parameter. No temperature was estimated here as the points of x versus u fall off the chart at the low end. The calculated temperature estimates for both NWA 6991 black and white fractions are plotted in Figure 4.14.
Table 4.10. Calculated temperature estimates for NWA 6991 from multiple calibration curves from the literature.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Model</th>
<th>α and β (kJ/mol)</th>
<th>NWA 6991 (white fraction)</th>
<th>NWA 6991 (black fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T (K) Error Range</td>
<td>T (K) Error Range</td>
<td></td>
</tr>
<tr>
<td>Peterson et al. 1991</td>
<td>$[1] \Delta G^* = \alpha + 2\beta x = -RT \ln(x^2/(1-x)(2-x))$</td>
<td>$\alpha = -31 \pm 1$ $\beta = -10 \pm 3$</td>
<td>464 444-488</td>
<td>546 523-579</td>
</tr>
<tr>
<td>Maekawa et al. 1997</td>
<td>$[1] \ln K = -(\alpha + 2\beta x)/RT$</td>
<td>$\alpha = 35 \pm 5$ $\beta = -32 \pm 5$</td>
<td>507 425-594</td>
<td>579 479-688</td>
</tr>
<tr>
<td>Millard et al. 1992</td>
<td>$[1][2] \Delta H_D = \alpha x + \beta x^2$</td>
<td>$\alpha = 25 \pm 5$ $\beta = 5.8 \pm 9.5$</td>
<td>386 300-476</td>
<td>466 357-586</td>
</tr>
<tr>
<td>Redfern et al. 1999</td>
<td>$[1] \alpha + 2\beta x = -RT \ln(x^2/(1-x)(2-x))$</td>
<td>$\alpha = 32.8 \pm 0.9$ $\beta = 4.7 \pm 2$</td>
<td>504 485-526</td>
<td>606 586-637</td>
</tr>
<tr>
<td>Princivalle et al. 1999</td>
<td>$[3] T(K) = (6440 \times B) + 273.15$</td>
<td></td>
<td>360 357-364</td>
<td>434 434-443</td>
</tr>
<tr>
<td>Andreozzi &amp; Princivalle 2002</td>
<td>$[4] x = 21.396 - 80.714u$</td>
<td>Temperature was not defined on graph at u = 0.265 (too low) (Figure 4.15).</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$[1]$ These models are based on O’Neill and Navrotsky 1983 model.

$[2]$ This model is also based on the Navrotsky and Kleppa 1967 model.


$[4]$ This model uses the oxygen position parameter (u). The model calculates inversion parameter (x) vs u for various temperatures, showing a linear relation. It was used to estimate a u parameter and a temperature.
The inversion parameter calculated for NWA 2364 was 0.0770. The B-value was calculated at 0.0385. These values were substituted into the appropriate calibration curves to produce a temperature estimate (Table 4.11). NWA 2364 had a calculated temperature range of 521 to 707 K (error range 399 to 772 K). Peterson et al. (1991) yielded 621 K (576 to 671 K), Maekawa et al. (1997) yielded 634 K (507 to 772), Millard et al. (1992) yielded 546 K (399 to 708 K), Redfern et al. (1999) yielded 707 K (661 to 758 K), and Princivalle et al. (1999) yielded 521 K (501 to 542 K). The model of $x$ versus $u$ from Andreozzi and Princivalle (2002) was used to estimate a $u$ parameter from the calculated $x$ parameter. No temperature was estimated using this model as the points of $x$ versus $u$ fall off the chart at the low end. The calculated temperature estimates for NWA 2364 are plotted in Figure 4.16.

**Figure 4.14.** Calculated temperature estimates (K) for NWA 6991 black and white fractions using mathematical models.

### 4.5.2 NWA 2364

The inversion parameter calculated for NWA 2364 was 0.0770. The B-value was calculated at 0.0385. These values were substituted into the appropriate calibration curves to produce a temperature estimate (Table 4.11). NWA 2364 had a calculated temperature range of 521 to 707 K (error range 399 to 772 K). Peterson et al. (1991) yielded 621 K (576 to 671 K), Maekawa et al. (1997) yielded 634 K (507 to 772), Millard et al. (1992) yielded 546 K (399 to 708 K), Redfern et al. (1999) yielded 707 K (661 to 758 K), and Princivalle et al. (1999) yielded 521 K (501 to 542 K). The model of $x$ versus $u$ from Andreozzi and Princivalle (2002) was used to estimate a $u$ parameter from the calculated $x$ parameter. No temperature was estimated using this model as the points of $x$ versus $u$ fall off the chart at the low end. The calculated temperature estimates for NWA 2364 are plotted in Figure 4.16.
Table 4.11. Calculated temperature estimates for NWA 2364 from multiple calibration curves from the literature.

<table>
<thead>
<tr>
<th>Source</th>
<th>Model</th>
<th>$\alpha$ and $\beta$ (kJ/mol)</th>
<th>$T$ (K)</th>
<th>Error (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peterson et al. 1991</td>
<td>$^{[1]}\Delta G^* = \alpha + 2\beta x = -RT\ln x(1-x) - 1(2-x) - 1$</td>
<td>$\alpha = -31 \pm 1$, $\beta = -10 \pm 3$</td>
<td>621</td>
<td>576-671</td>
</tr>
<tr>
<td>Maekawa et al. 1997</td>
<td>$^{[1]}\ln K = -(\alpha + 2\beta x)/RT$</td>
<td>$\alpha = 35 \pm 5$, $\beta = -32 \pm 5$</td>
<td>634</td>
<td>507-772</td>
</tr>
<tr>
<td>Millard et al. 1992</td>
<td>$^{[1][2]}\Delta HD = \alpha x + \beta x^2$</td>
<td>$\alpha = 25 \pm 5$, $\beta = 5.8 \pm 9.5$</td>
<td>546</td>
<td>399-708</td>
</tr>
<tr>
<td>Redfern et al. 1999</td>
<td>$^{[1]}RT\ln(x2/((1-x)(2-x))) = \alpha + 2\beta x$</td>
<td>$\alpha = 32.8 \pm 0.9$, $\beta = 4.7 \pm 2$</td>
<td>707</td>
<td>661-758</td>
</tr>
<tr>
<td>Princivalle et al. 1999</td>
<td>$^{[3]}T(\degree C) = 6440 \times B$</td>
<td></td>
<td>521</td>
<td>501-542</td>
</tr>
<tr>
<td>Andreozzi and Princivalle 2002</td>
<td>$^{[4]}x = 21.396 - 80.714u$</td>
<td>Temperature was not defined on graph at $u = 0.265$ (too low) (Figure 4.15).</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{[1]}$These models are based on O’Neill and Navrotsky 1983 model.

$^{[2]}$This model is also based on the Navrotsky and Kleppa 1967 model.

$^{[3]}$Princivalle et al. 1999 uses B value instead of x-value, where $B = ^{[4]}Al/Al_{total}$ for pure MgAl$_2$O$_4$ spinel.

$^{[4]}$This model uses the oxygen position parameter (u). The model calculates inversion parameter (x) vs u for various temperatures, showing a linear relation. It was used to estimate a u parameter and a temperature.
Figure 4.15. Graph of oxygen positional parameter, u, vs. x-value for different temperatures. The values of $u = 0.264$ and 0.265 corresponds with the calculated x-values for NWA 2364 and NWA 6991, respectively. This graph shows the temperature is significantly less than 600 °C (873.15 K). Modified from Andreozzi and Princivalle (2002).
The temperature estimates for NWA 2364 and NWA 6991 are similar, as are the u-values (0.264 and 0.265, respectively) from Andreozzi and Princivalle (2002). NWA 6991 (white fraction) had temperature estimates ranging from 360 K to 507 K. NWA 6991 (black fraction) temperature estimates ranged from 434 K to 606 K. NWA 2364 ranged from 521 K to 707 K. These temperatures are relatively similar (overlapping). This similarity may be partly due to both CAIs undergoing partial melting (Friedrich et al. 2005, Bullock et al. 2014). Both NWA 6991 fractions have estimates more similar to each other than to NWA 2364. This similarity is expected as they are from the same CAI. The estimate from NWA 6991 (black fraction) is likely less accurate than that from NWA 6991 (white fraction) because no two-dimensional $^{27}$Al 3Q MAS NMR spectra was collected for the black fraction. Based on the one-dimensional $^{27}$Al MAS NMR spectrum of NWA 6991 (black fraction), the black fraction appears to contain more fassaite than the white fraction. This difference was taken into account during fitting.

Figure 4.16. Calculated temperature estimates (K) for NWA 2364 CAI from mathematical models.

4.6 Discussion

The temperature estimates for NWA 2364 and NWA 6991 are similar, as are the u-values (0.264 and 0.265, respectively) from Andreozzi and Princivalle (2002). NWA 6991 (white fraction) had temperature estimates ranging from 360 K to 507 K. NWA 6991 (black fraction) temperature estimates ranged from 434 K to 606 K. NWA 2364 ranged from 521 K to 707 K. These temperatures are relatively similar (overlapping). This similarity may be partly due to both CAIs undergoing partial melting (Friedrich et al. 2005, Bullock et al. 2014). Both NWA 6991 fractions have estimates more similar to each other than to NWA 2364. This similarity is expected as they are from the same CAI. The estimate from NWA 6991 (black fraction) is likely less accurate than that from NWA 6991 (white fraction) because no two-dimensional $^{27}$Al 3Q MAS NMR spectra was collected for the black fraction. Based on the one-dimensional $^{27}$Al MAS NMR spectrum of NWA 6991 (black fraction), the black fraction appears to contain more fassaite than the white fraction. This difference was taken into account during fitting.
NWA 2364 had a higher temperature range than the NWA 6991 samples. NWA 2364 is a compact Type B CAI and shows more evidence of extreme heating events than NWA 6991 (Friedrich et al. 2005, Bullock et al. 2014). NWA 6991 is in the middle of the continuum from Type A to Type B CAIs (Bullock et al. 2014). These differences in thermal histories are reflected in the temperature estimates from cation ordering.

The temperatures are too low for nebular condensation temperatures. These temperatures therefore may represent melting in the nebula or melting on a parent body. Models of alteration on the carbonaceous chondrite parent body(ies) show peak temperature ranges of 90 °C (363.15 K) to 180 °C (453.15 K) (Travis and Schubert 2005). Grimm and McSween (1989) used maximum temperatures of 350 °C (623.15 K) for their parent body models. Using Travis and Schubert (2005) temperatures, these temperature estimates are too high to be planetary processing. But using Grimm and McSween (1989), these estimates are within planetary processing temperatures. The unusual shape of The Crucible CAI (i.e. enclosing some of its host matrix) was interpreted to be planetary processing (Friedrich et al. 2005). These temperatures may be nebular or parent body processing. Better constraints on temperatures in the parent bodies are needed to make any definitive claims.

These temperatures may be minimum temperatures. These minimum temperatures could have been recorded as a result of reordering on cooling. Millard et al. (1992) found that approximately 1300 K was the limit for quenched samples, the limit for samples cooled more slowly may be lower. Despite potential limitation, this technique can provide insight into the temperature regimes experienced in the nebula or on parent bodies.

4.7 Conclusions

The CAIs from NWA 2364 and NWA 6991 were shown to be slightly disordered. Disorder increases with increasing temperature. The disorder represents high temperature processing, which was quantified using $^{27}$Al MAS NMR. NWA 6991 (white fraction) had temperature estimates ranging from 360 K to 507 K. NWA 6991 (black fraction) estimates ranged from 434 K to 606 K. NWA 2364 ranged from 521 K to 707 K. These temperatures likely represent nebular processing after condensation but could be parent body processing.
Temperatures are higher than some models of the carbonaceous chondrite parent body, but lower than other models (Grimm and McSween Jr. 1989, Travis and Schubert 2005). Some aqueous alteration is documented in NWA 2364 (Johnson et al. 2017). Kojima and Tomoeka 1996 discussed alteration on the CV3 parent body. They argued that aqueous alteration was followed by thermal metamorphism. These meteorites would have originated at different locations on the parent body. These locations may have seen aqueous alteration but not thermal metamorphism.

The temperatures likely represent minimum temperatures. Cooling can cause re-ordering of cations to some extent. In the future, more CAIs and more pristine samples should be examined. More samples will help determine if there is an upper limit on recorded temperatures. Recorded temperatures may come closer to nebular condensation temperatures in more pristine samples, which have not been altered at high temperatures on the parent body. Pristine samples are therefore less likely to record parent body temperatures and may retain nebular temperatures given a quench event in the nebula. $^{27}$Al MAS NMR is a useful independent technique for determining the thermal and alteration history of CAIs and their host meteorites. It can also provide insight into parent body processing.

### 4.8 Acknowledgements

I thank Dr. Laurence Garvie for his loan of NWA 2364. I thank Dr. Denton Ebel for his loan of NWA 6991. I thank Sarah McFadden for characterization of the gehlenite standard used. Access to the 900 MHz NMR spectrometer was provided by the National Ultrahigh-Field NMR facility for solids (Ottawa, Canada). The facility is funded by the Canadian Foundation for Innovations (CFI), the Ontario Trust, Recherche Quebec, the National Research Council of Canada (NRC), and Bruker Biospin. The facility is managed by the University of Ottawa (nmr900.ca). The Natural Sciences and Engineering Council of Canada (NSERC) is acknowledged for a Major Resources Support grant.
4.9 References


Chapter 5

5 Cation Ordering in Spinel from a Calcium-Aluminium-Rich Inclusion in Allende CV3 using $^{27}$Al Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy

5.1 Executive Summary

Four Allende CV3 samples were surveyed for CAIs which contained spinel ($\sim$MgAl$_2$O$_4$) using in situ $\mu$XRD. $^{27}$Al MAS NMR collected on two Allende CAIs in 2011/2012 were confirmed by $\mu$XRD to contain spinel (Allende 3529 and TS62b). The MAS NMR of these samples was used to determine cation ordering in spinel from the CAIs. The spinel was found to be an ordered normal spinel in both samples. Fully ordered normal spinel yielded temperatures approaching 0 °C. This temperature is lower than expected for nebular temperatures and likely represents prolonged low temperature alteration on the parent body.

5.2 Introduction

Calcium-Aluminium-Rich Inclusions (CAIs) have been dated as the oldest materials in the solar system, at 4 567.9 ± 0.3 My (Bouvier and Wadhwa 2010). They are thought to be the first solids to condense out of the gas of the solar nebula (Grossman 1972). However, CAIs are also thought to have undergone subsequent processing including complex cycles of heating and cooling (Kerridge 1993, Brearley and Jones 1998, MacPherson 2003, MacPherson et al. 2005). CAIs consist mainly of the minerals spinel, fassaite, melilite, and anorthite (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016, Rubin and Ma 2017). They are divided into types based on mineralogy and grain size (McSween 1977a, Brearley and Jones 1998, Ivanova 2016). Type A CAIs are rich in spinel and melilite (Brearley and Jones 1998, Ivanova 2016). Type B CAIs are rich in melilite, fassaite, spinel, and anorthite (Brearley and Jones 1998, Ivanova 2016). Type C CAIs are rich in fassaite and anorthite and can contain spinel (Brearley and Jones 1998, MacPherson et al. 2005, Ivanova 2016). Fine-grained CAIs include Fluffy Type As, which are considered closest to nebular condensates (Brearley and Jones 1998, MacPherson et al. 2005). Coarse-grained CAIs can be either Compact Type A, Type B, or Type C (Brearley and Jones 1998, Ivanova 2016).
2016). These CAIs are generally considered to have undergone partial melting in the nebula after initial condensation (McSween 1977a, Friedrich et al. 2005, Bullock et al. 2014, Ivanova 2016).

CAIs, and other early solar system materials such as chondrules, dust, and metal form and are processed in the nebula (Grossman 1972, Kerridge 1993, Shu et al. 1996, 2001, MacPherson 2003, Henning and Semenov 2013, Ivanova 2016). These small particles begin to accrete together, forming larger and larger bodies (Goldreich and Ward 1973, Montmerle et al. 2006). These large bodies are referred to as planetesimals or parent bodies. Meteorites are matched with potential parent bodies. One way this matching can be done is with Infrared (IR) Spectroscopy (Gaffey 1976, Gaffey et al. 1993, McSween Jr. 1999). Asteroid bodies with spectra similar to certain meteorites are potential parent bodies for that meteorite (Gaffey 1976, Gaffey et al. 1993, McSween Jr. 1999). While in the parent body, meteoritic material can undergo parent body or secondary processing (Kerridge 1993, Brearley and Jones 1998, McSween Jr. 1999). This alteration on the parent body can obscure the primary processing that occurred in the nebula (Kerridge 1993). The amount of alteration experienced by meteorites varies, even among meteorites from the same parent body (McSween 1977b, Brearley and Jones 1998, McSween Jr. 1999, Travis and Schubert 2005).

CAIs are found in carbonaceous chondrites (CC), a sub group of chondrites (McSween 1977a, Brearley and Jones 1998, McSween Jr. 1999). Carbonaceous chondrites are some of the most primitive and unaltered materials (Kerridge 1993, Brearley and Jones 1998, McSween Jr. 1999, Ivanova 2016). Most CCs show evidence of aqueous alteration (Brearley and Jones 1998, McSween Jr. 1999, MacPherson 2003). CV3 CCs are a subtype of CC. CV3 CCs have the largest number of CAIs, and the CAIs tend to be larger than in other types (Brearley and Jones 1998, McSween Jr. 1999, Ivanova 2016). Allende is a well-studied CV3 chondrite because of the large amount of material recovered after its observed fall in 1969 (two tonnes of material) (Brearley and Jones 1998). Allende is an oxidized CV3. The dominant opaque phase in its matrix is magnetite, and metal is rare (McSween 1977b, Brearley and Jones 1998).
Spinel (MgAl$_2$O$_4$) is common in CAIs (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016, Rubin and Ma 2017). It has a cubic closest packed lattice of oxygen anions. The spaces between the oxygen form tetrahedral and octahedral sites. In space group Fd3m, 1/8 and 1/2 of the tetrahedral and octahedral sites are filled, respectively. Mg$^{2+}$ and Al$^{3+}$ substitute into these sites to offset the negative charge on the oxygen anions. Different formation temperatures will change the distribution of the cations between the sites (Wood et al. 1986, Peterson et al. 1991, Millard et al. 1992, Maekawa et al. 1997, Princivalle et al. 1999, Redfern et al. 1999, Andreozzi and Princivalle 2002). At higher temperatures, the spinel will become disordered, where some Al$^{3+}$ replaces the Mg$^{2+}$ in the tetrahedral site (O’Neill and Navrotsky 1983, Navrotsky 1994, Andreozzi and Princivalle 2002). Disorder can be represented by the inversion parameter, x, defined in $^{[4]}(\text{Mg}_{1-x}\text{Al}_x)^{[6]}(\text{Al}_{2-x}\text{Mg}_x)\text{O}_4$, as the amount of Al$^{3+}$ in the tetrahedral site. By measuring x, this method can be used to determine the formation temperature, or most recent equilibration temperature, of the spinel. Previous studies of natural and synthetic spinel provide calibration curves of temperature versus cation ordering. Cation ordering measurements were done either in situ at high temperatures or on quenched samples at room temperature (Peterson et al. 1991, Millard et al. 1992, Maekawa et al. 1997, Princivalle et al. 1999, Redfern et al. 1999, Andreozzi and Princivalle 2002).

The cation ordering of spinel can be measured directly using $^{27}$Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy (Wood et al. 1986, Millard et al. 1992, Maekawa et al. 1997). $^{27}$Al MAS NMR can determine the environment around the Al atoms in the sample (Harris 1986, Kirkpatrick 1988, Navrotsky 1994). With this information, the ratio of octahedral to tetrahedral Al$^{3+}$ can be obtained. This ratio can be used to calculate x where $x = 2/(1+^{[6]}\text{Al}/^{[4]}\text{Al})$ (Millard et al. 1992). That x-value can then be used, with calibration curves from the literature, to provide a formation temperature estimate. These temperatures need to be interpreted in the context of other known or hypothesized information about the formation and any subsequent alteration of the spinel being studied.

The primitive materials in carbonaceous chondrites are not always as pristine as when they first formed in the solar nebula (McSween 1977a, 1977b, Kerridge 1993, Brearley and
Jones 1998, MacPherson 2003, Ivanova 2016). The materials were accreted into parent bodies and have been exposed to secondary processing on those parent bodies (Kerridge 1993, McSween Jr. 1999). Therefore, meteorites, and even different fragments within the same meteorite, have experienced varying degrees of alteration (McSween 1977b, Brearley and Jones 1998, Travis and Schubert 2005). Materials, such as Dark Lithic Inclusions (DIs), in Allende, show evidence of having experienced aqueous alteration and subsequent thermal dehydration (Johnson et al. 1990, Kojima and Tomeoka 1996). Kojima and Tomoeoka (1996) describe textures that appear related to aqueous interaction (e.g. veins and play textured silicates), but with no minerals typical of aqueous alteration present. This relationship suggests that aqueous alteration occurred (creating textures) and was followed by high temperature dehydration (altering minerals related to aqueous interactions) (Kojima and Tomeoka 1996). Allende CAIs show evidence of metasomatic alteration (Brearley and Jones 1998). This alteration is evidenced by the presence of secondary minerals, grossular, sodalite, and nepheline, for example (Brearley and Jones 1998). There is evidence for some heating in Allende, even indicating slight metamorphism, for example, the olivine content has a homogenous composition, indicating metamorphic equilibration (McSween 1977b, Brearley and Jones 1998). This alteration suggests that its primary materials may not be pristine and may represent parent body processing rather than nebular processing.

Given Allende’s evidence of parent body alteration, the measured temperature may be nebular, but is more likely to be from planetary processing. Using the cation-ordering in spinel from an Allende CAI, most recent equilibration temperature will be inferred.

5.3 Methods

5.3.1 Sample Preparation

Three samples of Allende were examined initially. Allende TS62b is on loan from Dr. Steve Simon and Dr. Lawrence Grossman from the University of Chicago, Chicago, Illinois, USA. Dr. Steve Simon is now at the Institute of Meteoritics (IOM), Albuquerque, New Mexico, USA. The sample is a thin section of an Allende CAI, which has had fassaite removed from the center. Allende Cr 3.17 and Cr 3.7c (Allende Cr-Samples) are on loan from Dr. Carl Agee at the University of New Mexico, Albuquerque, New Mexico, USA.
The sample is a collection of fragments of Allende resulting from freeze-thaw cycles preformed in 2012 at Western University. Allende 3529 is on loan from Dr. Tim McCoy at the Smithsonian Institution’s National Museum of Natural History (USNM), Washington D.C., USA. The sample is a whole CAI that has been crushed for use in the NMR spectrometer.

5.3.2 Micro X-ray Diffraction

Initial phase identification of the sample was done using micro X-ray diffraction (Flemming 2007). A Bruker D8 Discover Microdiffractometer having a Co X-ray source (CoKα = 1.78897 Å) with a 60 mm Co Gobel mirror, and a 300 μm nominal beam diameter was used. The microdiffractometer has theta-theta geometry so the sample remains stationary while the source moves through θ₁ and the detector through θ₂. The source and detector were rotated around the sample using omega scan mode, to increase the number of lattice planes observed in single crystals. In omega scan mode the beam and detector simultaneously rotate clockwise around the sample at the same rate, over a set number of degrees (ω). This motion imitates rotating the sample. The source and detector start at angles θ₁ and θ₂, respectively. They both move clockwise through ω degrees. θ₁ + θ₂ = 2θ, which remains constant through rotation for each frame. All three samples were examined (omega scan parameters are in Table 5.1). Phase identification by μXRD was used to confirm the presence of spinel and identify other phases present that may be required as NMR standards.

The data are collected as a General Area Detector Diffraction system (GADDS) image by the Vantec 500 detector. The GADDS image can be integrated along 2θ to produce a conventional intensity versus 2θ plot. The resulting diffractogram was analyzed using DIFFRAC.EVA software 2016 release, part of a set of programs DIFFRAC.SUITE (Bruker AXS 2010-2016), interfaced with the International Centre for Diffraction Data (ICDD) database for phase identification using diffraction patterns of known minerals.
Table 5.1. Parameters used to collect μXRD data for Allende TS62b, Allende Cr-
Samples, and USNM Allende 3529

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS62b</td>
<td>June 2014</td>
<td>15</td>
<td>25.5</td>
<td>15</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Frame 2</td>
<td>38.5</td>
<td>40</td>
<td>15</td>
<td>75</td>
</tr>
<tr>
<td>Cr-samples</td>
<td>June 2016</td>
<td>14.5</td>
<td>22</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Frame 2</td>
<td>35.5</td>
<td>40</td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td>Allende 3529</td>
<td>May 2016</td>
<td>14.5</td>
<td>40</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Frame 2</td>
<td>33.5</td>
<td>40</td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>June 2017*</td>
<td>14.5</td>
<td>21</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Frame 2</td>
<td>33.5</td>
<td>40</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>

*A new detector was installed before collection of these data. Data collected with the new detector were consistent with the previous data.

5.3.3 $^{27}$Al Magic Angle Spinning (MAS) Nuclear Magnetic Resonance Spectroscopy (NMR)

$^{27}$Al MAS NMR was done on a Bruker Avance II 21.1T 900 MHz (Al at 234.6 MHz) NMR spectrometer at the Ultrahigh Field NMR facility for solids at the National Research Council in Ottawa, Ontario, Canada. MAS NMR and two-dimensional triple-quantum (3Q) MAS NMR data were collected. Spectra were originally collected by Monika Haring, Dr. Victor Terskikh, and Dr. Roberta Flemming in 2012 as part of a fassaite thesis project.
(Haring et al. 2012, Haring 2013). For more details about the technique see Chapter 1 section 1.2.2 and Chapter 2 section 2.5. $^{27}$Al MAS NMR spectra were collected at a spinning frequency of 31.25 kHz, with a pulse width of 0.5 μs which produced a tip angle of 30° ($\pi/6$) to the solid. The relaxation delay was 5 seconds. Relative intensities of the tetrahedral and octahedral peaks were monitored at various relaxation delays to ensure quantitative data. $^{27}$Al 3Q MAS NMR spectra were collected at 31.25 kHz. The spectra were collected using a standard 3-pulse experiment, using a zero quantum filter (Amoureux et al. 1996). Spectra were rotor-synchronized in the indirect F1 dimension. In the isotropic dimension (F1 axis) of the spectrum, the anisotropic effects are removed, by the pulse sequence. The P1 excitation pulse was 2.6 μs. The P2 conversion pulse was 0.9 μs. The P3 90-degree soft selective pulse was 10 μs. Each t1 time increment lasted 32 μs. For Allende 3529, 960 transient scans were collected during each t1 increment. 24 t1 increments were collected, with a relaxation time of 2 seconds. Total collection time was one day. For Allende TS62b, 2160 transient scans were collected during each t1 increment. 72 t1 increments were collected, with a relaxation time of 2 seconds.

DMfit software (Massiot et al. 2002) was used to analyze the $^{27}$Al MAS NMR and the $^{27}$Al 3Q MAS NMR spectra. $^{27}$Al MAS NMR spectra, under the aforementioned experimental conditions, is quantitative. The software was used to create a model of the whole spectrum with individual peaks, which are then integrated. Integration gives the area under the peaks, which were then used to calculate the inversion parameter $x$. The $^{27}$Al 3Q MAS NMR spectra of the sample and the standards were used to help determine peak locations of the different phases present. This method helped in identifying extra phases and choosing the Al peaks representing the spinel, and confirmed the absence or presence of tetrahedral Al spinel. Peak shapes were also constrained using information from Stebbins et al. (1995).

5.3.4 Calibration Curves

Temperature estimates were made using calibration curves from previous studies. The studies examined cation ordering in spinel in relation to temperature. Studies were completed on both synthetic and natural spinel. Different techniques looked at the cation
ordering in situ at high temperatures or after quenching or cooling of samples. A summary of the models determined by each previous study used in this study is below (Table 5.2).

Table 5.2. Summary of literature calibration curves used in this study.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Nature or Synthetic Spinel</th>
<th>High Temperature or Quenched/ Cooled Samples</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peterson et al. 1991</td>
<td>Synthetic</td>
<td>High Temperature in situ</td>
<td>$^{[1]} \Delta G^\circ = \alpha + 2\beta x = -RT\ln(x^2(1-x)^{1\over 2}(2-x))^{-1}$ $(\alpha = -31 \pm 1 \text{ kJ/mol}, \beta = -10 \pm 3 \text{ kJ/mol})$</td>
</tr>
<tr>
<td>Millard et al. 1992</td>
<td>Synthetic</td>
<td>Quenched</td>
<td>$^{[1][2]} \Delta H_D = \alpha x + \beta x^2$ $(\alpha = 25 \pm 5 \text{ kJ/mol}, \beta = 5.8 \pm 9.5 \text{ kJ/mol})$</td>
</tr>
<tr>
<td>Maekawa et al. 1997</td>
<td>Natural</td>
<td>Both (Quenched and in situ high temperature)</td>
<td>$^{[1][2]} \ln K = -(\alpha + 2\beta x)/RT$ $(\alpha = 35 \pm 5 \text{ kJ/mol}, \beta = -32 \pm 5 \text{ kJ/mol})$</td>
</tr>
<tr>
<td>Princivalle et al. 1999</td>
<td>Natural</td>
<td>Cooled</td>
<td>$^{[3]} T(°C) = 6440 \times B$ $(B = [^4] \text{Al/Al}_{	ext{total}})$</td>
</tr>
<tr>
<td>Redfern et al. 1999</td>
<td>Synthetic</td>
<td>Room temperature and high temperature</td>
<td>$^{[1]} -RT\ln(x^2/((1-x)(2-x))) = \alpha + 2\beta x$ $(\alpha = 32.8 \pm 0.9 \text{ kJ/mol}, \beta = 4.7 \pm 2 \text{ kJ/mol})$</td>
</tr>
<tr>
<td>Andreozzi and Princivalle 2002</td>
<td>Synthetic</td>
<td>Quenched</td>
<td>$^{[4]} x = 21.396 - 80.714u$</td>
</tr>
</tbody>
</table>

$^{[1]}$ These models are based on O’Neill and Navrotsky 1983 model.
$^{[2]}$ This model is also based on the Navrotsky and Kleppa 1967 model.
$^{[3]}$ Princivalle et al. 1999 uses B value instead of x-value, where $B = [^4] \text{Al/Al}_{	ext{total}}$ for pure MgAl$_2$O$_4$ spinel.
$^{[4]}$ This model uses the oxygen position parameter (u). The model calculates inversion parameter (x) versus u for various temperatures, showing a linear relation. This model is used to estimate u and temperature.
5.4 Results

5.4.1 XRD

5.4.1.1 Allende TS62b

Phase identification using μXRD showed CAI mineralogy, as expected. Phases included spinel, fassaite, grossular, and anorthite (Figure 5.1). Some olivine was also identified.

Figure 5.1. Representative μXRD of TS62b showing all phases identified. First image is context of the whole CAI. Green: Spinel (MgAl₂O₄, PDF 21-1152); Light Blue: Forsterite (Mg₁.₈₀₈Fe₀.₁₉₂SiO₄, PDF 83-1536); Pink: Grossular (Ca₃Al₂(SiO₄)₃, PDF 75-1551); Orange: Anorthite (CaAl₂Si₂O₈, PDF 03-0505); Red: Gehlenite (Ca₂Al₂SiO₇·H₂O, PDF 16-0388); and Blue: Fassaite (Ca₁.₀₀Mg₀.₁₉₁Ti₀.₃₈₁Al₀.₁₃(Al₀.₇₄Si₁.₂₆)O₆, PDF 71-1541).
5.4.1.2 Allende Cr-Samples

Phase identification using μXRD identified one spot which had some refractory mineralogy, but no spinel (Figure 5.2). All other inclusions examined were identified as olivine and pyroxene of various compositions (Figure 5.3).

Figure 5.2. μXRD of a fluffy white inclusion in Allende Cr3.17. The inclusion contains olivine and pyroxene, the refractory mineral gehlenite, and the secondary mineral grossular. Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552); Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 72-1251); Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$, PDF 89-1489); and Blue: Hedenbergite (CaFeSi$_2$O$_6$, PDF 71-1498). (Scale bar = 500 μm)
Figure 5.3. μXRD of a coarse-grained inclusion in Allende Cr3.17. The inclusion contains olivine and pyroxene. Light Blue: Forsterite (Mg$_{1.824}$Fe$_{0.176}$SiO$_4$, PDF 83-1541); and Blue: Hedenbergite (Ca$_{0.79}$Al$_{0.06}$Fe$_{0.81}$Mg$_{0.47}$Fe$_{0.60}$Si$_2$O$_6$, PDF 74-2425). (Scale bar = 500 μm)
5.4.1.3 Allende 3529

Phase identification using XRD, most importantly, showed the presence of spinel in Allende 3529 (Figure 5.4). Fassaite, anorthite, melilite, and grossular were also identified (Figure 5.5). All phases present have NMR visible Al, so standards for each of these minerals were chosen to be collected on the NMR.

Figure 5.4. μXRD of a grain from Allende 3529 powder. The results show spinel and anorthite. In the 2D GADDS image, the spinel is the spotty rings (aggregates of crystals) and the anorthite is single spots (large single crystals). The white mineral is likely the spinel, while the black mineral is likely the anorthite. Green: Spinel (MgAl$_2$O$_4$, PDF 82-2424); Orange: Anorthite (CaAl$_2$Si$_2$O$_8$, PDF 41-1486). (Scale bar = 500 μm)
Al MAS NMR was collected on Allende 3529 and the fassaite removed from Allende TS62b. The TS62b sample came to us as a carbon-coated thin section, and we did not have permission from the loaners to pick out more than the fassaite they had picked out for us. The TS62b fassaite, is not pure fassaite. It contains some spinel. Data collected on the sample in 2012 was also used in this study (Haring 2013). NMR was not collected for Allende Cr-Samples, as no spinel was found. 3Q MAS NMR of the sample, combined with 3Q MAS NMR of the standards, show the approximate location of tetrahedral and...
octahedral spinel peaks as well as the location of peaks of the other phases present. Any disorder will be represented by Al in the tetrahedral spinel site.

5.4.2.1 Allende 3529

$^{27}$Al 3Q MAS NMR of Allende 3529 overlain by standards shows that the spinel in Allende 3529 has no tetrahedral peak but shows a prominent octahedral spinel peak (Figure 5.6 and Figure 5.7). This lack of a tetrahedral peak indicates that the spinel is an ordered normal spinel. The lack of tetrahedral peak is not evident in the one-dimensional MAS NMR (Figure 5.7). As there is no Al in the tetrahedral site, the inversion parameter for an ordered normal spinel is $x = 0$, indicating that the spinel is fully ordered normal.
Figure 5.6. Top: Two-dimensional $^{27}$Al 3Q MAS NMR spectrum for Allende 3529 (multi-coloured contoured). Bottom: The same spectrum Allende 3529 (blue), with NMR standards overlain. Synthetic spinel (MEQ 003) standard is green, natural fassaite standard (Allende TS62b) is blue, natural gehlenite standard (DANA #3461) is red, synthetic grossular (RM 003A) standard is pink. From these spectra, the sample contains fassaite, grossular, and some gehlenite, and no tetrahedral site for spinel. Arrows indicate the location the spinel tetrahedral peak would be.
The fassaite from Allende TS62b was used as a fassaite $^{27}$Al 3Q MAS NMR standard. However, as this standard is not pure fassaite and contains some impurities, such as spinel, a second standard for $^{27}$Al MAS NMR was used. The synthetic $\text{Di}_{75}\text{CaTs}_{25}$ (RM 009A) standard in the one-dimensional $^{27}$Al MAS NMR spectrum, shows that the fassaite peaks

![Graph](image)

**Figure 5.7.** a) $^{27}$Al MAS NMR spectra of the Allende 3529 (black) and the synthetic spinel (MEQ 003) standard (green). Note that it is not obvious by one-dimensional NMR alone that the tetrahedral site in the Allende 3529 spectrum does not show tetrahedral Al in the spinel. b) Allende 3529 $^{27}$Al MAS NMR spectrum (black), with synthetic $\text{Di}_{75}\text{CaTs}_{25}$ (RM 009D) standard (blue), showing the approximate locations of a pure fassaite sample. The phase under the tetrahedral peak at ~80 ppm is gehlenite. There is also anorthite under the tetrahedral peak, as anorthite was found by μXRD.
do not overlap the octahedral spinel peak, but have some overlap in the tetrahedral peak (Figure 5.7).

5.4.2.2 Allende TS62b

$^{27}$Al 3Q MAS NMR of Allende TS62b overlain by standards shows that the spinel in Allende TS62b has no tetrahedral peak but shows a prominent octahedral spinel peak (Figure 5.8). This lack of a tetrahedral peak indicates that the spinel is an ordered normal spinel. The inversion parameter for an ordered normal spinel is $x = 0$, as there is no Al in the tetrahedral site.
Figure 5.8. Top: $^{27}$Al 3Q MAS NMR spectrum for Allende TS62b. Bottom: The same spectrum of Allende TS62b, with NMR standards overlain. Synthetic spinel standard (MEQ 003) is green, natural fassaite standard is blue (which is Allende TS62b), natural gehlenite standard (DANA #3461) is red, synthetic grossular standard (RM 003A) is pink. From these spectra, the sample contains fassaite, grossular, and some gehlenite, and spinel. No overlap in the tetrahedral site by spinel standard indicates there is no tetrahedral Al in the spinel (location shown by arrows).
5.4.3 Temperature Estimates

The ordered spinel means the inversion parameter, x, equals 0, where x = 2/(1+[6]Al/[4]Al). There is no tetrahedral Al^{3+}. The x-value is therefore undefined using this equation. However, in an ordered spinel, by definition, x = 0. Therefore, we can use x = 0 for all calibration curve calculations. The calibration curves all approach 0 °C (273.15 K) using an x-value of 0. Temperature estimates based on the models using x = 0 are shown in Table 5.3. The calibration curves all have temperatures approaching 0 °C or equal to 0 °C when x = 0.

Table 5.3. Table showing models used and temperature estimates based on x-values of 0. The R-value used is 8.314 x 10^{-3} kJ/K/mol.

<table>
<thead>
<tr>
<th>Source</th>
<th>Model</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peterson et al. 1991</td>
<td>[1]ΔG° = α + 2βx = -RTln(x^2(1-x)^{-1}(1-2x)^{-1}) (α = -31 ± 1 kJ/mol, β = -10 ± 3 kJ/mol)</td>
<td>Undefined (approaching 0 °C = 273.15 K)</td>
</tr>
<tr>
<td>Millard et al. 1992</td>
<td>[1][2]ΔH_D = αx + βx^2 (α = 25 ± 5 kJ/mol, β = 5.8 ± 9.5kJ/mol)</td>
<td>0 °C = 273.15 K or undefined (depending on model used)</td>
</tr>
<tr>
<td>Maekawa et al. 1997</td>
<td>[1] lnK = -(α + 2βx)/RT (α = 35 ± 5 kJ/mol, β = -32 ± 5 kJ/mol)</td>
<td>Undefined (approaching 0 °C = 273.15 K)</td>
</tr>
<tr>
<td>Princivalle et al. 1999</td>
<td>T(°C) = 6440 * B (B = [4]Al/[Al_total])</td>
<td>0 °C = 273.15 K</td>
</tr>
<tr>
<td>Redfern et al. 1999</td>
<td>[1]-RTln(x^2/((1-x)(2-x))) = α + 2βx (α = 32.8 ± 0.9 kJ/mol, β = 4.7 ± 2kJ/mol)</td>
<td>Undefined (approaching 0 °C = 273.15 K)</td>
</tr>
<tr>
<td>Andreozzi and Princivalle 2002</td>
<td>[3]x = 21.396 – 80.714u</td>
<td>Temperature was not defined on graph at u = 0.265 (too low)</td>
</tr>
</tbody>
</table>

[1] These models are based on O’Neill and Navrotsky 1983 model.
[2] This model is also based on the Navrotsky and Kleppa 1967 model.
[3] This model uses the oxygen position parameter (u). The model calculates inversion parameter (x) versus u for various temperatures, showing a linear relation. This model is used to estimate u and temperature.
5.5 Discussion

The temperature estimates for x = 0 are maximum temperatures. Because ordering increases with decreasing temperature, once the spinel is completely ordered at one temperature, it cannot record any lower temperatures. Therefore, these temperature estimates are maximum temperatures. The spinel may have experienced lower temperatures without being able to record those by cation ordering. The temperature models for spinel cation ordering consistently have an undefined temperature approaching 0 °C or a temperature estimate of 0 °C. The difference is seen in the equations used to model the cation ordering and temperature. Those models which use ln give an undefined temperature approaching 0 °C as the ln(0) is undefined. Models that do not rely on ln and are linear or quadratic give a temperature estimate of exactly 0 °C. As temperatures approach 0 K, x-values approach 0, for normal spinel (O’Neill and Navrotsky 1983, Andreozzi and Princivalle 2002). No experimental measurements of cation ordering have been attempted at these near 0 °C temperatures (273.15 K).

The measured cation ordering temperatures for Allende (≤273 K) are much lower than nebular condensation temperatures (1300 – 1500 K) (Grossman 1972, Brearley and Jones 1998, Henning and Semenov 2013, Ivanova 2016). Ordering increases with decreasing temperature as entropy of disorder (ΔS_dis) becomes negligible. Because Allende CAIs contain ordered spinel, the meteorite must have equilibrated at temperatures far lower than nebular temperatures for a prolonged period of time. Did this alternate temperature regime occur in the nebula or on a parent body? Given the evidence for aqueous alteration with subsequent thermal dehydration in some Allende constituents (Kojima and Tomeoka 1996) and the evidence of metamorphic alteration in Allende (Brearley and Jones 1998) it is plausible that the temperatures recorded are from secondary parent body processing. Simply cooling in the nebula should not have affected the cation ordering to the extent recorded here, as seen in quench experiments from high temperatures (Millard et al. 1992, Maekawa et al. 1997). Re-ordering of cations during cooling and quenching was thought to be the reason for an upper limit of 1000 °C on temperatures measured by cation ordering of the spinel (Millard et al. 1992). The CAI may have cooled slowly in the parent body to
near 273.15 K. Reactions, even cation exchange reactions, are likely to proceed slowly at such low temperatures. This slow kinetics may indicate that Allende remained on the parent body long after it had cooled. Aqueous alteration on the Allende parent body continued for approximately 6 My after it cooled from peak temperatures (Elkins-Tanton et al. 2011). Timing of ejection events may play a role in the cation ordering of spinel in CAIs. The ejection event itself is not likely to produce high temperatures for long enough to affect cation ordering. Impact events occur on time scales of seconds (Gucsik 2009), whereas ordering requires at least minutes depending on the temperature (Andreozzi and Princivalle 2002). Ejection will affect how long the meteorite can be exposed to the temperature regime on the parent body, and how much cation reordering can occur before begin quenched on ejection. Models of carbonaceous chondrite parent bodies show that heating from $^{26}$Al decay is not very long lived (Grimm and McSween Jr. 1989, Travis and Schubert 2005). The heating is enough to melt ice to produce liquid water in the parent body and can result in low temperature aqueous alteration (90 °C to 180 °C) (Travis and Schubert 2005). Allende may have remained on the parent body past this period of aqueous alteration, giving the spinel time to re-order, upwards of 6 My after peak temperatures on Allende parent body (Elkins-Tanton et al. 2011).

Even without numerical temperature estimates, the fact that the spinel is ordered is significant. The high temperatures in the nebula are expected to result in disorder in the spinel. Disorder increases with increasing temperatures. This high degree of ordering (e.g. complete ordering) implies that Allende experienced a temperature regime very different than nebular for a prolonged period of time. Ordering at low temperatures would require a long time (O’Neill and Navrotsky 1983, Redfern et al. 1999, Andreozzi and Princivalle 2002) and a slow cooling rate to ensure a higher temperature isn’t recorded during a quench event.

Spinel is recording temperatures lower than estimates made for fassaite by Haring et al. (2012) and Haring (2013) of approximately 870 K. This temperature estimate is for an ordered fassaite and represents a maximum temperature recorded. Spinel and fassaite are therefore both ordered in the Allende samples. The different maximum temperatures could be a result of differing kinetics in ordering, similar to how minerals react differently to
shock events (Stöffler et al. 1991, 2018). More minerals from Allende CAIs should be examined for temperature estimates to establish a more constrained range of temperatures experienced.

5.6 Conclusions

$^{27}$Al MAS NMR of a CAI from Allende showed the spinel ($\text{MgAl}_2\text{O}_4$) to be fully ordered normal. Temperature estimates for the formation of an ordered spinel are only maximum temperatures, as once ordered, any lower temperatures would not be recorded by cation ordering. The maximum temperature experienced by this CAI is 273.15 K or 0 °C. This temperature is much lower than expected nebular condensation temperatures or hypothesized nebular heating events. Therefore, this temperature represents a maximum temperature experienced during thermal processing on the CV3 parent body. The degree of alteration seen in CV chondrites is varied (McSween 1977b, Brearley and Jones 1998). The processing that led to Allende spinel being ordered may have been localized on the parent body. The re-ordering would be a slow process at such low temperatures, there may be some relation to the time Allende spent on the parent body before being ejected.

In future, more Allende CAIs should be tested using this technique to determine if all spinel in Allende is ordered. This would help in determining the extent of alteration on the CV3 parent body. Additionally, other CAIs from CV type chondrites and other chondrites should be used to test the collective thermal histories, either recorded on the parent body or in the nebula. For these samples specifically, more thorough investigation of the Allende Cr-Samples would likely turn up CAIs to study further.

5.7 Acknowledgements

I thank Dr. Steve Simon and Dr. Lawrence Grossman for their loan of Allende TS62b. I thank Dr. Tim McCoy for his loan of Allende 3529. I thank Dr. Carl Agee for his loan of Allende Cr3.17 and Allende Cr3.7c. I thank Sarah McFadden for characterization of the gehlenite standard used. I thank Monika Haring for collecting samples and NMR data in 2012. Access to the 900 MHz NMR spectrometer was provided by the National Ultrahigh-Field NMR facility for solids (Ottawa, Canada). The facility is funded by the Canadian Foundation for Innovations (CFI), the Ontario Trust, Recherche Quebec, the National
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5.8 References


Haring, M.M. 2013. Crystal structure and Al/Si cation ordering in “Fassaite": A combined single crystal, $^{27}$Al and $^{29}$Si NMR study. The University of Western Ontario.


Millard, R.L., Peterson, R.C., and Hunter, B.K. 1992. Temperature dependence of cation disorder in MgAl<sub>2</sub>O<sub>4</sub> <sup>27</sup>Al and <sup>17</sup>O magic-angle spinning NMR. American Mineralogist, **77**: 44–52.


Chapter 6

6 Survey of Inclusions from the Tagish Lake C2 Carbonaceous Chondrite by Micro X-ray Diffraction

6.1 Executive Summary

Four samples of Tagish Lake C2 were surveyed in situ using µXRD; the matrix and many inclusions were examined. The intent of this survey was to find CAIs for potential extraction. Most inclusions were not CAIs. The main phases in the majority of inclusions were forsterite and pyroxene. One CAI was found but deemed to be too small for extraction. Inclusions and matrix of four Tagish Lake C2 samples are described.

6.2 Introduction

Tagish Lake C2 is possibly the most primitive meteorite on Earth found to date (Zolensky et al. 2002). The Tagish Lake C2 meteorite is an unclassified C2 carbonaceous chondrite. It is unclassified because of its dissimilarity to any known carbonaceous chondrite clan (i.e. CV, CO, CI, etc.) (Zolensky et al. 2002). Tagish Lake C2 is a friable meteorite, meaning it is easily broken up. It has a dark black matrix with many small white inclusions. Multiple lithologies have been identified in Tagish Lake C2 (Zolensky et al. 2002, Izawa et al. 2010b). These lithologies are divided based on the dominant mineralogy of the matrix. The identified lithologies include carbonate-rich (calcite dominated), carbonate-poor, inclusion-poor magnetite- and sulphide-rich, and carbonate-rich (siderite dominated) (Zolensky et al. 2002, Izawa et al. 2010b, 2010a). Tagish Lake is rich in phyllosilicates, sulphides, carbonates, and fine-grained magnetite, as a result of the high amount of aqueous alteration it experienced on its parent body (Zolensky et al. 2002, 2008). The C2 parent body is suggested to be a D-type asteroid (Hiroi et al. 2001). D-type asteroids have low porosity, high phyllosilicates, low abundance of high temperature nebular materials (CAIs, and chondrules), which they have in common with the Tagish Lake meteorite (Hiroi et al. 2001, Zolensky et al. 2002).

Calcium-Aluminium-Rich Inclusions (CAIs), dated at 4 567.9 ± 0.3 My (Bouvier and Wadhwa 2010), are the oldest materials in the solar system (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). They are thought to be solar nebular condensates,

This study of Tagish Lake C2 inclusions was inspired by a larger relict CAI found in Tagish Lake by Izawa et al. (2010a). The CAI was aqueously altered and contained mostly spinel and dolomite (Figure 6.1). It was not available for examination in during this project.
In this study, I attempted to find CAIs in Tagish Lake C2. I performed a survey of Tagish Lake C2 inclusions and matrix. Measurements were done using Micro X-ray Diffraction (μXRD). CAIs found would be extracted and used in a $^{27}$Al Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectroscopy study of spinel in CAIs. The study would measure the cation ordering in the spinel. This information could be used to determine formation temperature. The most recent equilibration temperature may be recorded instead of formation temperature. The temperature recorded depends on the amount of processing the CAI has undergone since its formation. Cation ordering in MgAl$_2$O$_4$ is predicted to be sluggish at low temperatures (Navrotsky and Kleppa 1967, Redfern et al. 1999), so high formation temperatures might be preserved despite aqueous alteration on the C2 parent body.

Figure 6.1. Relict CAI found in Tagish Lake containing spinel and dolomite. Modified from Izawa et al., (2010a).
6.3 Methods

A survey of the inclusions and different matrix lithologies was performed on four samples of Tagish Lake. For each sample, inclusions were examined and one or two spots on the matrix were collected. Samples included HG 48a, HG48b, MM01 26c, and PM 032 (Table 6.1).

Table 6.1. Samples of Tagish Lake Examined

<table>
<thead>
<tr>
<th>Sample</th>
<th>Image</th>
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</thead>
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<tr>
<td>HG 48a</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>HG 48b</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
</tbody>
</table>
6.3.1 Micro X-Ray Diffraction

Examination was done using a Bruker D8 Discover Diffractometer (theta-theta geometry) (Figure 6.2) using a Co X-ray source (Co kα radiation = 1.78897 Å), with a 60 mm Cobalt Gobel mirror, and a 300 μm nominal beam diameter (Flemming 2007). The diffractometer uses theta-theta geometry, where the source and detector move through θ₁ and θ₂ respectively. The sample remains stationary and the apparatus rotate around the sample. μXRD identifies the structure of minerals using Bragg’s Law: nλ = 2dsinθ (Navrotsky 1994). Where n is assumed to be one, lambda (λ) is the wavelength of the X-ray source,
and $d$ is the perpendicular distance between lattice planes. Theta ($\theta$) is an angle related to the geometry of the diffractometer.

Data were collected using omega scan mode. The snout angle relative to the sample is called $\theta_1$ and the detector angle relative to the sample is $\theta_2$. $\theta_1$ plus $\theta_2$ is the observed $2\theta$.

Figure 6.2. Top: Bruker D8 Discover Microdiffractometer showing X-ray source (beam) and collimator, drive-able XYZ stage, and Vantec 500 detector with GADDS software. Diagram shows how $2\theta$ is calculated based on the geometry of the diffractometer. Bottom: Two merged frames of a GADDS image showing $2\theta$ is the center of the detector. The range of each frame goes from $2\theta \pm$ the radius of the detector ($r = 25$ degrees of $2\theta$ at a 12 cm distance). The value of $2\theta$ remains constant during each frame, as the beam and detector are moving at the same rate clockwise around the stage. The value of $2\theta$ in the unlabeled frame is higher than $2\theta$ for the labelled frame.
angle in the center of the diffraction pattern, spanning 50° of 2θ (Figure 6.2). Parameters for μXRD in this project describe two frames collected by the omega scan function. The omega scans collect two frames with some overlapping degrees of 2θ. The frames are stitched together to give a range of 10-110° 2θ. θ₁ and θ₂ are the starting angles for the beam and detector, respectively. Omega (ω) is the number of degrees the beam and detector will move through. Both the source and detector rotate simultaneously clockwise around the sample to preserve a constant 2θ (θ₁ + θ₂ = 2θ). The time is the total collection time for the frame.

6.3.2 Sample Preparation

All samples were mounted in tinfoil on the μXRD to keep them from touching the plasticine mounting medium. Samples were examined using similar μXRD parameters (Table 6.2). PM 032 was collected with higher angle parameters because of the bumpy surface. Higher angles avoided the X-rays being blocked by the local highs on the sample surface.

Table 6.2. Parameters for collection of μXRD data for all Tagish Lake C2 samples examined

<table>
<thead>
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<th>Frame 2</th>
</tr>
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<tbody>
<tr>
<td></td>
<td># of spots</td>
<td>θ₁</td>
<td>θ₂</td>
</tr>
<tr>
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<td>February and March 2017</td>
<td>9</td>
<td>14.5</td>
</tr>
<tr>
<td>HG 48a (side b)</td>
<td>February and March 2017</td>
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<td>Date</td>
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<td>-----------------------------</td>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td></td>
<td># of</td>
<td>θ₁</td>
</tr>
<tr>
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<td>February and March 2017</td>
<td>18</td>
<td>14.5</td>
</tr>
<tr>
<td>HG 48b (side b)</td>
<td>February and March 2017</td>
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<td>14.5</td>
</tr>
<tr>
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<td>April 2017</td>
<td>20</td>
<td>14.5</td>
</tr>
<tr>
<td>PM 032</td>
<td>June 2016</td>
<td>4</td>
<td>21</td>
</tr>
</tbody>
</table>

### 6.4 Results

Examination of the matrix by μXRD commonly shows forsterite, magnetite, pyrrhotite, siderite, and saponite (Figure 6.3 to Figure 6.5). The distribution of matrix phases in HG 48a, HG 48b, and MM01 26c is very different than the distribution in the matrix of PM 032. The clast in MM01 26c has the same mineralogy as the rest of the matrix in the sample (Figure 6.6). Most inclusions were olivine-rich (Figure 6.7 and Figure 6.8). Some contained enstatite or pyroxene (Figure 6.6). One inclusion was a likely CAI, containing spinel (Figure 6.9).
Figure 6.3. μXRD of matrix in HG 48a, showing forsterite, magnetite, pyrrhotite, gypsum, siderite, and saponite. Olivine is coarse-grained (produces spots in GADDS image). The rest of the phases are fine-grained (< 5 μm, producing complete homogenous Debye rings). Saponite shows turbostratic stacking, typical of clay minerals (the initial peak is followed by a tail of decreasing intensity).

Light Blue: Forsterite (Mg₂(SiO₄), PDF 08-0783); Pink: Magnetite (Fe₃O₄, PDF 85-1436); Purple: Pyrrhotite (FeS, PDF 02-1241); Orange: Gypsum (CaSO₄ · 2H₂O, PDF 06-0046); Blue: Siderite (FeCO₃, PDF 12-0531); Red: Saponite-18A (Ca₀.₃Mg₃(Si,Al)₄O₁₀(OH)₂ · H₂O, PDF 06-0002). (Scale bar = 500 μm)
Figure 6.4. μXRD of matrix in HG 48a, showing forsterite, magnetite, pyrrhotite, gypsum, siderite, and saponite. Olivine is coarse-grained (produces spots in GADDS image). The rest of the phases are fine-grained (< 5 μm, producing complete homogenous Debye rings). Saponite shows turbostratic stacking, typical of clay minerals (the initial peak is followed by a tail of decreasing intensity).

Light Blue: Forsterite (Mg$_2$(SiO$_4$), PDF 08-0783); Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436); Purple: Pyrrhotite (FeS, PDF 02-1241); Blue: Siderite (FeCO$_3$, PDF 12-0531); Red: Saponite-18A (Ca$_{0.3}$Mg$_3$(Si,Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002). (Scale bar = 500 μm)
Figure 6.5. µXRD of matrix in MM01 26c, showing forsterite, magnetite, pyrrhotite, siderite, and saponite. Olivine is coarse-grained (spots in GADDS image). The other phases are fine-grained (< 5 μm, producing complete homogenous Debye rings). Saponite shows turbostratic stacking, typical of clay minerals (the initial peak is followed by a tail of decreasing intensity). The location of the target is producing a poor X-ray signal.

Light Blue: Forsterite (Mg$_2$(SiO$_4$), PDF 08-0783); Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436); Purple: Pyrrhotite (FeS, PDF 02-1241); Blue: Siderite (FeCO$_3$, PDF 12-0531); Red: Saponite-18A (Ca$_{0.3}$Mg$_3$(Si,Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002). (Scale bar = 500 μm)
Figure 6.6. μXRD of the unusual clast in MM01 26c, showing forsterite, magnetite, pyrrhotite, gypsum, siderite, and saponite. Olivine is coarse-grained (produces spots in GADDS image). The rest of the phases are fine-grained (< 5 μm, producing complete homogenous Debye rings). Saponite shows turbostratic stacking, typical of clay minerals (the initial peak is followed by a tail of decreasing intensity). This spot also has an amorphous phase (bright broad spot on the right side of the GADDS image, and the noisy signal at the front of the EVA pattern from 10 to ~30 degrees 2Theta) which was present only on the clast.

Light Blue: Forsterite (Mg$_2$(SiO$_4$), PDF 08-0783); Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436); Purple: Pyrrhotite (FeS, PDF 02-1241); Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046); Blue: Siderite (FeCO$_3$, PDF 12-0531); Red: Saponite-18A (Ca$_{0.3}$Mg$_3$(Si,Al)$_4$O$_{10}$(OH)$_2$ · H$_2$O, PDF 06-0002). (Scale bar = 500 μm)
Figure 6.7. μXRD of a massive grey inclusion in HG 48b, showing forsterite, magnetite, saponite, and clinoenstatite. Olivine and clinoenstatite are coarse-grained (produces rows of spots in GADDS image, 15-50 μm grain size (Bramble et al. 2015)). The rest of the phases are fine-grained (< 5 μm, producing complete homogenous Debye rings).

Light Blue: Forsterite (Mg₂(SiO₄), PDF 08-0783); Pink: Magnetite (Fe₃O₄, PDF 85-1436); Purple: Pyrrhotite (FeS, PDF 02-1241); Red: Saponite-18A (Ca₀.₃Mg₃(Si,Al)₄O₁₀(OH)₂ · H₂O, PDF 06-0002); Blue: Clinoenstatite (MgSiO₃, PDF 76-0526). (Scale bar = 500 μm)
Figure 6.8. μXRD of an inclusion in HG 48a, showing forsterite, magnetite, pyrrhotite, gypsum, siderite, and saponite. The forsterite is a large single crystal (spots on GADDS image). The rest of the phases are fine-grained (< 5 μm, producing complete homogenous Debye rings).

Light Blue: Forsterite (Mg_2(SiO_4), PDF 08-0783); Pink: Magnetite (Fe_3O_4, PDF 85-1436); Purple: Pyrrhotite (FeS, PDF 02-1241); Orange: Gypsum (CaSO_4 · 2H_2O, PDF 06-0046); Blue: Siderite (FeCO_3, PDF 12-0531); Red: Saponite-18A (Ca_0.3Mg_3(Si,Al)_4O_10(OH)_2 · H_2O, PDF 06-0002). (Scale bar = 500 μm)
Figure 6.9. μXRD of an inclusion in HG 48b showing spinel, forsterite, magnetite, pyrrhotite, gypsum, siderite, and saponite. The forsterite is a large single crystal (spots on GADDS image). The rest of the phases are fine-grained (< 5 μm, producing complete homogenous Debye rings). Saponite shows turbostratic stacking, typical of clay minerals (the initial peak is followed by a tail of decreasing intensity).

Light Blue: Forsterite (Mg$_2$(SiO$_4$), PDF 08-0783); Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436); Purple: Pyrrhotite (FeS, PDF 02-1241); Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046); Blue: Siderite (FeCO$_3$, PDF 12-0531); Red: Saponite-18A (Ca$_{0.3}$Mg$_3$(Si,Al)$_4$O$_{10}$(OH)$_2$ · H$_2$O, PDF 06-0002); Green: Spinel (MgAl$_2$O$_4$, PDF 05-0672). (Scale bar = 500 μm)
6.5 Discussion

Inspired by the large aqueously altered CAI found by Izawa et al (2010a), an in situ survey was performed on Tagish Lake inclusions. There are coarse-grained grey inclusions, single crystal inclusions, and fine-grained white inclusions. Types of inclusions known in Tagish Lake C2 include Ameboid Olivine Aggregates (AOAs), chondrules, olivine grains, pyroxene, CAIs, carbonate nodules, and coarse-grained phyllosilicates (Zolensky et al. 2002, Bland et al. 2004, Izawa et al. 2010b). The coarse-grained grey inclusions here are probably chondrules or pyroxene inclusions. The single crystal inclusions are olivine grains. The white inclusions are AOAs or CAIs. Most of the inclusions studied here are likely olivine and pyroxene grains. There is only one which contains refractory minerals associated with CAIs.

The matrix examined shows previously documented lithologies. The samples here represent the new lithology, carbonate-rich siderite dominated (Izawa et al. 2010b). Previously documented samples, show a large CAI in the carbonate-rich calcite dominated lithology (Izawa et al. 2010a). Samples of that lithology were not available to be examined here but may be the best lithology in which to find CAIs.

The matrix clast in MM01 26c is the same composition as the host matrix. The clast, however, has a different appearance. It is darker than the surrounding matrix. This distinction implies a difference in processing between the clast and the matrix.

One inclusion surveyed is likely a CAI, containing spinel. With Tagish Lake C2 being aqueously altered, other phases normally present in CAIs may be altered. Spinel is a common mineral in refractory inclusions and is not very susceptible to aqueous alteration. It was decided that the CAI was too small to remove an adequate amount of sample for NMR (minimum 3 mg). The matrix is also heavily oxidized and contains magnetite due to aqueous alteration on the parent body (Zolensky et al. 2002, 2008). The large amount of magnetite may interfere with the NMR magnet.
6.6 Conclusions

Four samples of Tagish Lake C2 were examined by μXRD: HG-48a, HG-48b, MM01 26c, and PM 032. Data were collected on white and grey inclusions in the sample. Most inclusions appear to be grains of olivine and pyroxene. One inclusion that contained spinel, is likely to be a CAI, but was deemed too small for extraction. Matrix and inclusions from the four samples were characterized.

Matrix was also examined. The matrix displayed carbonate-rich siderite dominated lithology, consistent with that described by Izawa et al. (2010b). Sample MM01 26c possesses a clast of matrix. The clast appears distinct from the rest of the matrix but has the same mineralogy as the surrounding matrix. It is mechanically distinct and may represent different processing of the matrix.

Ultimately, the small CAI found was not extracted for study by $^{27}$Al MAS NMR. The inclusion is very small (400 μm) and would likely not provide enough sample for NMR spectroscopy. The large amount of magnetite in the sample also poses a problem in using NMR spectroscopy. Paramagnetic minerals interfere with the signal, and magnetic samples can’t be spun freely in the NMR probe.

In the future, more Tagish Lake C2 samples should be examined for CAIs. Large CAIs will diminish the risk of contamination with magnetite. They will also provide more starting material. After picking out matrix and removal of magnetite enough sample should remain to collect good quality NMR data (minimum 3 to 5 mg). The carbonate-rich lithology may be the most likely to contain large CAIs and could be examined. Studying CAIs in Tagish Lake C2 will help provide insight into early solar system processes and the processing in the Tagish Lake C2 parent body. Tagish Lake C2 has not undergone much thermal metamorphism on the parent body and so may hold a record of early solar system temperatures. Tagish Lake C2 is currently unclassified; it is the only meteorite of its kind. More information about it can enrich our understanding of carbonaceous chondrites as a whole.
6.7 Acknowledgements

I thank Dr. Phil McCausland and Dr. Audrey Bouvier for sample selection and loans from Western University’s Meteorite Collection.
6.8 References


Chapter 7

7 Survey of Inclusions in NWA 4502 and NWA 7678

7.1 Executive Summary

Two samples of NWA 4502 and one of NWA 7678 were examined in situ with µXRD. Inclusions in the samples were characterized mineralogically. The inclusions were surveyed with the intent of finding CAIs for extraction to use in an NMR study. One CAI was found in NWA 4502. The CAI was too small for extraction of enough sample for NMR. The majority of the inclusions in NWA 4502 were olivine- and pyroxene-rich, likely chondrules. A fluffy white inclusion examined in NWA 7678 may be an Ameboid Olivine Aggregate (AOA). The main phase in the inclusion is forsterite with some minor pyroxene. AOAs containing spinel would be an interesting candidate for $^{27}$Al MAS NMR.

7.2 Introduction

Calcium-Aluminium-Rich Inclusions (CAIs) are refractory inclusions in chondrites, which formed in the solar nebula (Grossman 1972, Kerridge 1993, Brearley and Jones 1998, McSween Jr. 1999, Ivanova 2016). They are the oldest materials in the solar system and consist mainly of melilite (gehlenite), spinel, fassaite, and anorthite (Brearley and Jones 1998, MacPherson 2003, Ivanova 2016). CAIs are thought to form by condensation in the nebula, often with subsequent nebular heating events altering the CAIs (Grossman 1972, Kerridge 1993, Brearley and Jones 1998, McSween Jr. 1999, Ivanova 2016). CAI mineralogy and formation is described in more detail in Chapter 1 Section 1.2.3. The spinel in CAIs is nearly pure MgAl$_2$O$_4$ (Brearley and Jones 1998, Ivanova 2016). The distribution of Al$^{3+}$ and Mg$^{2+}$ cations in sites between the oxygen anions is related to the formation temperature of the spinel (described in Chapter 1 Section 1.2.1) (O’Neill and Navrotsky 1984, Wood et al. 1986, Peterson et al. 1991, Millard et al. 1992, Maekawa et al. 1997, Princivalle et al. 1999, Redfern et al. 1999, Andreozzi and Princivalle 2002).

Ameboid Olivine Aggregates (AOAs) are another type of refractory inclusion, which have an irregular shape. They are rich in fine-grained forsterite or aggregates of forsterite crystals and typically contain pyroxene and spinel as minor phases (Brearley and Jones 1998, MacPherson 2003, MacPherson et al. 2005). They can enclose other types of
refractory inclusions, including small CAI fragments (Brearley and Jones 1998, MacPherson 2003, MacPherson et al. 2005). AOAs are less refractory than CAIs and their formation mechanism is not well understood (Brearley and Jones 1998, MacPherson 2003, MacPherson et al. 2005).

Studying minerals in these inclusions can provide insight into their formation conditions in the nebula. Two CV3 carbonaceous chondrites will be studied. NWA 7678, purchased from The Meteorite Exchange and two samples of NWA 4502. One is on loan from Dr. Melissa Strait at Alma College, Alma, Michigan, USA (NWA 4502). The other is on loan from Dr. Kim Tait at the Royal Ontario Museum (ROM), Toronto, Ontario, Canada (NWA 4502 ROM). NWA 7678 and NWA 4502 will be examined by μXRD to look for spinel-bearing CAIs to be extracted. Upon successful extraction, CAIs would be examined using $^{27}\text{Al}$ MAS NMR spectroscopy. The cation ordering in the spinel can provide a formation or most recent equilibration temperature for the spinel. This temperature would provide insight into the temperature regimes in the nebula or on the CV3 parent body.

This study aims to examine samples of NWA 4502 and NWA 7678. Using μXRD the inclusions in the sample were tested to see if they are CAIs. Only one small CAI was found during this examination. The mineralogy of the inclusions is reported.

7.3 Methods

7.3.1 Micro X-ray Diffraction

Examination of the samples was done with a Bruker D8 Discover Microdiffractometer with X-ray source (Co kα radiation wavelength = 1.78897 Å), a 60 mm Cobalt Gobel Mirror and a 300 μm nominal beam diameter (Flemming 2007). Spots to examine were chosen based on a “fluffy”/irregular appearance and/or a white or light colour. The data is collected as a GADDs image by the Vantec 500 detector with a 50° 2θ range. The GADDs image can be integrated along 2θ. 2θ is the sum of the angles between the source and the sample and between the detector and the sample (Figure 7.1). The resulting diffractograms are analyzed using Diffrac.SUITE EVA software (Bruker-AXS 2010-2016, 2016 release). The software matches the diffraction pattern to those in the International Centre for Diffraction Data (ICDD) database. The source and detector rotate clockwise around the
sample at the same rate. This motion imitates rotating the sample. The movement is done over a set number of degrees (ω), chosen based on the diffractometer.

![Diagram of diffractometer](image)

Figure 7.1. Top: Bruker D8 Discover Microdiffractometer showing X-ray source (beam) and collimator, drive-able XYZ stage, and Vantec 500 detector with GADDS software. Figure shows how 2θ is calculated based on the geometry of the diffractometer. Bottom: Two frames of a merged GADDS image labelled to show the direction of increasing 2θ and the location of 2θ as the center of the detector. The range of the scan goes from 2θ to 2θ plus and minus the radius of the detector (r = 25 degrees of 2θ). The value of 2θ remains constant during each frame, as the beam and detector are moving simultaneously clockwise around the stage.

7.3.2 Extraction

Extraction of CAIs was done using a metal pick to chisel out the CAI. Chiseling was done under ethanol to prevent any sample from being lost. We attempted to keep contamination
of the CAI powder from the matrix to a minimum. The sample was hand-picked under ethanol after extraction to clean out any matrix or other contamination.

7.3.3 Sample Preparation

7.3.3.1 NWA 4502

NWA 4502 came as a large irregular piece (Figure 7.2). It had a metal hanger attached at the top of the sample. The hanger was used for a previous artificial shock study performed by Dr. Melissa Strait. The shock experiment used low energy impacts, intended to create craters. The impact event lasted for 2 μs and may have heated the sample for 85 μs, however ordering to equilibrium can require minutes (4 minutes at 900 °C) (Andreozzi and Princivalle 2002). All the material affected by the impact was ejected from the sample. The shock study is not expected to have affected cation order of spinel. During this previous study, the sample was also examined by Micro Computed Tomography (μCT) scanning. The μCT scans show density differences throughout the slab. It is a non-destructive technique. X-rays are focused on the sample and a detector collects the X-ray images. The imaging is done at various angles by rotating the sample or the X-ray source. Virtual slices of the sample are created in a computer from the X-ray images, which can be scrolled through on a 3-D model of the sample. The scans were collected on a GE eXplore speCZT. Collection parameters used were defined by McCausland et al. (2010) and Charles et al. (2018). Collection energies ranged from 80 – 110 kV. Scans were 900 separate images over one full 360° rotation. Detector is a CdZnTe array surrounding the

Figure 7.2. Left: NWA 4502 sample prior to cutting, white line shows approximate cut location of the first cut. Right: Slice A, resulting from the first cut.
sample. Scan files were viewed and manipulated using MicroView software. Scans were used to determine cut location in NWA 4502 (Figure 7.3). Cut locations were chosen based on the irregular shape of inclusions visible in the μCT scans. After the sample was cut, the cut pieces were examined using μXRD (Table 7.1).

Table 7.1. Parameters used for collecting μXRD data for NWA 4502

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>January 2018</td>
<td>14.5</td>
<td>20.5</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>Frame 2</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>

7.3.3.2 NWA 4502 ROM

NWA 4502 ROM came as a small slice. The surface of the slice was examined by μXRD (Table 7.2). CAIs are typically white in colour. No white inclusions were seen in the sample upon visual examination.

Table 7.2. Parameters used for collecting μXRD data for NWA 4502 ROM

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 2017</td>
<td>14.5</td>
<td>20.5</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>Frame 2</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>

7.3.3.3 NWA 7678

NWA 7678 was purchased as a cut slab. It was examined as is using μXRD (Table 7.3). One large, white, irregularly shaped inclusion was examined. Other smaller white inclusions were also studied. The large inclusion (~0.5 cm) would provide a good size for extraction.
Table 7.3. Parameters used for collecting μXRD data for NWA 7678

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
<th>Theta2 (θ₂)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 2018</td>
<td>14.5</td>
<td>25.5</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>Frame 2</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>90</td>
</tr>
</tbody>
</table>

7.4 Results

7.4.1 NWA 4502

Using μCT scans, a large, irregular inclusion was observed. This inclusion determined the cut location. The inclusion seen using the μCT scans was determined to be olivine and pyroxene by μXRD (Figure 7.4). This inclusion was not visually very different from the matrix. Two white inclusions were also examined, which were not visible by μCT. One was a gehlenite inclusion (Figure 7.5). The other was a small CAI with spinel, fassaite, gehlenite, and forsterite (Figure 7.6). The small CAI identified was chosen for extraction. Extraction was attempted using a metal pick in a glass petri dish filled with ethanol. As a result of complications during extraction, which resulted in contamination of the sample with the glass from the petri dish in which the CAI was being extracted, the CAI was not examined by $^{27}$Al NMR spectroscopy.
Extraction of the CAI from NWA 4502 was difficult. The CAI was very small. We attempted to pick the CAI out with a metal pick. The goal was to do so without much matrix contamination. The CAI was smaller than the tip of the pick. The size prevented the CAI from being scraped. We decided to try to chisel out the sample by tapping the pick into the inclusion. Metal wrenches of different sizes and masses were used to hit the metal pick. The different wrenches allowed for various amounts of pressure when extracting the inclusion. The picking was done under ethanol and in a glass petri dish. The glass petri dish shattered under the pressure of chiseling. Some of the sample was lost and the rest was contaminated with glass pieces. Picking out the glass, the recovered sample was only 0.4 mg. This amount is too little for NMR spectroscopy.

A better extraction technique is needed for future CAIs. Scraping, rather than chiseling, should provide more control. Extraction is easier with larger CAIs. Scraping larger CAIs will be easier and less likely to cause matrix contamination. Also a plastic petri dish should be used to prevent breakage of a glass petri dish during extraction.
Figure 7.4. XRD of the large, irregular inclusion in NWA 4502 seen in the μCT scans indicated by arrow. The two main phases are forsterite and diopside. GADDS image reveals homogenous rings indicating that sample target is fine-grained (< 5 μm).

Light Blue: Forsterite (Mg$_{1.812}$Fe$_{0.188}$(SiO$_4$); PDF 83-1537) and Dark Blue: Diopside (CaMg(SiO$_3$)$_2$; PDF 02-0663).
Figure 7.5. $\mu$XRD of a rounded grey inclusion in NWA 4502. The main phase is gehlenite. Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$; PDF 35-0755).
No inclusions examined on the surface of the intact piece of NWA 4502 ROM contained spinel (Figure 7.7). They were mostly olivine-rich inclusions, likely chondrules (Figure 7.8). Some were very weathered, showing the presence of goethite (Figure 7.8 and 7.9).
Figure 7.7. Context photo of NWA 4502 ROM. Arrows indicate the location of the spots displayed below. (Left arrow shows location of spot in Figure 7.8 and right arrow is Figure 7.9)
Figure 7.8. μXRD of an olivine-rich inclusion in NWA 4502 ROM. This inclusion has forsterite, enstatite, and diopside. Light Blue: Forsterite ferroan (Mg$_{1.83}$Fe$_{0.18}$SiO$_4$, PDF 72-2462); Dark Blue: Fassaite (Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$; PDF 83-2075); and Pink: Goethite (Fe$_2$O$_3$·H$_2$O, PDF 02-0272). (Scale bar = 500 μm)
The large, white, irregular inclusion examined was found to be olivine and pyroxene (Figure 7.10). The inclusion in NWA 7678 is not a CAI and contained no spinel. No extraction was attempted using this sample. The inclusion would not be useful in this $^{27}$Al NMR study of spinel.

Figure 7.9. μXRD of an olivine-rich inclusion in NWA 4502 ROM that is highly weathered. This inclusion has forsterite, clinoenstatite, and goethite. Blue: Clinoenstatite (MgSiO$_3$, PDF 73-1758); Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117); and Pink: Goethite (Fe$_2$O$_3 \cdot$ H$_2$O, PDF 02-0273). (Scale bar = 500 μm)

7.4.3 NWA 7678

The large, white, irregular inclusion examined, was found to be olivine and pyroxene (Figure 7.10). The inclusion in NWA 7678 is not a CAI and contained no spinel. No extraction was attempted using this sample. The inclusion would not be useful in this $^{27}$Al NMR study of spinel.
Figure 7.10. μXRD of the large white inclusion in NWA 7678 (indicated by arrow in context image). There are two phases present: Light Blue: Forsterite \(((\text{Mg}_{1.86}\text{Fe}_{0.14})\text{Si}_4\text{O}_4)\); PDF 77-1025) and Dark Blue: Diopside \((\text{CaMgSi}_2\text{O}_6)\); PDF 03-0860).
7.5 Discussion

The fluffy white inclusion in NWA 7678 is likely an Amoeboid Olivine Aggregate (AOA). AOAAs are common refractory inclusions in carbonaceous chondrites (Brearley and Jones 1998, MacPherson 2003, MacPherson et al. 2005). The main phase in these is forsterite (Fo$_{93}$ according to ICDD card PDF 77-1025 with formula (Mg$_{1.86}$Fe$_{0.14}$)(SiO$_4$)). The lack of iron in this olivine contributes to the white colour of these inclusions. μXRD is a non-destructive technique for examining refractory inclusions in meteorites. It can differentiate between CAIs and AOAAs based on mineralogy.

The pyroxene in this AOA is structurally similar to diopside. In future, chemical analysis can be used to determine pyroxene is in this AOA. A common refractory pyroxene is fassaite, which has a similar structure to diopside. Fassaite is an aluminous-diopside and may be the pyroxene seen here.

The gehlenite inclusion in NWA 4502, may be a type of melilite-rich CAI. Gehlenite and akermanite are end members of the melilite solid solution. The Al-rich gehlenite end member is found in CAIs. Because the inclusion does not contain spinel, it could not be used in this study. The small CAI in NWA 4502 has minerals expected in CAIs: spinel, fassaite, and gehlenite. Its μXRD results also showed forsterite. This forsterite is likely being picked-up from the matrix as the beam diameter extends beyond the inclusion.

7.6 Conclusions

Inclusions from NWA 7678 and NWA 4502 were examined and characterized. NWA 7678 did not contain any CAIs for extraction. NWA 4502 had one small spinel-containing CAI that was chosen for extraction. Despite hand-picking under ethanol, not enough clean sample was recovered to be used in NMR spectroscopy. Future extractions will be done on larger CAIs. The inclusions will be scraped out, rather than chiseled. Scraping will allow for greater control on which areas are picked.

AOAs are similar to refractory inclusions like CAIs. Little is known about their formation mechanism. Temperature measurements from spinel in AOAAs and from CAIs enclosed in AOA would be an interesting comparison. Would the CAIs in AOAAs record similar
temperatures to individual CAIs, or would they record the formation temperature of the AOA?

7.7 Acknowledgements

I thank Dr. Melissa Strait for her loan of NWA 4502 and her collaborators Dr. George Flynn at the State University of New York-Plattsburgh and Dr. Dan Durda at the Southwest Research Institute, for allowing me to use their sample. I thank Dr. Kim Tait for her loan of NWA 4502 ROM. I thank Ivan Barker for allowing me to use the precision-tipped tweezers from his lab during picking and for his guidance on picking technique.
7.8 References


Chapter 8

8 Discussion and Conclusions

Seven carbonaceous chondrites (CCs) were examined using Micro X-ray Diffraction (μXRD), Calcium-Aluminium-Rich Inclusions (CAIs) were provided for three of these CCs and the goal was to find spinel-containing CAIs to extract from the remaining CCs (Table 8.1). $^{27}$Al MAS NMR was collected on extracted CAIs to measure cation ordering in the spinel. Cation ordering in spinel was used to estimate formation or most recent equilibration temperature of the CAIs. Three of the sample meteorites had spinel-containing CAIs: Tagish Lake C2 sample HG48a, NWA 4502 CV3, and NWA 6603 CV3. Another four samples were of CAIs, from three different meteorites, which were confirmed to contain spinel: Allende CV3 (TS62b and USNM 3529), NWA 2364 CV3, and NWA 6991 CV3. Other samples were not found to contain spinel or CAIs: NWA 7678 CV3, Allende CV3 (Cr3.7c and Cr3.17), Tagish Lake C2 (HG 48b, MM01 26c, and PM 032). Unless otherwise stated, throughout the rest of this chapter, the meteorite type is CV3.

The CAI in Tagish Lake C2 was deemed to be too small to be useful for NMR, the amount of magnetite in the sample also posed a problem for NMR. The CAI in NWA 4502 was also small, but extraction was attempted. Ultimately, not enough sample was collected for NMR spectroscopy. The large CAI in NWA 6603 was successfully extracted. $^{27}$Al MAS NMR spectroscopy was acquired for the NWA 6603 (1-92), NWA 2364, NWA 6991 (black and white fractions), and Allende 3529 and TS62b. 3Q MAS NMR spectra were acquired for all but NWA 6991 (black fraction).

This study showed that nebular temperatures can be estimated using cation ordering in spinel from unaltered CAIs. It was the first to use this cation ordering technique on spinel in CAIs. Temperatures can also be measured in altered CAIs by this technique. These temperature estimates can be useful in understanding the alteration history of chondrites.
**Table 8.1 Summary of meteorite samples and CAIs found**

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Samples</th>
<th>Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende CV3</td>
<td>Cr 3.7c, Cr3.17, TS62b, 3529</td>
<td>No CAIs were found in Cr-samples, TS62b and 3529 are CAIs which contain spinel, NMR was collected on these in 2012 (Haring 2013)</td>
</tr>
<tr>
<td>Tagish Lake C2</td>
<td>HG 48a, HG 48b, MM01 26c, PM 032</td>
<td>One CAI was found in HG 48a. The CAI was deemed too small for extraction. No NMR was collected.</td>
</tr>
<tr>
<td>NWA 2364 CV3</td>
<td>The Crucible</td>
<td>The sample is a CAI. It was found to contain spinel. NMR was collected in 2017.</td>
</tr>
<tr>
<td>NWA 6991 CV3</td>
<td>B4 (black and white fractions)</td>
<td>The sample is a CAI. It was found to contain spinel. Sample was hand separated to concentrate spinel. NMR was collected on both separates in 2017.</td>
</tr>
<tr>
<td>NWA 4502 CV3</td>
<td>NWA 4502, NWA 4502 ROM</td>
<td>One small CAI was found in NWA 4502. Extraction was attempted. Complications prevented extraction of enough sample. No NMR was collected.</td>
</tr>
<tr>
<td>NWA 7678 CV3</td>
<td>NWA 7678 slice</td>
<td>No CAIs were found in NWA 7678.</td>
</tr>
<tr>
<td>NWA 6603 CV3</td>
<td>NWA 6603 1-92, NWA 6603 16-7</td>
<td>One CAI was found in 1-92 and one in 16-2. The CAI from 1-92 was extracted. NMR was collected in 2018.</td>
</tr>
</tbody>
</table>
8.1 Results Review

Cation ordering was measured in spinel from five CAIs. The CAIs were from four different meteorites (Table 8.1). Cation ordering was measured using $^{27}$Al MAS NMR spectroscopy. Six calibration curves from the literature were used to calculate temperatures from the cation ordering in the spinel (Table 8.2 and 8.3). Figure 8.1 summarizes the temperature estimates for each meteorite from each mathematical calibration model. Calibration curve graphs are displayed in Figures 8.2 to 8.7. Temperature estimates from the calibration curve graphs are summarized in Table 8.4. The errors for the high temperature NWA 6603 estimates are larger than the errors for the other estimates. The high errors are partly a result of the model used. Most of the models have shallow slopes at the high and low range of temperatures. This results in larger variation in temperature estimates within a range of similar $x$-values, than is seen for the mid-range temperatures where the model is approximately linear. This effect is not seen using the Princivalle et al. (1999) model because their model uses a linear relationship throughout. The temperature estimates from Andreozzi and Princivalle (2002) are extrapolations beyond the modelled data. These are therefore less accurate estimates than those provided by other models.

Table 8.2 Calibration curves from the literature used in this project

<table>
<thead>
<tr>
<th>Source</th>
<th>Natural or Synthetic Spinel</th>
<th>High Temperature or Quenched/Cooled Samples</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peterson et al. 1991</td>
<td>Synthetic</td>
<td>High temperature in situ</td>
<td>$^{[1]}\Delta G^o = \alpha + 2\beta x = -RT\ln(x^2(1-x)^{-1}(2-x)^{-1})$&lt;br&gt;$(\alpha = -31 \pm 1 \text{ kJ}, \beta = -10 \pm 3 \text{ kJ})$</td>
</tr>
<tr>
<td>Millard et al. 1992</td>
<td>Synthetic</td>
<td>Quenched</td>
<td>$^{[1][2]}H_D = \alpha x + \beta x^2$&lt;br&gt;$(\alpha = 25 \pm 5 \text{ kJ}, \beta = 5.8 \pm 9.5 \text{kJ})$</td>
</tr>
<tr>
<td>Source</td>
<td>Natural or Synthetic Spinel</td>
<td>High Temperature or Quenched/ Cooled Samples</td>
<td>Model</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------</td>
<td>---------------------------------------------</td>
<td>-----------------------------------------------------------------------</td>
</tr>
<tr>
<td>Maekawa et al. 1997</td>
<td>Natural</td>
<td>Both (Quenched and in situ high temperature)</td>
<td>[^{[1][2]}\ln K = -(\alpha + 2\beta x)/RT] \n(\alpha = 35 \pm 5 \text{ kJ}, \beta = -32 \pm 5 \text{ kJ})</td>
</tr>
<tr>
<td>Princivalle et al. 1999</td>
<td>Natural</td>
<td>Cooled</td>
<td>[^{[3]}\text{T(°C)} = 6440 \times B] \n(B = [^{[4]}\text{Al/Al}_{\text{total}})</td>
</tr>
<tr>
<td>Redfern et al. 1999</td>
<td>Synthetic</td>
<td>Room temperature and high temperature</td>
<td>[^{[1]}\text{RTln}(x^2/((1-x)(2-x))) = \alpha + 2\beta x] \n(\alpha = 32.8 \pm 0.9 \text{ kJ}, \beta = 4.7 \pm 2\text{ kJ})</td>
</tr>
<tr>
<td>Andreozzi and Princivalle 2002</td>
<td>Synthetic</td>
<td>Quenched</td>
<td>[^{[4]}x = 21.396 – 80.714u]</td>
</tr>
</tbody>
</table>

\[^{[1]}\text{These models are based on O’Neill and Navrotsky 1983 model.}\]

\[^{[2]}\text{This model is also based on the Navrotsky and Kleppa 1967 model.}\]

\[^{[3]}\text{Princivalle et al. 1999 uses B value instead of x-value, where B = \[^{[4]}\text{Al/Al}_{\text{total}}\) for pure MgAl}_2\text{O}_4\] spinel.\]
This model uses the oxygen position parameter (u). The model calculates inversion parameter (x) vs u for various temperatures, showing a linear relation. This model is used to estimate both u and temperature.

Table 8.3 Calculated x-value, B-value, temperature range and error for each CAI studied. Temperature ranges are taken from all calibration models presented in Table 8.2

<table>
<thead>
<tr>
<th>CAI Sample</th>
<th>x-value</th>
<th>B-value</th>
<th>Temperature Range</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende 3529</td>
<td>0</td>
<td>0</td>
<td>≤ 0 °C / 273.15 K</td>
<td>n/a</td>
</tr>
<tr>
<td>Allende TS62b</td>
<td>0</td>
<td>0</td>
<td>≤ 0 °C / 273.15 K</td>
<td>n/a</td>
</tr>
<tr>
<td>The Crucible</td>
<td>0.0770</td>
<td>0.0385</td>
<td>521-707 K</td>
<td>399-772 K</td>
</tr>
<tr>
<td>B4 (white fraction)</td>
<td>0.0268</td>
<td>0.0135</td>
<td>360-507 K</td>
<td>300-594 K</td>
</tr>
<tr>
<td>B4 (black fraction)</td>
<td>0.0501</td>
<td>0.0250</td>
<td>434-606 K</td>
<td>357-688 K</td>
</tr>
<tr>
<td>[1] NWA 6603 1-92 CAI</td>
<td>0.3027</td>
<td>0.1513</td>
<td>~1173-1675 K</td>
<td>835-1936 K</td>
</tr>
</tbody>
</table>

[1] This range does not include the estimate from Maekawa et al. (1997), which gave a comparatively low estimate for the bottom of the range. The range including this value is 735-1675 K (error: 330-1936 K). This low estimate is not seen when using the model graph from Maekawa et al. (1997).
Figure 8.1. Calculated temperature estimates (K) for all CAI samples using mathematical models. Yellow line shows the estimate from Maekawa et al. (1997) mathematical model, and blue spots show the graphical estimate from Maekawa et al. (1997).
Figure 8.2. Calibration curve of inversion parameter, $x$, versus temperature (K) from Peterson et al. (1991). Lines show where the CAIs tested here fall on the curve, Allende falls at 0, 0.00. Blue: NWA 6603 1-92 CAI, $\sim$ 1150 K; Red: NWA 2364 The Crucible, $\sim$ 625 K; Black: NWA 6991 (black fraction), $\sim$ 550 K; and Purple: NWA 6991 (white fraction), $\sim$ 500 K. Modified from Peterson et al. (1991).
Figure 8.3. Calibration curve of inversion parameter, $x$, versus temperature (K) from Millard et al. (1992). Lines show where the CAIs tested here fall on the curve, Allende falls off the chart at $x = 0$. Blue: NWA 6603 1-92 CAI, ~1300 K; Red: NWA 2364 The Crucible, ~600 K; Black: NWA 6991 (black fraction), ~550 K; and Purple: NWA 6991 (white fraction), ~500 K. Modified from Millard et al. (1992).
Figure 8.4. Calibration curve of inversion parameter, $x$, versus temperature ($^\circ$C) from Maekawa et al. (1997). Lines show where the CAIs tested here fall on the curve, Allende falls off the chart at $x = 0$. Blue: NWA 6603 1-92 CAI, $\sim$1200 $^\circ$C (1473.15 K); Red: NWA 2364 The Crucible, $\sim$500 $^\circ$C (773.15 K); Black: NWA 6991 (black fraction), $\sim$400 $^\circ$C (673.15 K); and Purple: NWA 6991 (white fraction), $\sim$300 $^\circ$C (573.15 K). Modified from Maekawa et al. (1997).
Figure 8.5. Calibration curve of temperature (°C) versus B-value, B, from Princivalle et al. (1999). Lines show where the CAIs tested here fall on the curve, Allende falls at 0.00, 0. Blue: NWA 6603 1-92 CAI, ~1000 °C (1273.15 K); Red: NWA 2364 The Crucible, ~200 °C (473.15 K); Black: NWA 6991 (black fraction), ~175 °C (448.15 K); and Purple: NWA 6991 (white fraction), ~100 °C (373.15 K). Modified from Princivalle et al. (1999).
Figure 8.6. Calibration curve of inversion parameter, $x$, versus temperature (K) from Redfern et al. (1999). Lines show where the CAIs tested here fall on the curve, Allende falls off the chart at $x = 0$. NWA 2364, NWA 6991 (both fractions), fall off the chart at $x = 0.02-0.07$, below ~700 K. Blue: NWA 6603 1-92 CAI, ~1650 K. Modified from Redfern et al. (1999).
Temperature estimates varied among the models used. Overall, the models gave similar temperature ranges for each CAI examined, with some small discrepancies. Temperature estimates from Redfern et al. (1999) were higher than the other models. Their dataset only covered high temperatures and may have skewed the estimates. The mathematical model from Maekawa et al. (1997) and the graphical curve of their model disagreed at high temperatures. Andreozzi and Princivalle (2002), had no low temperature data in their oxygen positional parameter ($u$) versus inversion parameter ($x$) graph, making this model less useful for lower temperature materials. The Millard et al. (1992) model most closely approximates the linear model created using the average of the data collected in this study.

Figure 8.7. Calibration curve of oxygen positional parameter, $u$, versus inversion parameter, $x$, from Andreozzi and Princivalle (2002). Blue circles show where the calculated $x$-values and $u$-values would fall. NWA 6603 (blue) extrapolates to the top, in high temperatures (~1200 °C, ~1473 K). Allende, NWA 2364 (red), and NWA 6991 (both fractions, black and purple) extrapolate to the bottom, in low temperatures (< 600 °C, < 873 K).
(Figure 8.8 and 8.9). The Peterson et al. (1991) and Princivalle et al. (1999) models were in close agreement. The model from Princivalle et al. (1999) uses a simple linear model. I would recommend using Princivalle et al. (1999) for its simplicity, in conjunction with one of either Millard et al. (1992) or Peterson et al. (1991). Using these models provides a low and high end of the temperature range. Using two models will help constrain a temperature range that is more likely to encompass the actual temperature experienced by the CAI.

Table 8.4 Temperatures estimated for each meteorite sample (Allende had the same temperature for both CAIs examined) from calibration curve graphs (Figures 8.1 to 8.6)

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Allende</td>
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<td>273 K</td>
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<td>&lt; 870 K</td>
</tr>
<tr>
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<td>1473 K</td>
<td>1273 K</td>
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<td>448 K</td>
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<tr>
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<td>500 K</td>
<td>573 K</td>
<td>373 K</td>
<td>&lt; 700 K</td>
<td>&lt; 870 K</td>
</tr>
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8.2 Temperature Versus Inversion Parameter Plots

All models, except for the Maekawa et al. (1997) mathematical model at high temperatures, show similar relationships for inversion parameter (x) versus temperature (K) (Figure 8.8).
The discrepancy in the Maekawa et al. (1997) plots is one reason I chose not to use their mathematical model when discussing high temperature estimates from NWA 6603. All models, except the Maekawa et al. (1997) mathematical model, were fit with a linear trend line. The Maekawa et al. (1997) mathematical model was best fit with an exponential function. A plot showing temperature derived from inversion parameter data from multiple models is shown in Figure 8.9. Using the data from only four meteorite samples, the relationship between temperature and inversion parameter is linear. All models, except the Maekawa et al. (1997) mathematical model, show similar slopes.
Figure 8.8. Inversion parameter, x, versus temperature (K) for each mathematical model used. Both the mathematical estimate and the graphical estimate from Maekawa et al. (1997) are shown. Points are median temperatures and x-values from each model.
Allende has documented evidence of aqueous alteration on a parent body (Brearley and Jones 1998). Both Allende temperature estimates give low temperatures approaching 0 °C. These temperatures are maximum temperatures for the low temperature regime which caused re-ordering. Once fully ordered, the spinel cannot record lower temperatures. X-values for temperatures as low as 273 K are not measured in any of these literature studies. The temperature estimates for Allende may not be exactly 273 K and may be a result of the theoretical models used in previous studies, where most model curves tend toward 0 K. More studies with slower cooling rates need to be done to attempt to record these low temperatures on cooling. The temperature estimate for Allende is lower than the temperatures recorded in the other samples studied in this project. The temperatures recorded here are lower than estimates of parent body temperature during aqueous alteration (Grimm and McSween Jr. 1989, Travis and Schubert 2005). Travis and Schubert (2005) modelled the Carbonaceous Chondrite parent body being heated by $^{26}$Al decay. Their modelled temperatures reached peaks of 90 to 180 °C depending on starting...
conditions. Similar models by Grimm and McSween Jr. (1989) estimated a maximum temperature of 350 °C. If the temperature recorded in spinel in the Allende CAIs was from this period of aqueous alteration, the temperature would be higher. It is possible the temperature recorded in Allende CAIs are from after this period of aqueous alteration, once the parent body had cooled. The temperature in Allende CAIs could indicate the length of time Allende remained on the parent body or reflect its post ejection temperature. The material could have remained on the parent body until the heat from accretion and $^{26}$Al decay had dissipated. Cation re-ordering at low temperatures would take a long time as the kinetics would be slow.

Fassaite from Allende, examined by Haring (2013), showed ordered fassaite, representing a maximum temperature of 870 K. This maximum temperature is in close agreement to a peak temperature determined using a chromium-olivine thermometer on chondrules in Allende (Weinbruch et al. 1994). Both studies estimated maximum temperatures of around 800 K on the Allende parent body (Weinbruch et al. 1994, Haring 2013). These temperatures could represent the peak local temperatures reached on the CV parent body. Spinel, which records a maximum temperature of 273 K, could represent the lower end of the temperatures reached on the parent body, after cooling. Combining temperature estimates from multiple sources in the Allende meteorite can help constrain the local temperature regime on the parent body.

8.4 NWA 2364 (The Crucible) and NWA 6991 (B4) CV3s

Temperature estimates from The Crucible (521-707 K) and B4 360-507 K (white) and 434-606 K (black)) are similar. The Crucible CAI is a compact Type B CAI (Friedrich et al. 2005). It has undergone some igneous and aqueous processing since its formation in the nebula (Friedrich et al. 2005, Johnson et al. 2017). B4 is compact Type A CAI (Bullock et al. 2014). Its mineralogy suggests it was moving towards becoming a Type B (Bullock et al. 2014). Compact Type A and Type B CAIs appear to be on a continuum of alteration (Bullock et al. 2014). Both CAIs have undergone some processing since their formation in the nebula. The temperature estimates from their spinels are consistent with this
scenario. The temperatures are lower than nebular formation (>1300 - 1500 K). The Crucible and B4 temperatures could represent nebular or parent body processing.

The temperatures on modelled parent bodies reach a maximum of around 350 °C (623 K) at 5-8 km depths (Grimm and McSween Jr. 1989, Travis and Schubert 2005, Elkins-Tanton et al. 2011) or up to <600 °C (873 K) (Cody et al. 2008, Elkins-Tanton et al. 2011). The temperatures from these CAIs could be consistent with parent body processing. The CAIs could have also recorded temperatures during cooling in the nebula. They would have had to remain at a location in the nebula at those temperatures for a prolonged period. The parent body may be a more stable location for prolonged temperature regimes. But models show peak temperatures are only reached on carbonaceous chondrite parent bodies for a short period of time. It may be long enough to re-order cations, but these may also have reordered during its time in the nebula.

8.5 NWA 6603 CV3

The temperature estimates from spinel in NWA 6603 1-92 CAI bracket nebular condensation temperatures. NWA 6603 1-92 CAI is likely a Fluffy Type A CAI, based on irregular shape, and the large amount of melilitite (gehlenite) and spinel. The CAI records high nebular temperatures between 1173 and 1675 K. These temperatures may be original condensation temperatures or subsequent high temperature nebular processing. NWA 6603 material was not in lower temperature regimes for long enough to re-order the cations in spinel.

The temperatures estimated for NWA 6603 (~1173 to 1675 K), are around the upper limit of temperatures expected to be recorded by cation ordering in spinel. The upper limit for temperatures recorded during quenching is between 1273 and 1573 K (Millard et al. 1992, Redfern et al. 1999). Calculating temperature estimates higher than this may not be plausible with this technique, as a result of the rapid reordering of cations on quenching (Redfern et al. 1999). Nebular temperatures are expected to range from ~1100 to 1700 K (Grossman 1972, Henning and Semenov 2013). This technique can therefore measure temperatures at the low to mid-range of expected nebular temperatures. The technique could be used in conjunction with other mineral thermometers, such as melilitite and fassaite
(Benisek et al. 2007, Etzel et al. 2007, Etzel and Benisek 2008, Florian et al. 2012). From multiple independent temperature estimates, a more complete thermal history of a CAI can be understood. Spinel could reliably record high temperatures from the nebula up to about 1573 K (Redfern et al. 1999). Constraining minimum cooling rates of spinel to record these high temperatures from the nebula, can be used to constrain the cooling rates in the nebula.

Despite not necessarily recording the highest temperatures reached in the nebula, cation ordering in spinel can still be used to help differentiate between the X-wind and the shock or transient heating events models of CAI formation. The X-wind model should produce CAIs which have experienced similar temperatures and cooling rates. The transient heating model should produce CAIs which have experienced a variety of temperatures and cooling rates. If nebular temperature estimates from multiple CAIs record similar temperatures, the X-wind model would be favourable. If nebular temperature estimates from multiple CAIs record various temperatures, the transient heating event model would be favoured.

8.6 Comparison

The four meteorites displayed a range of temperatures. The temperatures calculated for Allende were the lowest. NWA 2364 and NWA 6991 gave moderate temperatures. The highest temperature estimates were seen in NWA 6603. These temperatures are consistent with the presumed processing of each CAI. Allende is the most altered in this study, a CV3.2, it shows evidence of metasomatism (Brearley and Jones 1998). NWA 2364 The Crucible is a Type B CAI, which has undergone some high temperature alteration (Friedrich et al. 2005). NWA 6991 B4 is a Compact Type A CAI, with some Type B characteristics, indicating some alteration (Bullock et al. 2014). NWA 6603 CAI is a Fluffy Type A CAI, which are considered to be closest to nebular condensates (McSween 1977, Brearley and Jones 1998, Ivanova 2016). The $^{27}\text{Al}$ MAS NMR spectrum for NWA 6603 1-92 CAI is unique from the other CAIs studied. It has a tetrahedral site that is larger than the octahedral site. There is less Al$^{3+}$ in the octahedral coordination than in other CAIs. This difference is a result of the small amount of Al$^{3+}$ in the octahedral spinel and the large amount of gehlenite in the sample, having tetrahedral Al.
Travis and Schubert (2005) showed that heterogeneous processing on a parent body was possible. Thus, The Crucible, B4, Allende, and NWA 6603 1-92 CAI can be from the same parent body but show variations in alteration. The different temperatures measured from cation ordering suggest a different type, amount, or length of processing for each meteorite. CAIs retaining the spinel cation ordering of high temperatures indicate that no re-ordering occurred, such as reordering seen in Allende CAIs in this study. This lack of re-ordering could suggest a shorter lifetime on the parent body and a longer time in space as a smaller meteorite after being ejected from the parent body. The temperatures in space reach near absolute zero, so cation exchange reaction rate would be negligible as a result of slow kinetics. Ejection may act like a quench experiment.

The CV3 meteorites in this study may have all undergone different amounts of processing on the same parent body. Being from the same parent body is an assumption based on their similarity in composition, being all CV3 meteorites. Allende was thermally altered at high temperatures. The ordered spinel in Allende suggests that it underwent significant cooling after metamorphism. NWA 2364 (The Crucible) and NWA 6991 (B4) were also altered at high temperature, though not to the same extent as Allende. These two meteorites did not undergo slow cooling after this metamorphism, as their spinel cation ordering records the high temperatures. NWA 6603 1-92 CAI was not altered at high temperatures on the parent body nor did it undergo any slow cooling event, as its spinel records temperatures high enough to be nebular. The location on the parent body is likely part of the reason for the different amounts of alteration. Another factor affecting alteration, relating to spinel cation ordering, could be timing of ejection of the meteorite material.

### 8.7 Integration with Models of the Carbonaceous Chondrite Parent Body

Grimm and McSween Jr. (1989) proposed two heating and ejection mechanisms for the CC parent body:

1. Heating internally by $^{26}$Al decay followed by catastrophic breakup of the parent body
2. Heating and melting via impacts, which also resulted in ejection of material.

The reality could be a combination of the two heat sources and ejection methods.
Travis and Schubert (2005) modelled heating of potential CC parent bodies. They used $^{26}$Al decay as the heat source. Temperatures were high enough to allow for metasomatism (Travis and Schubert 2005). Travis and Schubert (2005) and Grimm and McSween Jr. (1989)’s models found the top few kilometers of the crust remained frozen by this method. This heat source alone would need catastrophic breakup of the parent body to eject CCs with the amount of alteration we see today (Grimm and McSween Jr. 1989). Elkins-Tanton et al. (2011), modelled CC parent bodies. They found that differentiation of the parent body could occur (Elkins-Tanton et al. 2011). Their model suggests the origin of CCs is the metamorphosed crust of a differentiated body. Their model invokes a convecting mantle to bring heat closer to the surface of the parent body. More altered CCs are deeper in the crust (Elkins-Tanton et al. 2011). By Elkins-Tanton et al. (2011)’s model, NWA 6603 would be closest to the surface, NWA 2364 and NWA 6991 would be deeper than NWA 6603 and Allende would be deeper still (see Figure 8.10).

Peak temperature estimates have been made by mineralogical and organic chemistry constraints (Grimm and McSween Jr. 1989, Cody et al. 2008). These estimates are between 300 and less than 600 °C ($573 – 873$ K). If Allende was deep in the crust it would constantly have been subjected to heat. The very low temperatures given from Allende CAIs, suggest it had experienced low temperatures for prolonged periods. The ordering of cations could take place in two locations: on the parent body or in outer space after ejection. If re-ordering occurred in space the time taken to re-order would have been very long; temperatures approach 0 K in space, where motion of atoms is negligible, and approach 0 °C in the solar system around the location of the asteroid belt. The cation ordering reaction for spinel requires an activation energy of $197 \pm 22$ kJ/mol, which would be difficult to overcome at low temperatures (Andreozzi and Princivalle 2002). It is unlikely that reordering would occur in space. This activation temperature would also make reordering on Earth unlikely to occur. Temperatures reached during ejection impacts and delivery would likely not last long enough for the reaction to proceed to equilibrium and may not penetrate very far into the meteorite as a result of the short time scales. Therefore, any reordering is likely to have occurred on the parent body or in the nebula. Both are locations where high temperatures could exist long enough to cause reordering and overcome the
activation energy. Re-ordering in the early solar nebula, where temperatures were higher, would take less time than ordering on the parent body.

Allende would need to have stayed on the parent body long enough to be metamorphosed. It is unlikely the re-ordering occurred in the space. If re-ordering had occurred on the parent body, Allende would have been first metamorphosed. The ordering could have occurred after the whole parent body had cooled, or after a local change in the temperature regime at Allende’s location. Location on the parent body and amount of time spent on the parent body play a role in the alteration of CAIs, which would affect the cation ordering.

NWA 2364 and NWA 6991 were in a different location on the parent body than Allende. They experienced less alteration than Allende. They may have been ejected earlier than Allende because they do not show complete reordering; they were not on the parent body when it cooled.
NWA 6603 was also in a different location than the other three meteorites. It experienced less alteration than Allende, NWA 6991 and NWA 2364. It may have been ejected earlier than these other meteorites as well, as it was not subjected to low temperatures alterations. The discussion of the Elkins-Tanton et al. (2011) model is pictured below (Figure 8.10).

![Diagram of CV parent body](image)

**Figure 8.10.** Model of the CV parent body showing possible locations of sample meteorites. Allende would have been heated within the crust and then remained on the parent body as it cooled. NWA 6603 would have experienced little aqueous alteration on the surface of the parent body, and may have been ejected early, avoiding high temperature alteration. NWA 2364 and NWA 6991 would have been heated in the crust and then experienced rapid cooling. This may have been an igneous event which brought them to the surface or ejection while they were heated, acting as a quench. Modified from Elkins-Tanton et al. 2011).

The heat of $^{26}$Al decay may not have been sufficient to create a heated crust, as other models suggest (Grimm and McSween Jr. 1989, Travis and Schubert 2005). In this case, heterogeneous processing at different locations can still account for some variation in the alteration. As the heat dissipated, Allende may have been in a location that lost heat sooner than the other meteorite materials. Catastrophic breakup of the parent body would be needed to eject the altered material under the frozen crust.
Combining the two models, heat from both $^{26}$Al decay, and impacts could cause heterogeneous alteration and allow for different residence times on the parent body. This combination can account for variations in both degree of alteration and recorded temperature.

More CAIs should be examined from different types of chondrites. CAIs have been documented in all types of chondrites except Enstatite and CI chondrites (MacPherson 2003). Differences in parent body or nebular processing temperatures may be observed among the chondrite groups. Tagish Lake C2, especially carbonate-rich lithology, should be surveyed to find and extract CAIs for this technique. Tagish Lake C2 is the only one of its kind and may have a unique thermal history. Large aggregates of spinel in the Paris CM2 meteorite are also a good candidate for study. The meteorite is considered to be the least altered CM chondrite to date (Rubin 2015), so would likely provide nebular temperature estimates.

Ameboid Olivine Aggregates (AOAs), which contain spinel should also be examined with the technique. Constraints on the thermal history of AOAs will help our understanding of their formation mechanism. Spinel in CAIs enclosed in AOAs should also be examined to compare to other CAIs in the sample and to the AOA in which it is enclosed.

To produce more accurate temperature estimates, better constraints are needed on the spinel peak sizes and positions in the $^{27}$Al MAS NMR spectra. Rietveld refinement of XRD data could be used to determine modal percentages of the different mineral phases in the CAIs. This would help constrain the relative peak heights of the phases in the NMR spectra. Collecting NMR spectra on a higher field strength NMR spectrometer would produce narrower peaks in the NMR spectra of spin > 1/2 nuclei (1 GHz fields are now available). This would help constrain the peak locations in the NMR spectra. Both of these techniques can be done without destruction of the powdered CAI and without the need to completely separate the mineral phases in the CAI.

This technique of measuring cation ordering of spinel in CAIs can be used to gain temperature information useful for understanding both nebular conditions and parent body
processing. The temperatures derived from this technique can be incorporated into models of accretion and parent body processing. The temperatures are also relatable to nebular conditions. The application of cation ordering in spinel to measure temperatures experienced by CAIs is new to planetary science. This study showed that cation ordering in spinel is a useful independent parameter for quantifying temperature and understanding both nebular formation of CAIs and parent body alteration seen in CAIs.

8.8 Conclusions

Cation-ordering in spinel from CAIs can be used to measure temperature of formation or most recent equilibration temperature of CAIs. The cation ordering can be measured directly using $^{27}$Al MAS NMR spectroscopy.

Five CAIs from four different meteorites were examined with $^{27}$Al MAS NMR and $^{27}$Al 3Q MAS NMR spectroscopy. Two-dimensional $^{27}$Al 3Q MAS NMR is useful for determining the peak locations for the different phases in the CAIs. This technique makes it possible to fit the one-dimensional $^{27}$Al MAS NMR even when it contains multiple phases, especially in the tetrahedral Al site. $^{27}$Al MAS NMR spectra were collected using parameters that ensured quantitative data, necessary for calculating the inversion parameter. DMfit software (Massiot et al. 2002) was used to create a model of the whole spectrum, using individual peaks, which were then integrated, using the same software. Integration gives the area under the peaks used to calculate the inversion parameter $x$. Peak shapes were constrained using information from Stebbins et al. (1995) and by fitting NMR standards as starting parameters. The temperatures calculated using this method varied depending on the amount of processing the CAI had undergone. Temperatures ranged from less than 0 °C (273 K) to greater than 827 °C (1100 K). Phases other than spinel in the CAI do not need to be removed to use this technique, they just need to be included in the fit. The powdered CAI is not destroyed during NMR collection, in this sense NMR is a non-destructive technique, and the powder can be used for other experiments. This ability to recover material is useful when dealing with CAIs, which are usually small, uncommon, and scientifically valuable.
Allende CV3 was the most processed meteorite studied. The temperatures from Allende were calculated at a maximum of 0 °C (273 K). These temperatures resulted from prolonged parent body processing. These also represent a maximum temperature. Once the spinel is fully ordered, it can’t record lower temperatures. Temperatures calculated for NWA 6991 ranged from 360-606 K and for NWA 2364 ranged from 521 to 707 K. These likely represent parent body temperatures, as parent body temperatures are thought to be between 98 and 623 K but can be anything less than 600 °C (873 K) (Grimm and McSween Jr. 1989, Travis and Schubert 2005, Cody et al. 2008, Elkins-Tanton et al. 2011). Temperatures from NWA 6603 1-92 CAI show nebular temperatures between 1173 and 1675 K. These represent nebular condensation or processing temperatures. They are too high for parent body processing and overlap well with nebular temperature ranges (1300-1500 K) (Grossman 1972, Henning and Semenov 2013).

This technique can measure temperatures recorded in spinel from CAIs. It is not necessary to completely isolate the spinel, as two-dimensional $^{27}$Al 3Q MAS NMR spectroscopy can help discern peak locations. This technique can provide insight into temperature regimes in the nebula and in chondrite parent bodies. It can be used on any spinel, terrestrial or planetary to estimate formation or processing temperatures. This project has successfully demonstrated that nebular temperatures can be measured in unaltered CAIs, and parent body processing temperatures can be measured in altered CAIs.
8.9 References


Haring, M.M. 2013. Crystal structure and Al/Si cation ordering in “Fassaite”: A combined single crystal, $^{27}$Al and $^{29}$Si NMR study. The University of Western Ontario.


Appendices

Appendix A: Micro X-ray Diffraction of All Meteorite Samples
Micro X-Ray Diffraction of NWA 6603

1. NWA 6603 1-92 (small)
2. NWA 6603 16-7 (large)
NWA 6603 I-92
Context Map and Parameters

Context map of NWA 6603 I-92, showing the spots examined by μXRD. The numbering continues from another run, both numbers are listed.

Table showing parameters used to collect μXRD data on NWA 6603 I-92, scan type was omega scan

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μXRD diffraction pattern of NWA 6603 1-92 slab showing clinoenstatite, forsterite and gehlenite.

Blue: Clinoenstatite (MgSiO$_3$, PDF 73-1758)
Light Blue: Forsterite (Mg$_{1.36}$Fe$_{0.64}$SiO$_4$, PDF 76-0552)
Red: Gehlenite (Al$_2$O$_3$(CaO)$_3$(SiO$_2$)$_2$, PDF 02-0823)
μXRD diffraction pattern of NWA 6603 1-92 slab showing forsterite and fassaite.

Light Blue: Forsterite (Mg_{1.86}Fe_{0.14})(SiO_{4}), PDF 77-1025

Blue: Fassaite ((Ca_{0.968}Mg_{0.578}Fe_{0.220}Al_{0.161}Ti_{0.059})(Si_{1.728}Al_{0.272})O_{6}), PDF 83-2083
NWA 6603 1-92 Spot 3

\[ \text{\(\mu\)XRD diffraction pattern of NWA 6603 1-92 slab showing spinel, fassaite and forsterite.} \]

- **Green**: Spinel (Mg\(_{0.91}\)Fe\(_{0.09}\)O\(_4\)), PDF 02-1075
- **Blue**: Fassaite ((Ca\(_{0.968}\)Mg\(_{0.578}\)Fe\(_{0.220}\)Al\(_{0.161}\)Ti\(_{0.059}\))(Si\(_{1.728}\)Al\(_{0.272}\))O\(_6\)), PDF 83-2083
- **Light Blue**: Forsterite (Mg\(_{1.360}\)Fe\(_{0.640}\)SiO\(_4\)), PDF 07-0074

\[ 500 \mu \text{m} \]
μXRD diffraction pattern of NWA 6603 1-92 slab showing gehlenite. Red: Gehlenite (Ca$_{1.96}$Na$_{0.05}$)(Mg$_{2.4}$Al$_{6.4}$Fe$_{1.2}$)(Si$_{1.39}$Al$_{61.07}$), PDF 72-2128)
μXRD diffraction pattern of NWA 6603 1-92 slab showing gehlenite, spinel, fassaite, grossular and perovskite.

Red: Gehlenite \((\text{Ca}_{1.96}\text{Na}_{0.05})(\text{Mg}_{2.4}\text{Al}_{6.4}\text{Fe}_{1.2})(\text{Si}_{1.39}\text{Al}_{6.17}),\text{PDF }72-2128)\)

Green: Spinel, syn \(\text{Mg}(\text{Al}_{0.91}\text{Fe}_{0.09})\text{O}_4\), PDF 02-1075

Blue: Fassaite \(((\text{Ca}_{1}\text{Mg}_{0.39}\text{Ti}_{0.35}\text{Ti}_{0.13}\text{Al}_{0.13}\text{Al}_{0.74}\text{Si}_{1.26})\text{O}_6),\text{PDF }71-1541)\)

Pink: Grossular \((\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12},\text{PDF }03-0826)\)

Brown: Perovskite \((\text{CaTiO}_3,\text{PDF }75-2100)\)
NWA 6603 1-92 Spot 6

μXRD diffraction pattern of NWA 6603 1-92 slab showing clinoenstatite and forsterite.  
Blue: Clinoenstatite (MgSiO$_3$, PDF 73-1758)  
Light Blue: Forsterite (Mg$_{1.808}$Fe$_{0.192}$SiO$_4$, PDF 83-1536)
NWA 6603 1-92 Spot 7

μXRD diffraction pattern of NWA 6603 1-92 slab showing fassaite and forsterite. Blue: Fassaite \((\text{Ca}^{0.968}\text{Mg}^{0.578}\text{Fe}^{0.220}\text{Al}^{0.161}\text{Ti}^{0.059})(\text{Si}^{1.728}\text{Al}^{0.272})\text{O}_6\), PDF 83-2083
Light Blue: Forsterite \((\text{Mg}^{1.36}\text{Fe}^{0.64}\text{SiO}_4\), PDF 76-0552)
NWA 6603 16-7
Context Map and Parameters

Context map of NWA 6603 16-7, showing the spots examined by μXRD. The slice broke in two along a plane of weakness during mounting.

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μXRD diffraction pattern of NWA 6603 16-7 slab showing gehlenite, forsterite and clinoenstatite.

Red: Gehlenite (Al$_2$O$_3$(CaO)(SiO$_2$), PDF 02-0823)
Light Blue: Forsterite (Mg$_{1.36}$Fe$_{0.64}$SiO$_4$, PDF 76-0552)
Blue: Clinoenstatite (MgSiO$_3$, PDF 73-1758)
μXRD diffraction pattern of NWA 6603 16-7 slab showing forsterite, grossular, fassaite, gehlenite and spinel.

**Light Blue:** Forsterite ($\text{Mg}_{1.36}\text{Fe}_{0.64}\text{SiO}_4$, PDF 76-0552)

**Pink:** Grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, PDF 75-1551)

**Blue:** Fassaite ($\text{(Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})\text{(Si}_{1.726}\text{Al}_{0.272})\text{O}_6$, PDF 83-2083)

**Red:** Gehlenite ($\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_7(\text{Ca})_2(\text{Al}_2\text{O}_3\text{Si}_2\text{O}_2$, PDF 04-0690)

**Green:** Spinel ($\text{MgAl}_2\text{O}_4$, PDF 21-1152)
μXRD diffraction pattern of NWA 6603 16-7 slab showing forsterite, grossular and gehlenite.

Light Blue: Forsterite (Mg$_{1.36}$Fe$_{0.64}$SiO$_4$, PDF 76-0552)
Pink: Grossular (Ca$_3$Al$_2$Si$_3$O$_{12}$, PDF 75-1551)
Red: Gehlenite (Ca$_2$Al$_2$Si$_7$(Ca)$_2$(Al$_2$O$_3$SiO$_2$, PDF 04-0690)
NWA 6603 16-7 Spot 4

μXRD diffraction pattern of NWA 6603 16-7 slab showing forsterite, fassaite and gehlenite.

Light Blue: Forsterite (Mg$_{1.36}$Fe$_{0.64}$SiO$_4$, PDF 76-0552)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.228}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083)
Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$(Ca)$_2$(Al$_2$O$_3$SiO$_2$), PDF 04-0690)
μXRD diffraction pattern of NWA 6603 16-7 slab showing gehlenite and grossular.
Red: Gehlenite syn. (Ca$_2$Al$_2$SiO$_7$, PDF 35-0755)
Pink: Grossular (Ca$_3$Al$_2$Si$_3$O$_{12}$, PDF 03-0627)
μXRD diffraction pattern of NWA 6603 16-7 slab showing gehlenite, fassaite, spinel and grossular.

Red: Gehlenite \((\text{Ca}_{1.96}\text{Na}_{0.05})(\text{Mg}_{2.4}\text{Al}_{0.64}\text{Fe}_{0.12})(\text{Si}_{1.39}\text{Al}_{0.61})\), PDF 72-2128

Blue: Fassaite \((\text{Ca}_1\text{Mg}_{0.39}\text{Ti}_{0.35}\text{Ti}_{0.13}\text{Al}_{0.13}(\text{Al}_{0.74}\text{Si}_{1.26}))\), PDF 71-1541

Green: Spinel \((\text{MgAl}_2\text{O}_4)\), PDF 03-0901

Pink: Grossular \((\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3)\), PDF 03-0827
μXRD diffraction pattern of NWA 6603 16-7 slab showing gehlenite, fassaite, spinel and grossular.

Red: Gehlenite \( \text{(Ca}_{1.96}\text{Na}_{0.05}) \text{(Mg}_{2.4}\text{Al}_{6.4}\text{Fe}_{1.2})(\text{Si}_{1.39}\text{Al}_{6.17}) \), PDF 72-2128

Blue: Fassaite \((\text{Ca}_{1}\text{Mg}_{0.39}\text{Ti}_{0.13}\text{Al}_{0.74}\text{Si}_{1.26})\text{O}_{6} \), PDF 71-1541

Green: Spinel, syn MgAl\(_2\)O\(_4\), PDF 05-0672

Pink: Grossular \( \text{(Ca}_{3}\text{Al}_{2}\text{Si}_{3}\text{O}_{12}) \), PDF 03-0826
μXRD diffraction pattern of NWA 6603 16-7 slab showing forsterite, fassaite and grossular.

**Light Blue:** Forsterite ($\text{Mg}_{1.36}\text{Fe}_{0.64}\text{SiO}_4$, PDF 76-0552)

**Blue:** Fassaite ($\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059}(\text{Si}_{1.728}\text{Al}_{0.272})\text{O}_6$, PDF 83-2083)

**Pink:** Grossular ($\text{Al}_2\text{Ca}_3(\text{SiO}_4)_3$, PDF 02-0944)
μXRD diffraction pattern of NWA 6603 16-7 slab showing forsterite, fassaite and grossular.

Light Blue: Forsterite \((\text{Mg}_{1.808}\text{Fe}_{0.192}\text{SiO}_4)\), PDF 83-1536

Blue: Fassaite \(((\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})\text{Si}_{1.728}\text{Al}_{0.272}\text{O}_6)\), PDF 83-2083

Pink: Grossular \((\text{Al}_2\text{Ca}_3\text{Si}_4\text{O}_{12})\), PDF 02-0944
μXRD diffraction pattern of NWA 6603 16-7 slab showing forsterite, fassaite, gehlenite and spinel.

- **Light Blue**: Forsterite (Mg$_{1.36}$Fe$_{0.64}$SiO$_4$, PDF 76-0552)
- **Blue**: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083)
- **Red**: Gehlenite (Ca$_2$Al$_2$SiO$_7$Ca$_2$(Al$_2$O$_3$SiO$_2$, PDF 04-0690)
- **Green**: Spinel, syn Mg$_2$Al$_2$O$_4$, PDF 21-1152
Micro X-Ray
Diffraction of NWA 6991
NWA 6991
Context Map and Parameters

Context map of NWA 6991 powder, showing the spots examined by μXRD.

Table showing parameters used to collect μXRD data on NWA 6991, scan type was omega scan

<table>
<thead>
<tr>
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<td></td>
<td>Frame 2 40</td>
<td>40</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>
μXRD diffraction pattern of NWA 6991 powder showing fassaite, grossular, gehlenite and spinel.

Blue: Fassaite \((\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})(\text{Si}_{1.728}\text{Al}_{0.272})\text{O}_6, \text{PDF 83-2083})\)

Pink: Grossular \((\text{Al}_2\text{Ca}_3(\text{SiO}_4)_3, \text{PDF 02-0944})\)

Red: Gehlenite \((\text{Ca}_2\text{Al}(\text{AlSi})_2\text{O}_7, \text{PDF 25-0123})\)

Green: Spinel \((\text{MgAl}_2\text{O}_4, \text{PDF 03-0901})\)
μXRD diffraction pattern of NWA 6991 powder showing fassaite, spinel and gehlenite. 
Blue: Fassaite \(((\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})_{(\text{Si}_{1.728}\text{Al}_{0.272})}\text{O}_6\), PDF 83-2083)
Green: Spinel \((\text{MgAl}_2\text{O}_4\), PDF 05-0672)
Red: Gehlenite \(((\text{CaO})_2\text{Al}_2\text{O}_3\text{SiO}_2\), PDF 01-0982)
μXRD diffraction pattern of NWA 6991 powder showing fassaite, spinel and gehlenite.  
Blue: Fassaite \((\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})(\text{Si}_{1.728}\text{Al}_{0.272})\text{O}_6\), PDF 83-2083
Green: Spinel (\(\text{MgAl}_2\text{O}_4\)), PDF 05-0672
Red: Gehlenite \((\text{CaO})_2\text{Al}_2\text{O}_3\text{SiO}_2\), PDF 01-0982
Micro X-Ray Diffraction of NWA 2364
NWA 2364
Context Map and Parameters

Context map of NWA 2364 powder, showing the spots examined by μXRD.

Table showing parameters used to collect μXRD data on NWA 2364, scan type was omega scan

<table>
<thead>
<tr>
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<td>40</td>
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NWA 2364 Spot 4

μXRD diffraction pattern of NWA 2364 spot 4 showing fassaite, spinel, grossular and gehlenite. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Blue: Fassaite \((\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})(\text{Si}_{1.728}\text{Al}_{0.272})\text{O}_6\), PDF 83-2083

Green: Spinel \((\text{MgAl}_2\text{O}_4\), PDF 05-0672)

Pink: Grossular \((\text{Al}_2\text{Ca}_3(\text{SiO}_4)_3\), PDF 02-0944)

Red: Gehlenite \((\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_7\), PDF 09-0216)
μXRD diffraction pattern of NWA 2364 spot 5 showing fassaite, spinel, gehlenite and grossular. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Blue: Fassaite \(((\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})(\text{Si}_{1.728}\text{Al}_{0.272})\text{O}_6, \text{PDF 83-2083})\)

Green: Spinel \((\text{MgAl}_2\text{O}_4, \text{PDF 05-0672})\)

Red: Gehlenite \((\text{Al}_2\text{O}_3 \cdot 3\text{Ca} \cdot 2\text{SiO}_2, \text{PDF 02-0823})\)

Pink: Grossular \((\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}, \text{PDF 03-0826})\)
μXRD diffraction pattern of NWA 2364 spot 6 showing grossular, fassaite and spinel. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Pink: Grossular \((\text{Al}_2\text{Ca}_3(\text{SiO}_4)_3, \text{PDF 02-0944})\)

Blue: Fassaite \((\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})(\text{Si}_{1.728}\text{Al}_{0.272})\text{O}_6, \text{PDF 83-2083})\)

Green: Spinel \((\text{MgAl}_2\text{O}_4, \text{PDF 05-0672})\)
Micro X-Ray
Diffraction of Allende Samples

1. Allende TS62b
2. Allende Cr3.17
3. Allende Cr3.7c
4. Allende 3529
Allende TS62b
Context Map and Parameters

Context map of TS62b showing the ten spots examined by μXRD

Table showing parameters used to collect μXRD data on Allende TS62b, scan type was omega scan

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<td>Frame 2</td>
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<td>40</td>
<td>15</td>
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</tbody>
</table>
For TS62b, the beam was lower than the crosshairs. Spots measured are therefore lower than the spot pictured on the crosshairs, where the red spot on the image above marks the highest intensity of x-rays.

Beam location measured on April 23, 2014.
μXRD diffractogram of TS62b spot 1 showing all phases identified. All phases but anorthite are fine-grained (rings on GADDS image), anorthite is coarse-grained (spots on GADDS image).

Green: Spinel (MgAl₂O₄, PDF 21-1152)
Light Blue: Forsterite (Mg₁₈₀₈Feₒ₁₉₂SiO₄, PDF 83-1536)
Pink: Grossular (Ca₃Al₂(SiO₄)₃, PDF 75-1551)
Orange: Anorthite (CaAl₂SiO₄, PDF 03-0505)
Red: Gehlenite (Ca₂Al₂SiO₅·H₂O, PDF 16-0388)
Blue: Fassaite (Ca₁₁₀₀Mg₀₃₀₉Tiₒ₃₅Alₒ₁₃(Alₒ₇₄Si₁₂₆)O₆, PDF 71-1541).
μXRD diffractogram of TS62b spot 2 showing all phases identified. All phases but anorthite are fine-grained (rings on GADDS image), anorthite is coarse-grained (spots on GADDS image).

Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Light Blue: Forsterite (Mg$_{1,808}$Fe$_{0.192}$SiO$_4$, PDF 83-1536)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Orange: Anorthite (CaAl$_2$Si$_2$O$_8$, PDF 03-0505)
Blue: Fassaite (Ca$_{1.000}$Mg$_{0.39}$Ti$_{0.35}$T$_{0.13}$Al$_{0.13}$(Al$_{0.74}$Si$_{1.26}$)O$_6$, PDF 71-1541).
μXRD diffractogram of TS62b spot 3 showing all phases identified. All phases but anorthite are fine-grained (rings on GADDS image), anorthite is coarse-grained (spots on GADDS image).

Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Light Blue: Forsterite (Mg$_{1.808}$Fe$_{0.192}$SiO$_4$, PDF 83-1536)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Orange: Anorthite (CaAl$_2$Si$_2$O$_8$, PDF 03-0505)
Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$·H$_2$O, PDF 16-0388)
Blue: Fassaite (Ca$_{1.00}$Mg$_{0.39}$Ti$_{0.35}$Ti$_{0.13}$Al$_{0.13}$(Al$_{0.74}$Si$_{1.26}$)O$_6$, PDF 71-1541).
μXRD diffractogram of TS62b spot 4 showing all phases identified. All phases but anorthite are fine-grained (rings on GADDS image), anorthite is coarse-grained (spots on GADDS image).

Green: Spinel (MgAl<sub>2</sub>O<sub>4</sub>, PDF 21-1152)
Light Blue: Forsterite (Mg<sub>1.808</sub>Fe<sub>0.192</sub>SiO<sub>4</sub>, PDF 83-1536)
Pink: Grossular (Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>, PDF 75-1551)
Orange: Anorthite (CaAl<sub>2</sub>SiO<sub>8</sub>, PDF 03-0505)
Red: Gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>·H<sub>2</sub>O, PDF 16-0388)
Blue: Fassaite (Ca<sub>1.00</sub>Mg<sub>0.39</sub>Ti<sub>0.35</sub>Ti<sub>0.13</sub>Al<sub>0.13</sub>(Al<sub>0.74</sub>Si<sub>1.26</sub>)O<sub>6</sub>, PDF 71-1541).
μXRD diffractogram of TS62b spot 5 showing all phases identified. Spinel is the almost fine-grained (spotty rings in GADDS image), grossular is large streaky spots in GADDS image (likely due to cracks in sample), gehlenite is coarse-grained (spots in GADDS image).

Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Red: Gehlenite (Ca$_2$Al(Al, Si)O$_7$, PDF 79-2421)
μXRD diffractogram of TS62b spot 5 showing all phases identified. Spinel is the almost fine-grained (spotty rings in GADDS image), grossular is large streaky spots in GADDS image (likely due to cracks in sample), gehlenite is coarse-grained (spots in GADDS image).

Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Red: Gehlenite (Ca$_2$Al(Al, Si)O$_7$, PDF 79-2421)
μXRD diffractogram of TS62b spot 6 showing all phases identified. Anorthite and spinel are fine-grained (rings on GADDS image), gehlenite is coarse-grained (spots on GADDS image), and fassaite is a strained single crystal (streaks on GADDS image).

Orange: Anorthite (Ca\(_{2}\)Al\(_2\)Si\(_2\)O\(_8\), PDF 03-0505)

Blue: Fassaite ((Ca\(_{0.968}\)Mg\(_{0.578}\)Fe\(_{0.220}\)Al\(_{0.161}\)Ti\(_{0.059}\))(Si\(_{1.728}\)Al\(_{0.272}\))O\(_6\), PDF 83-2083)

Red: Gehlenite (Cr-bearing) (Ca\(_2\)Al\(_2\)SiO\(_7\), PDF 87-0969)

Green: Spinel (MgAl\(_2\)O\(_4\), PDF 03-0901).
μXRD diffractogram of TS62b spot 6 showing all phases identified. Anorthite and spinel are fine-grained (rings on GADDS image), gehlenite is coarse-grained (spots on GADDS image), and fassaite is a strained single crystal (streaks on GADDS image).

Orange: Anorthite (CaAl$_2$Si$_2$O$_8$, PDF 03-0505)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083)
Red: Gehlenite (Cr-bearing) (Ca$_2$Al$_2$SiO$_7$, PDF 87-0969)
Green: Spinel (MgAl$_2$O$_4$, PDF 03-0901).

Allende TS62b Spot 6 (zoom in on EVA image)
μXRD diffractogram of TS62b spot 7 showing all phases identified. Anorthite and gehlenite are coarse-grained (spots on GADDS image). Spinel and grossular are fine-grained (rings on GADDS image). Forsterite is nearly fine-grained (spotty rings on GADDS image). Fassaite is streaky rings in GADDS image (mostly fine-grained but with some strained larger crystals).

Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Light Blue: Forsterite (Mg$_{1.808}$Fe$_{0.192}$SiO$_4$, PDF 83-1536)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Orange: Anorthite (CaAl$_2$Si$_2$O$_8$, PDF 03-0505)
Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$·H$_2$O, PDF 16-0388)
Blue: Fassaite (Ca$_{1.00}$Mg$_{0.39}$Ti$_{0.35}$Ti$_{0.13}$Al$_{0.13}$(Al$_{0.74}$Si$_{1.26}$)O$_6$, PDF 71-1541)
μXRD diffractogram of TS62b spot 7 showing all phases identified. Anorthite and gehlenite are coarse-grained (spots on GADDS image). Spinel and grossular are fine-grained (rings on GADDS image). Forsterite is nearly fine-grained (spotty rings on GADDS image). Fassaite is streaky rings in GADDS image (mostly fine-grained but with some strained larger crystals).

Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Light Blue: Forsterite (Mg$_{1.808}$Fe$_{0.192}$SiO$_4$, PDF 83-1536)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Orange: Anorthite (Ca$_2$Al$_2$Si$_2$O$_7$, PDF 03-0505)
Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$·H$_2$O, PDF 16-0388)
Blue: Fassaite (Ca$_{1.00}$Mg$_{0.30}$Ti$_{0.35}$Al$_{0.13}$Si$_{1.26}$O$_6$, PDF 71-1541).
μXRD diffractogram of TS62b spot 8 showing all phases identified. All phases but anorthite are fine-grained (rings on GADDS image), anorthite is coarse-grained (spots on GADDS image).

Green: Spinel (MgAl₂O₄, PDF 21-1152)
Light Blue: Forsterite (Mg₁.₈₀₈Fe₀.₁₉₂SiO₄, PDF 83-1536)
Pink: Grossular (Ca₃Al₂(SiO₄)₃, PDF 75-1551)
Orange: Anorthite (CaAl₂Si₂O₈, PDF 03-0505)
Red: Gehlenite (Ca₂Al₂SiO₇·H₂O, PDF 16-0388)
Blue: Fassaite (Ca₁.₀₀Mg₀.₃₉Ti₀.₃₅Al₀.₁₃(Al₀.₇₄Si₁.₂₆)O₆, PDF 71-1541).

Allende TS62b Spot 8

μXRD diffractogram of TS62b spot 8 showing all phases identified. All phases but anorthite are fine-grained (rings on GADDS image), anorthite is coarse-grained (spots on GADDS image).

Green: Spinel (MgAl₂O₄, PDF 21-1152)
Light Blue: Forsterite (Mg₁.₈₀₈Fe₀.₁₉₂SiO₄, PDF 83-1536)
Pink: Grossular (Ca₃Al₂(SiO₄)₃, PDF 75-1551)
Orange: Anorthite (CaAl₂Si₂O₈, PDF 03-0505)
Red: Gehlenite (Ca₂Al₂SiO₇·H₂O, PDF 16-0388)
Blue: Fassaite (Ca₁.₀₀Mg₀.₃₉Ti₀.₃₅Al₀.₁₃(Al₀.₇₄Si₁.₂₆)O₆, PDF 71-1541).
Allende TS62b Spot 9

μXRD diffractogram of TS62b spot 9 showing all phases identified. Anorthite, gehlenite and forsterite are coarse-grained (spots on GADDS image). Spinel is fine-grained (rings on GADDS image). Fassaite and grossular are strained (streaks on GADDS image).

Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Light Blue: Forsterite (Mg$_{1.808}$Fe$_{0.192}$SiO$_4$, PDF 83-1536)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Orange: Anorthite (Ca$_{1.00}$Al$_{2}$Si$_2$O$_8$, PDF 03-0505)
Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$·H$_2$O, PDF 16-0388)
Blue: Fassaite (Ca$_{1.00}$Mg$_{0.39}$Ti$_{0.35}$Al$_{0.13}$Al$_{0.74}$Si$_{1.26}$O$_6$, PDF 71-1541).
μXRD diffractogram of TS62b spot 10 showing all phases identified. Anorthite is coarse-grained (spots on GADDS image). Spinel, grossular, and forsterite are fine-grained (rings on GADDS image). Fassaite and gehlenite are strained (streaks on GADDS image).

Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Orange: Anorthite (CaAl$_2$Si$_2$O$_8$, PDF 03-0505)
Red: Gehlenite (Ca$_3$Al$_2$SiO$_7$·H$_2$O, PDF 16-0388)
Blue: Fassaite (Ca$_{1.00}$Mg$_{0.39}$Ti$_{0.35}$Al$_{0.13}$Al$_{0.13}$(Al$_{0.74}$Si$_{1.26}$)O$_6$, PDF 71-1541) Light Blue: Forsterite ferroan (Mg$_{1.83}$Fe$_{0.18}$SiO$_4$, PDF 72-2462).
Allende Cr3.17
Context Map and Parameters

Allende Cr3.17 sample context image, showing spots examined along two traverses

Table showing parameters used to collect μXRD data on Allende Cr3.17, scan type was omega scan

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<td>Frame 2</td>
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<td>18</td>
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μXRD of a fluffy white inclusion in Allende Cr3.17. The inclusion contains olivine (forsterite) and pyroxene (fassaite), the refractory mineral gehlenite, and the secondary mineral grossular.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 72-1251)
Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$, PDF 89-1489)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of matrix in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite or hedenbergite).

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
Allende Cr3.17 Spot 2 (hedenbergite)

μXRD of matrix in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite or hedenbergite).

Light Blue: Forsterite ($\text{Mg}_{1.360}\text{Fe}_{0.640}\text{Si}_4\text{O}_{10}$, PDF 76-0552)

Blue: Hedenbergite ($\text{CaFeSi}_2\text{O}_6$, PDF 71-1498).
μXRD of inclusion in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite).

Light Blue: Forsterite ($\text{Mg}_{1.360}\text{Fe}_{0.640}\text{SiO}_4$, PDF 76-0552)

Blue: Fassaite (($\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})(\text{Si}_{1.728}\text{Al}_{0.272})\text{O}_6$, PDF 83-2083).
Allende Cr3.17 Spot 4

μXRD of a small inclusion in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite).

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of a coarse-grained inclusion in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite). The olivine appears as both fine-grained (rings in GADDS image) and coarse-grained (spots in GADDS image).

Light Blue: Forsterite ferroan (Mg$_{1.80}$Fe$_{0.20}$SiO$_4$, PDF 72-2461)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of matrix near a fluffy white inclusion in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite). The presence of gehlenite is likely being picked up from the nearby fluffy inclusion.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$, PDF 89-1489)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of matrix near an inclusion in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite).

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of an inclusion in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite).

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of matrix near some small inclusions in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite).

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of an inclusion and some matrix in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite). The different textures in the 2D GADDS image likely represent the different forsterite and pyroxene in the matrix vs the inclusion.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of an inclusion in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite). The different textures in the 2D GADDs image likely represent the different grain sizes of forsterite and pyroxene in the inclusion.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).

Allende Cr3.17 Spot 11
μXRD of matrix near an inclusion (from spot 11) in Allende Cr3.17, containing olivine (forsterite) and pyroxene (fassaite). The different textures in the 2D GADDS image likely represent the different grain sizes of forsterite and pyroxene in the inclusion and the matrix.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
Allende Cr3.7c Samples Summary

Outside of possible CAI

Small fragment of CAI A

Large fragment of CAI A

Small fragment of CAI B

Large fragment of CAI B

Fragment of CAI

500 μm
Allende Cr3.7c: Outside of Potential CAI
Context Map and Parameters

Table showing parameters used to collect μXRD data on Allende Cr3.7c
Outside of Potential CAI, scan type was omega scan

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<td>Frame 2</td>
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500 μm

Allende Cr3.7c: Outside of Potential CAI sample context image, showing spots examined along a traverse
μXRD of outside of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite), enstatite, and grossular.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 72-1251)
Blue: Enstatite (MgSiO$_3$, PDF 73-1937).
μXRD of outside of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite), enstatite, and grossular.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 72-1251)
Blue: Enstatite (MgSiO$_3$, PDF 73-1937).
μXRD of outside of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and enstatite.
Light Blue: Forsterite ($\text{Mg}_{1.360}\text{Fe}_{0.640}\text{SiO}_4$, PDF 76-0552)
Blue: Enstatite ($\text{MgSiO}_3$, PDF 73-1937).
Allende Cr3.7c: Outside of Potential CAI Spot 4

μXRD of outside of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and enstatite.
Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Enstatite (MgSiO$_3$, PDF 73-1937).
Allende Cr3.7c: Large CAI Fragment A and B
Context Map and Parameters

Allende Cr3.7c: Large CAI Fragment A (top) and B (bottom)
sample context image, showing spots examined

Table showing parameters used to collect μXRD data on Allende Cr3.7c Large CAI Fragments, scan type was omega scan

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<td>35.5</td>
<td>40</td>
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<td>25</td>
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</table>
μXRD of outside of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite.

Light Blue: Forsterite (Mg\(_{1.360}\)Fe\(_{0.640}\)Si\(_4\), PDF 76-0552)

Blue: Fassaite ((Ca\(_{0.968}\)Mg\(_{0.578}\)Fe\(_{0.220}\)Al\(_{0.161}\)Ti\(_{0.059}\))(Si\(_{1.728}\)Al\(_{0.272}\))O\(_6\), PDF 83-2083)

Orange: Albite (NaAlSi\(_3\)O\(_8\), PDF 03-0451).

[note that EVA would not merge the frames, so the GADDS images are separate]
μXRD of inside of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of inside of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite. It appears there is some preferred orientation in the forsterite (fine-grained rings but with one much larger in comparison to others).

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite and albite. It appears there is some preferred orientation in the forsterite (fine-grained rings but with one much larger in comparison to others).

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Fassaite ([Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$](Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083)
Orange: Albite (NaAlSi$_3$O$_8$, PDF 03-0451).
μXRD of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite and albite. It appears there is some preferred orientation in the forsterite (fine-grained rings but with one much larger in comparison to others).

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083)

Orange: Albite (NaAlSi$_3$O$_8$, PDF 03-0451).
Allende Cr3.7c: Small CAI Fragment A and B
Context Map and Parameters

Allende Cr3.7c: Small CAI Fragment A and B sample context image, showing spots examined, run at the same time as Large CAI Fragment A and B (numbering continues)

Table showing parameters used to collect μXRD data on Allende Cr3.7c Small CAI Fragments, scan type was omega scan

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µXRD of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite and albite. The amorphous phase at about 29 degrees two-theta, is likely the crystal bond used to mount the sample.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite), fassaite, albite, spinel, and grossular. This sample is likely a small CAI. The amorphous phase at about 29 degrees two-theta, is likely the crystal bond used to mount the sample.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Green: Spinel (Mg$_6$Al$_2$O$_{12}$, PDF 21-1152)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 72-1251)
Orange: Albite (NaAlSi$_3$O$_8$, PDF 03-0451)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_0.272$)O$_6$, PDF 83-2083).
μXRD of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite), fassaite, albite, and enstatite. The amorphous phase at about 25 degrees two-theta, is likely the crystal bond used to mount the sample.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Orange: Albite (NaAlSi$_3$O$_8$, PDF 03-0451)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083)
Purple: Enstatite (MgSiO$_3$, PDF 22-0714).
Allende Cr3.7c: Fragment of CAI
Context Map and Parameters

Allende Cr3.7c: Fragment of CAI sample context image, showing spots examined. There were some issues with shielding so data collected on some spots were not very good.

Table showing parameters used to collect μXRD data on Allende Cr3.7c CAI fragment, scan type was omega scan

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μXRD of a fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite. The amorphous phase at about 28 degrees two-theta, is likely the crystal bond used to mount the sample.

Light Blue: Forsterite (Mg\textsubscript{1.360}Fe\textsubscript{0.640}Si\textsubscript{4}, PDF 76-0552)

Blue: Fassaite ((Ca\textsubscript{0.968}Mg\textsubscript{0.578}Fe\textsubscript{0.220}Al\textsubscript{0.161}Ti\textsubscript{0.059})(Si\textsubscript{1.728}Al\textsubscript{0.272})O\textsubscript{6}, PDF 83-2083).
μXRD of a fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite.  
Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)  
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of a fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of a fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite. The amorphous phase at about 28 degrees two-theta, is likely the crystal bond used to mount the sample.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
Allende Cr3.7c: CAI Fragment Spot 5

μXRD of a fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite) and fassaite.

Light Blue: Forsterite \((\text{Mg}_{1.360}\text{Fe}_{0.640}\text{Si}_4\text{O}_{10})\), PDF 76-0552

Blue: Fassaite \(((\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})(\text{Si}_{1.728}\text{Al}_{0.272})\text{O}_6)\), PDF 83-2083.

\[500 \text{ μm}\]
μXRD of fragment thought to be a CAI from Allende Cr3.7c samples, containing olivine (forsterite), fassaite, albite, and enstatite. The amorphous phase at about 25 degrees two-theta, is likely the crystal bond used to mount the sample.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
Allende 3529 (first run)
Context Map and Parameters

Table showing parameters used to collect μXRD data on Allende 3529, scan type was omega scan

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Allende 3529 powder, context image.
μXRD of Allende 3529 powder, containing anorthite, spinel, grossular, and gehlenite. 
Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)  
Orange: Anorthite (CaAl$_2$Si$_2$O$_8$, PDF 03-0505)  
Pink: Grossular (Ca$_3$Al$_2$Si$_3$O$_{12}$, PDF 03-0627)  
Red: Gehlenite (Al$_2$O$_3$(CaO)$_3$(SiO$_2$)$_2$, PDF 02-0823).
μXRD of Allende 3529 powder, containing fassaite, spinel, and forsterite.
Green: Spinel (MgAl$_2$O$_4$, PDF 05-0672)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 01-1290)
Blue: Fassaite (Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.433}$Ti$_{0.059}$Si$_{1.728}$O$_6$, PDF 83-2075).
μXRD of Allende 3529 powder, containing anorthite, spinel, grossular, and fassaite.
Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Orange: Anorthite (Al$_2$Ca(SiO$_4$)$_2$, PDF 02-0537)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Blue: Fassaite (Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.433}$Ti$_{0.059}$Si$_{1.728}$O$_{6}$, PDF 83-2075).
Allende 3529 (second run)
Context Map and Parameters

Allende 3529 powder, context image.

Table showing parameters used to collect μXRD data on Allende 3529, scan type was omega scan

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Allende 3529 Spot 1

μXRD of Allende 3529 powder, containing anorthite, spinel, grossular, and gehlenite. Green: Spinel (MgAl$_2$O$_4$, PDF 82-2424) Orange: Anorthite (CaAl$_2$Si$_2$O$_8$, PDF 41-1486).
μXRD of Allende 3529 powder, containing anorthite, spinel, grossular, and fassaite.
Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Orange: Anorthite (Al$_2$Ca(SiO$_4$)$_2$, PDF 02-0537)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Blue: Fassaite (Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.433}$Ti$_{0.059}$Si$_{1.728}$O$_6$, PDF 83-2075).
μXRD of Allende 3529 powder, containing anorthite, spinel, grossular, and fassaite.

Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Orange: Anorthite (Al$_2$Ca(SiO$_4$)$_2$, PDF 02-0537)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Blue: Fassaite (Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.433}$Ti$_{0.059}$Si$_{1.728}$O$_6$, PDF 83-2075).
μXRD of Allende 3529 powder, containing anorthite, spinel, grossular, and fassaite.

Green: Spinel (MgAl₂O₄, PDF 82-2424)
Orange: Anorthite Ca(Al₂Si₂O₈), PDF 89-1459)
Pink: Grossular Al₂Ca₃(SiO₄)₃, PDF 74-1087)
Red: Gehlenite ((Ca₃MgNa₄.05)(Mg₀.24Fe₀.12)(Si₁.39Al₀.61O₇), PDF 72-2128)
Blue: Fassaite (Ca₀.968Mg₀.578Fe₀.220Al₀.433Ti₀.059Si₁.728O₆, PDF 83-2075).
Micro X-Ray
Diffraction of Tagish Lake Samples

1. HG 48a
2. Hg 48b
3. MM01 26c
4. PM 032
Tagish Lake HG48a Side a
Context Map and Parameters

Context map of Tagish Lake HG 48a Side a showing the spots examined by μXRD (red 9 not used as it was in a crevasse).

Table showing parameters used to collect μXRD data on Tagish Lake HG 48a Side a, scan type was omega scan

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Tagish Lake HG 48a Side a Spot 1

μXRD diffractogram of Tagish Lake HG 48a Side a spot 1 showing all phases identified.
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
μXRD diffractogram of Tagish Lake HG 48a Side a spot 2 showing all phases identified.

- **Light Blue**: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
- **Pink**: Magnetite (Fe$_3$O$_4$), PDF 85-1436
- **Purple**: Pyrhotite (FeS, PDF 02-1241)
- **Orange**: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
- **Blue**: Siderite (FeCO$_3$, PDF 12-0531)
- **Red**: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
- **Deep Dark Blue**: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
μXRD diffractogram of Tagish Lake HG 48a Side a spot 3 showing all phases identified.

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Pink: Magnetite (Fe$_3$O$_4$), PDF 85-1436
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Tagish Lake HG 48a Side a Spot 4

μXRD diffractogram of Tagish Lake HG 48a Side a spot 4 showing all phases identified.

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Pink: Magnetite (Fe$_3$O$_4$), PDF 85-1436
Purple: Pyrrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·$2\text{H}_2\text{O}$, PDF 06-0046)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
μXRD diffractogram of Tagish Lake HG 48a Side a Spot 4 showing all phases identified.

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Pink: Magnetite (Fe$_3$O$_4$), PDF 85-1436
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
μXRD diffractogram of Tagish Lake HG 48a Side a spot 5 showing all phases identified.
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Pink: Magnetite (Fe$_3$O$_4$), PDF 85-1436
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
μXRD diffractogram of Tagish Lake HG 48a Side a spot 6 showing all phases identified.

Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$Si$_2$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$), PDF 75-0449
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117)
Green: Spinel (MgAl$_2$O$_4$, PDF 03-0897)
μXRD diffractogram of Tagish Lake HG 48a Side a spot 7 showing all phases identified.

Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)

Blue: Siderite (FeCO$_3$, PDF 12-0531)

Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)

Pink: Magnetite (Fe$_3$O$_4$, PDF 75-0449)

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117)
Tagish Lake HG 48a Side a Spot 8

μXRD diffractogram of Tagish Lake HG 48a Side a spot 8 showing all phases identified.

Green: Spinel (MgAl₂O₄, PDF 03-0897).
Light Blue: Forsterite (Mg₂SiO₄, PDF 03-1117)
Pink: Magnetite (Fe₃O₄), PDF 75-0449
Red: Saponite (Ca₀.₃Mg₃(Si, Al)₄O₁₀(OH)₂ · 6H₂O, PDF 06-0002)
Orange: Gypsum (CaSO₄ · 2H₂O, PDF 06-0046)
μXRD diffractogram of Tagish Lake HG 48a Side a spot 9 showing all phases identified.

Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 84-0652)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Context map of Tagish Lake HG 48a Side b showing the ten spots examined by μXRD

Table showing parameters used to collect μXRD data on Tagish Lake HG 48a Side b, scan type was omega scan

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 ($\theta_1$)</th>
<th>Theta2 ($\theta_2$)</th>
<th>Width (ω)</th>
<th>Time (min)</th>
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<tbody>
<tr>
<td>February and March 2014</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frame 1</td>
<td>14.5</td>
<td>21</td>
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<tr>
<td>Frame 2</td>
<td>33.5</td>
<td>40</td>
<td>20</td>
<td>60</td>
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Tagish Lake HG 48a Side b Spot 1

μXRD diffractogram of Tagish Lake HG 48a Side b spot 1 showing all phases identified.

Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
μXRD diffractogram of Tagish Lake HG 48a Side b spot 2 showing all phases identified.

Red: Saponite \((Ca_{0.3}Mg_3(Si, Al)Al_4O_{10}(OH)_2 \cdot 6H_2O, PDF \text{ 06-0002})\)

Pink: Magnetite \((Fe_3O_4, PDF \text{ 85-1436})\)

Light Blue: Forsterite \((Mg_2SiO_4, PDF \text{ 80-0783})\)
μXRD diffractogram of Tagish Lake HG 48a Side b spot 3 showing all phases identified.

Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
μXRD diffractogram of Tagish Lake HG 48a Side b spot 4 showing all phases identified.

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Tagish Lake HG 48a Side b Spot 5

μXRD diffractogram of Tagish Lake HG 48a Side b spot 5 showing all phases identified.

Light Blue: Forsterite ($\text{Mg}_2 \text{SiO}_4$, PDF 80-0783)
Pink: Magnetite ($\text{Fe}_3 \text{O}_4$, PDF 85-1436)
Red: Saponite ($\text{Ca}_0.3 \text{Mg}_3 (\text{Si, Al})_4 \text{O}_{10} (\text{OH})_2 \cdot 6\text{H}_2\text{O}$, PDF 06-0002)
Deep Dark Blue: Clinoenstatite ($\text{MgSiO}_3$, PDF 03-0696)
μXRD diffractogram of Tagish Lake HG 48a Side b spot 6 showing all phases identified.

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
μXRD diffractogram of Tagish Lake HG 48a Side b spot 7 showing all phases identified.

- **Light Blue**: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
- **Orange**: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
- **Pink**: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
- **Purple**: Pyrhotite (FeS, PDF 02-1241)
- **Blue**: Siderite (FeCO$_3$, PDF 12-0531)
- **Red**: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
- **Deep Dark Blue**: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
μXRD diffractogram of Tagish Lake HG 48a Side b spot 8 showing all phases identified.

Light Blue: Forsterite ($\text{Mg}_2\text{SiO}_4$, PDF 80-0783)
Orange: Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, PDF 06-0046)
Pink: Magnetite ($\text{Fe}_3\text{O}_4$, PDF 85-1436)
Blue: Siderite ($\text{FeCO}_3$, PDF 12-0531)
Red: Saponite ($\text{Ca}_{0.3}\text{Mg}_3(\text{Si, Al})_4\text{O}_{10}($OH$)_2 \cdot 6\text{H}_2\text{O}$, PDF 06-0002)
μXRD diffractogram of Tagish Lake HG 48a Side b spot 9 showing all phases identified.

Light Blue: Forsterite (Mg₂SiO₄, PDF 80-0783)
Orange: Gypsum (CaSO₄ · 2H₂O, PDF 06-0046)
Pink: Magnetite (Fe₃O₄, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Blue: Siderite (FeCO₃, PDF 12-0531)
Red: Saponite (Ca₀.₃Mg₃(Si, Al)₄O₁₀(OH)₂ · 6H₂O, PDF 06-0002)
Deep Dark Blue: Clinoenstatite (MgSiO₃, PDF 03-0696)
Tagish Lake HG 48b Side a
Context Map and Parameters

Tagish Lake HG 48b Side a sample context image, showing spots examined along two traverses

Table showing parameters used to collect μXRD data on Tagish Lake HG 48b Side a, scan type was omega scan

<table>
<thead>
<tr>
<th>Date Collected</th>
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<tr>
<td></td>
<td>Frame 2</td>
<td>33.5</td>
<td>40</td>
<td>20</td>
</tr>
</tbody>
</table>
μXRD of Tagish Lake HG 48b Side a spot 1 showing all phases identified.

- **Pink:** Magnetite (Fe₃O₄, PDF 85-1436)
- **Purple:** Pyrhotite (FeS, PDF 02-1241)
- **Orange:** Gypsum (CaSO₄·2H₂O, PDF 06-0046)
- **Blue:** Siderite (FeCO₃, PDF 12-0531)
- **Red:** Saponite (Ca₀.₃Mg₃(Si, Al)₄O₁₀(OH)₂·6H₂O, PDF 06-0002)
- **Deep Dark Blue:** Clinoenstatite (MgSiO₃, PDF 03-0696)
- **Light Blue:** Forsterite (Mg₂SiO₄, PDF 07-0074)
μXRD of Tagish Lake HG 48b Side a spot 2 showing all phases identified.

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Tagish Lake HG 48b Side a Spot 3

μXRD of Tagish Lake HG 48b Side a spot 3 showing all phases identified.

- **Light Blue**: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117)
- **Pink**: Magnetite (Fe$_3$O$_4$, PDF 75-0449)
- **Red**: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
- **Purple**: Pyrhotite (FeS, PDF 02-1241)
- **Orange**: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
- **Blue**: Siderite (FeCO$_3$, PDF 12-0531)
- **Deep Dark Blue**: Clinoenstatite (MgSiO$_3$, PDF 03-0696)

[Diagram showing XRD patterns and phase assignments]
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Purple: Pyrrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Pink: Magnetite (Fe$_3$O$_4$), PDF 75-0449)
Green: Clinoenstatite (MgSiO$_3$, PDF 84-0652)
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite \((\text{Ca}_{0.3}\text{Mg}_3\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O}, \text{PDF 06-0002})\)
Purple: Pyrhotite \((\text{FeS}, \text{PDF 02-1241})\)
Orange: Gypsum \((\text{CaSO}_4\cdot 2\text{H}_2\text{O}, \text{PDF 06-0046})\)
Deep Dark Blue: Clinoenstatite \((\text{MgSiO}_3, \text{PDF 03-0696})\)
Pink: Magnetite \((\text{Fe}_3\text{O}_4, \text{PDF 85-1436})\)
Blue: Siderite \((\text{FeCO}_3, \text{PDF 12-0531})\)
Light Blue: Forsterite \((\text{Mg}_2\text{SiO}_4, \text{PDF07-0074})\)
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite \((\text{Ca}_{0.3}\text{Mg}_{3}(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O}, \text{PDF 06-0002})\)
Purple: Pyrhotite \((\text{FeS}, \text{PDF 02-1241})\)
Orange: Gypsum \((\text{CaSO}_4 \cdot 2\text{H}_2\text{O}, \text{PDF 06-0046})\)
Deep Dark Blue: Clinoenstatite \((\text{MgSiO}_3, \text{PDF 03-0696})\)
Pink: Magnetite \((\text{Fe}_3\text{O}_4, \text{PDF 85-1436})\)
Blue: Siderite \((\text{FeCO}_3, \text{PDF 12-0531})\)
Light Blue: Forsterite \((\text{Mg}_2\text{SiO}_4, \text{PDF07-0074})\)
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite \( (\text{Ca}_{0.3}\text{Mg}_3(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O}, \text{PDF 06-0002}) \)
Purple: Pyrhotite \( (\text{FeS}, \text{PDF 02-1241}) \)
Orange: Gypsum \( (\text{CaSO}_4 \cdot 2\text{H}_2\text{O}, \text{PDF 06-0046}) \)
Deep Dark Blue: Clinoenstatite \( (\text{MgSiO}_3, \text{PDF 03-0696}) \)
Pink: Magnetite \( (\text{Fe}_3\text{O}_4, \text{PDF 85-1436}) \)
Blue: Siderite \( (\text{FeCO}_3, \text{PDF 12-0531}) \)
Light Blue: Forsterite \( (\text{Mg}_2\text{SiO}_4, \text{PDF07-0074}) \)
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF07-0074)
Tagish Lake HG 48b Side a Spot 11

μXRD of Tagish Lake HG 48b Side a, showing all phases identified.

Red: Saponite (Ca$_{0.3}$Mg$_{3}$Si$_4$Al$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117)
Purple: Pyrhotite (FeS, PDF 02-1241)
Dark Blue: Orthopyroxene (Mg$_{1.12}$Fe$_{0.88}$Si$_2$O$_6$, PDF 76-0709)

μXRD WL=1.78897
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrohite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite \( \text{Ca}_{0.3} \text{Mg}_3 \text{Si}_4 \text{Al}_4 \text{O}_{10} \text{(OH)}_2 \cdot 6\text{H}_2\text{O} \), PDF 06-0002
Pink: Magnetite \( \text{Fe}_3 \text{O}_4 \), PDF 85-1436
Purple: Pyrhotite \( \text{FeS} \), PDF 02-1241
Orange: Gypsum \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \), PDF 06-0046
Blue: Siderite \( \text{FeCO}_3 \), PDF 12-0531
Deep Dark Blue: Clinoenstatite \( \text{MgSiO}_3 \), PDF 03-0696
Light Blue: Forsterite \( \text{Mg}_2 \text{SiO}_4 \), PDF 07-0074
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake HG 48b Side a Spot 16

Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake HG 48b Side a, showing all phases identified. 
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)  
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)  
Purple: Pyrhotite (FeS, PDF 02-1241)  
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)  
Blue: Siderite (FeCO$_3$, PDF 12-0531)  
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)  
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake HG 48b Side a, showing all phases identified.
Red: Saponite ($Ca_{0.3}Mg_3(Si, Al)_4O_{10}(OH)_2 \cdot 6H_2O$, PDF 06-0002)
Pink: Magnetite ($Fe_3O_4$, PDF 85-1436)
Purple: Pyrhotite ($FeS$, PDF 02-1241)
Orange: Gypsum ($CaSO_4 \cdot 2H_2O$, PDF 06-0046)
Blue: Siderite ($FeCO_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite ($MgSiO_3$, PDF 03-0696)
Light Blue: Forsterite ($Mg_2SiO_4$, PDF 07-0074)
Tagish Lake HG 48b Side b
Context Map and Parameters

Tagish Lake HG 48b Side b sample context image, showing spots examined along two traverses

Table showing parameters used to collect μXRD data on Tagish Lake HG 48b Side b, scan type was omega scan

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 (θ₁)</th>
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<td>14.5</td>
<td>21</td>
<td>10</td>
</tr>
</tbody>
</table>
μXRD of Tagish Lake HG 48b Side b, showing all phases identified.
Red: Saponite \((\text{Ca}_{0.3} \text{Mg}_3 (\text{Si, Al})_2 \text{O}_{10} (\text{OH})_2 \cdot 6\text{H}_2\text{O}, \text{PDF 06-0002})\)
Pink: Magnetite \((\text{Fe}_3 \text{O}_4, \text{PDF 85-1436})\)
Light Blue: Forsterite \((\text{Mg}_2 \text{SiO}_4, \text{PDF 80-0783})\)
Dark Blue: Clinoenstatite \((\text{MgSiO}_3, \text{PDF 76-0526})\)
μXRD of Tagish Lake HG 48b Side b, showing all phases identified.
Red: Saponite \( \text{Ca}_{0.3}\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O} \), PDF 06-0002)
Pink: Magnetite \( \text{Fe}_3\text{O}_4 \), PDF 85-1436
Purple: Pyrohotite \( \text{FeS} \), PDF 02-1241
Orange: Gypsum \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \), PDF 06-0046
Blue: Siderite \( \text{FeCO}_3 \), PDF 12-0531
Deep Dark Blue: Clinoenstatite \( \text{MgSiO}_3 \), PDF 03-0696
Light Blue: Forsterite \( \text{Mg}_2\text{SiO}_4 \), PDF 07-0074
μXRD of Tagish Lake HG 48b Side b, showing all phases identified. 
Red: Saponite (Ca_{0.3}Mg_3(Si, Al)_4O_{10}(OH)_2 · 6H_2O, PDF 06-0002) 
Pink: Magnetite (Fe_3O_4, PDF 85-1436) 
Purple: Pyrhotite (FeS, PDF 02-1241) 
Orange: Gypsum (CaSO_4 · 2H_2O, PDF 06-0046) 
Blue: Siderite (FeCO_3, PDF 12-0531) 
Deep Dark Blue: Clinopyroxene (MgSiO_3, PDF 03-0696) 
Light Blue: Forsterite (Mg_2SiO_4, PDF 07-0074)
μXRD of Tagish Lake HG 48b Side b, spot 4.
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Tagish Lake HG 48b Side b Spot 5

μXRD of Tagish Lake HG 48b Side b, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake HG 48b Side b, showing all phases identified. 
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002) 
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436) 
Purple: Pyrhotite (FeS, PDF 02-1241) 
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046) 
Blue: Siderite (FeCO$_3$, PDF 12-0531) 
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696) 
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake HG 48b Side b, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
 Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
 Purple: Pyrohotite (FeS, PDF 02-1241)
 Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
 Blue: Siderite (FeCO$_3$, PDF 12-0531)
 Deep Dark Blue: Clinomenstatite (MgSiO$_3$, PDF 03-0696)
 Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
Tagish Lake HG 48b Side b Spot 8

μXRD of Tagish Lake HG 48b Side b, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Tagish Lake HG 48b Side b Spot 9

μXRD of Tagish Lake HG 48b Side b, showing all phases identified:
- Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
- Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
- Purple: Pyrohite (FeS, PDF 02-1241)
- Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
- Blue: Siderite (FeCO$_3$, PDF 12-0531)
- Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
- Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake HG 48b Side b, showing all phases identified.

Red: Saponite \((\text{Ca}_{0.3}\text{Mg}_3(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O}, \text{PDF 06-0002})\)

Pink: Magnetite \((\text{Fe}_3\text{O}_4, \text{PDF 85-1436})\)

Purple: Pyrotite \((\text{FeS}, \text{PDF 02-1241})\)

Orange: Gypsum \((\text{CaSO}_4 \cdot 2\text{H}_2\text{O}, \text{PDF 06-0046})\)

Blue: Siderite \((\text{FeCO}_3, \text{PDF 12-0531})\)

Deep Dark Blue: Clinoenstatite \((\text{MgSiO}_3, \text{PDF 03-0696})\)

Light Blue: Forsterite \((\text{Mg}_2\text{SiO}_4, \text{PDF 07-0074})\)
Tagish Lake MM01 26c
Context Map and Parameters

Tagish Lake MM01 26c context map, showing locations on spots examined.

Table showing parameters used to collect μXRD data on Tagish Lake MM01 26c, scan type was omega scan

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<td>Frame 2</td>
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Tagish Lake MM01 26c Spot 1

μXRD of Tagish Lake MM01 26c samples, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
Tagish Lake MM01 26c Spot 2

μXRD of Tagish Lake MM01 26c showing all phases identified. Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002) Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436) Purple: Pyrhotite (FeS, PDF 02-1241) Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046) Blue: Siderite (FeCO$_3$, PDF 12-0531) Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696) Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite \((\text{Ca}_{0.3}\text{Mg}_3(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O, PDF 06-0002})\)
Pink: Magnetite \((\text{Fe}_3\text{O}_4, \text{PDF 85-1436})\)
Purple: Pyrhotite \((\text{FeS, PDF 02-1241})\)
Orange: Gypsum \((\text{CaSO}_4 \cdot 2\text{H}_2\text{O, PDF 06-0046})\)
Blue: Siderite \((\text{FeCO}_3, \text{PDF 12-0531})\)
Deep Dark Blue: Clinoenstatite \((\text{MgSiO}_3, \text{PDF 03-0696})\)
Light Blue: Forsterite \((\text{Mg}_2\text{SiO}_4, \text{PDF 07-0074})\)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca_{0.3}Mg_3(Si, Al)_4O_{10}(OH)_2 · 6H_2O, PDF 06-0002)
Pink: Magnetite (Fe_3O_4, PDF 85-1436)
Purple: Pyrrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO_4 · 2H_2O, PDF 06-0046)
Blue: Siderite (FeCO_3, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO_3, PDF 03-0696)
Light Blue: Forsterite (Mg_2SiO_4, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
Orange: Hedenbergite (CaFe(Si$_2$O$_6$), PDF 87-1695)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.

Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Pink: Magnetite (Fe$_3$O$_4$), PDF 75-0449
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117)
Green: Spinel (MgAl$_2$O$_4$, PDF 03-0897)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_2$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrohotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.

Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)

Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)

Purple: Pyrhotite (FeS, PDF 02-1241)

Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)

Blue: Siderite (FeCO$_3$, PDF 12-0531)

Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
Pink: Magnetite (Fe$_3$O$_4$), PDF 75-0449
Tagish Lake MM01 26c Spot 16

μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$Si$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
μXRD of Tagish Lake MM01 26c showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Purple: Pyrhotite (FeS, PDF 02-1241)
Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 80-0783)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Tagish Lake MM01 26c Spot 19

μXRD of Tagish Lake MM01 26c clast, showing all phases identified.
Red: Saponite \( \text{Ca}_{0.3}\text{Mg}_3(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O} \), PDF 06-0002
Pink: Magnetite \( \text{Fe}_3\text{O}_4 \), PDF 85-1436
Purple: Pyrhotite \( \text{FeS} \), PDF 02-1241
Orange: Gypsum \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \), PDF 06-0046
Blue: Siderite \( \text{FeCO}_3 \), PDF 12-0531
Deep Dark Blue: Clinoenstatite \( \text{MgSiO}_3 \), PDF 03-0696
Light Blue: Forsterite \( \text{Mg}_2\text{SiO}_4 \), PDF 07-0074
Tagish Lake MM01 26c Spot 20

μXRD of Tagish Lake MM01 26c matrix, showing all phases identified.
Red: Saponite \( \text{Ca}_{0.3} \text{Mg}_3 \text{Si}_4 \text{Al}_2 \text{O}_{10} \cdot 6\text{H}_2\text{O} \), PDF 06-0002
Pink: Magnetite \( \text{Fe}_3 \text{O}_4 \), PDF 85-1436
Purple: Pyrohotite \( \text{FeS} \), PDF 02-1241
Orange: Gypsum \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \), PDF 06-0046
Blue: Siderite \( \text{FeCO}_3 \), PDF 12-0531
Deep Dark Blue: Clinoenstatite \( \text{MgSiO}_3 \), PDF 03-0696
Light Blue: Forsterite \( \text{Mg}_2 \text{SiO}_4 \), PDF 07-0074

500 μm
Tagish Lake PM 032
Context Map and Parameters

Tagish Lake PM 032 context image, showing spots examined

Table showing parameters used to collect μXRD data on Tagish Lake PM 032, scan type was omega scan

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<th>Theta2 (θ2)</th>
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Tagish Lake PM 032 Spot 1

μXRD of Tagish Lake PM 032 inclusion, showing all phases identified.

Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
μXRD of Tagish Lake PM 032 inclusion, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrhotite (FeS, PDF 02-1241)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
μXRD of Tagish Lake PM 032 matrix, showing all phases identified.

Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Purple: Pyrohite (FeS, PDF 02-1241)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Tagish Lake PM 032 Spot 4

μXRD of Tagish Lake PM 032 inclusion, showing all phases identified.
Red: Saponite \((\text{Ca}_{0.3}\text{Mg}_3(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O})\), PDF 06-0002
Light Blue: Forsterite \((\text{Mg}_2\text{SiO}_4)\), PDF 03-1117
Pink: Magnetite \((\text{Fe}_3\text{O}_4)\), PDF 85-1436
Blue: Siderite \((\text{FeCO}_3)\), PDF 12-0531
Deep Dark Blue: Clinoenstatite \((\text{MgSiO}_3)\), PDF 03-0696
μXRD of Tagish Lake PM 032 inclusion, showing all phases identified.
Red: Saponite (Ca$_{0.3}$Mg$_{3}$(Si, Al)$_{4}$O$_{10}$(OH)$_{2}$ · 6H$_{2}$O, PDF 06-0002)
Light Blue: Forsterite (Mg$_{2}$SiO$_{4}$, PDF 03-1117)
Pink: Magnetite (Fe$_{3}$O$_{4}$, PDF 85-1436)
Blue: Siderite (FeCO$_{3}$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_{3}$, PDF 03-0696)
μXRD of Tagish Lake PM 032 inclusion, showing all phases identified. Red: Saponite (Ca$_{0.3}$Mg$_3$(Si, Al)$_4$O$_{10}$(OH)$_2$ · 6H$_2$O, PDF 06-0002) Orange: Gypsum (CaSO$_4$ · 2H$_2$O, PDF 06-0046) Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074) Pink: Magnetite (Fe$_3$O$_4$), PDF 75-0449)
μXRD of Tagish Lake PM 032 inclusion, showing all phases identified.
Red: Saponite ($\text{Ca}_{0.3}\text{Mg}_3(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, PDF 06-0002)
Light Blue: Forsterite ($\text{Mg}_2\text{SiO}_4$, PDF 03-1117)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Blue: Siderite (FeCO$_3$, PDF 12-0531)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Purple: Pyrhotite (FeS, PDF 02-1241)
μXRD of Tagish Lake PM 032 inclusion, showing all phases identified.
Red: Saponite \((\text{Ca}_{0.3}\text{Mg}_3(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O}, \text{PDF 06-0002})\)
Light Blue: Forsterite \((\text{Mg}_2\text{SiO}_4, \text{PDF 03-1117})\)
Pink: Magnetite \((\text{Fe}_3\text{O}_4, \text{PDF 85-1436})\)
Blue: Siderite \((\text{FeCO}_3, \text{PDF 12-0531})\)
Deep Dark Blue: Clinoenstatite \((\text{MgSiO}_3, \text{PDF 03-0696})\)
μXRD of Tagish Lake PM 032 inclusion, showing all phases identified.
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 03-1117)
Pink: Magnetite (Fe$_3$O$_4$, PDF 85-1436)
Deep Dark Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0696)
Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)
μXRD of inclusion from Tagish Lake PM 032 samples, showing all phases identified.

Orange: Gypsum (CaSO$_4$·2H$_2$O, PDF 06-0046)

Purple: Pyrhotite (FeS, PDF 02-1241)

Red: Saponite (Ca$_{0.3}$Mg$_{3}$Si$_4$O$_{10}$(OH)$_2$·6H$_2$O, PDF 06-0002)

Pink: Magnetite (Fe$_3$O$_4$), PDF 75-0449

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
Micro X-Ray Diffraction of NWA 4502 Samples

1. NWA 4502
2. NWA 4502_ROM
3. NWA 4502 Sawdust
Context map of NWA 4502 Slice A, showing the spots examined by μXRD. The slice broke in two along a plane of weakness during mounting.

Table showing parameters used to collect μXRD data on NWA 4502 Slice A, scan type was omega scan

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<tr>
<td></td>
<td>Frame 2</td>
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<td>40</td>
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</table>
NWA 4502 Slice A Spot 1

μXRD diffraction pattern of NWA 4502 Slice A spot 1 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Light Blue: Forsterite ($\text{Mg}_{1.86}\text{Fe}_{0.14}\text{SiO}_4$, PDF 77-1025)

Blue: Diopside ($\text{CaMg(SiO}_3)_2$, PDF 02-0663)
μXRD diffraction pattern of NWA 4502 Slice A spot 2 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.14}$SiO$_4$, PDF 77-1025)

Blue: Diopside (CaMg(SiO$_3$)$_2$, PDF 02-0663)
μXRD diffraction pattern of NWA 4502 Slice A spot 3 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.14}$SiO$_4$, PDF 77-1025)
Blue: Diopside (CaMg(SiO$_3$)$_2$, PDF 02-0663)
μXRD diffraction pattern of NWA 4502 Slice A spot 4 showing forsterite, fassaite, gehlenite, spinel and grossular. This spot is a small white inclusion, not seen in CT scans.

Green: Spinel (MgAl$_2$O$_4$, PDF 21-1152)
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$, PDF 0-0690)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083)
NWA 4502 Slice A Spot 5

μXRD diffraction pattern of NWA 4502 Slice A spot 5 showing forsterite and diopside. This spot is an inclusion with a rust colour.
Light Blue: Forsterite (Mg$_{1.46}$Fe$_{0.54}$SiO$_4$, PDF 75-0553)
Brown: Perovskite (TiO$_3$, PDF 86-1393)
Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404).
μXRD diffraction pattern of NWA 4502 Slice A spot 6 showing forsterite.
Light Blue: Forsterite (Mg$_{1.460}$Fe$_{0.540}$SiO$_4$, PDF 76-0553)
NWA 4502 Slice A Spot 7

μXRD diffraction pattern of an inclusion in NWA 4502 Slice A spot 7 showing forsterite and diopside.

Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.14}$SiO$_4$, PDF 77-1025)
μXRD diffraction pattern of an inclusion in NWA 4502 Slice A spot 8 showing forsterite, fassaite, and gehlenite.

Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.14}$SiO$_4$, PDF 77-1025)
Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$, PDF 0-0690)
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083)
μXRD diffraction pattern of an inclusion in NWA 4502 Slice A spot 9 showing forsterite and fassaite.

Light Blue: Forsterite ($\text{Mg}_{\text{1.86}}\text{Fe}_{0.14}\text{SiO}_4$, PDF 77-1025)
Blue: Fassaite ($\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059}\text{Si}_{1.728}\text{Al}_{0.272}\text{O}_6$, PDF 83-2083)
μXRD diffraction pattern of an inclusion in NWA 4502 Slice A spot 10 showing forsterite and clinoenstatite.

Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.14}$SiO$_4$, PDF 77-1025)
Blue: Clinoenstatite (MgSiO$_3$, PDF 03-0521)
μXRD diffraction pattern of an inclusion in NWA 4502 Slice A spot 11 showing forsterite, fassaite, and gehlenite.

Light Blue: Forsterite ($\text{Mg}_{1.86}\text{Fe}_{0.14}\text{SiO}_4$, PDF 77-1025)
Red: Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$, PDF 0-0690)
Blue: Fassaite (($\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})\text{Si}_{1.728}\text{Al}_{0.272}\text{O}_6$, PDF 83-2083)
NWA 4502 Slice A Spot 12

μXRD diffraction pattern of an inclusion in NWA 4502 Slice A spot 11 showing gehlenite.
Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$, PDF 35-0755)
NWA 4502 Slice A (take two)
Context Map and Parameters

NWA 4502 Slice A sample context image, showing spots examined, this was a second run done after finding one CAI to attempt to find another.

Table showing parameters used to collect μXRD data on NWA 4502, scan type was omega scan

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NWA 4502 Slice A Spot 1 (take two)

μXRD diffraction pattern of an inclusion in NWA 4502 Slice A spot 11 showing forsterite, fassaite, gehlenite, and grossular.

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
Red: Gehlenite (Ca$_2$Al$_2$SiO$_7$, PDF 0-0690)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551)
Blue: Fassaite ([Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$](Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083)
NWA 4502 Slice A Spot 2 (take two)

μXRD diffraction pattern of an inclusion in NWA 4502 Slice A spot 11 showing forsterite, and clinoenstatite.

Light Blue: Forsterite (Mg$_{1.36}$Fe$_{0.64}$SiO$_4$, PDF 76-0552)
Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
NWA 4502 Slice A Spot 3 (take two)

μXRD diffraction pattern of an inclusion in NWA 4502 Slice A spot 11 showing forsterite, and clinoenstatite.

Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)

Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
μXRD diffraction pattern of an inclusion in NWA 4502 Slice A spot 11 showing forsterite, and clinoenstatite.
Light Blue: Forsterite (Mg$_2$SiO$_4$, PDF 07-0074)
Blue: Clinoenstatite (MgSiO$_3$, PDF 13-0415)
NWA 4502 Slice B
Context Map and Parameters

NWA 4502 Slice B sample context image, showing spots examined.
Run at the same time as NWA 4502 Slice A (take two), so numbering continues from there.

Table showing parameters used to collect μXRD data on NWA 4502, scan type was omega scan

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µXRD of a small inclusion in NWA 4502 Slice B, containing olivine (forsterite) and clinoenstatite.
Light Blue: Forsterite (Mg$_{1.36}$Fe$_{0.64}$SiO$_4$, PDF 76-0552)
Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
NWA 4502 Slice B Spot 6

μXRD of a small inclusion in NWA 4502 Slice B, containing olivine (forsterite) and pyroxene (diopside).

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Diopside (CaMg(SiO$_3$)$_2$, PDF 02-0663)
μXRD of a small inclusion in NWA 4502 Slice B, containing olivine (forsterite) and clinoenstatite.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
μXRD of a small inclusion in NWA 4502 Slice B, containing olivine (forsterite) and clinoenstatite.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
μXRD of a small inclusion in NWA 4502 Slice B, containing olivine (forsterite) and clinoenstatite.
Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
μXRD of a small inclusion in NWA 4502 Slice B, containing olivine (forsterite) and clinoenstatite.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
μXRD of a small inclusion in NWA 4502 Slice B, containing olivine (forsterite) and clinoenstatite.

Light Blue: Forsterite (Mg_{1.360}Fe_{0.640}SiO_{4}, PDF 76-0552)
Blue: Clinoenstatite (MgSiO_{3}, PDF 75-1404)
μXRD of a small inclusion in NWA 4502 Slice B, containing olivine (forsterite) and clinoenstatite.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
μXRD of a small inclusion in NWA 4502 Slice B, containing olivine (forsterite) and clinoenstatite.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
NWA 4502 Sawdust

This sample is the off cut from the wire saw when cutting NWA 4502 Slice A. Powder is very fine-grained. The μXRD data were collected as a part of another run. The numbering begins at spot 3. The spectra were very noisy, could be run with longer times.

Table showing parameters used to collect μXRD data on NWA 4502 Slice A
Outside of Potential CAI, scan type was omega scan

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NWA 4502 Sawdust Spot 3

\[ \mu \text{XRD of off cut from NWA 4502 Slice A. This spot was a fairly consolidated piece compared to the rest of the powder. It contains forsterite and clinoenstatite.} \]

Light Blue: Forsterite (Mg\textsubscript{1.360}Fe\textsubscript{0.640}SiO\textsubscript{4}, PDF 76-0552)

Blue: Clinoenstatite (MgSiO\textsubscript{3}, PDF 75-1404)
NWA 4502 Sawdust Spot 4

μXRD of off cut from NWA 4502 Slice A, containing forsterite and clinoenstatite.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)

Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
NWA 4502 Sawdust Spot 5

μXRD of off cut from NWA 4502 Slice A, containing forsterite and clinoenstatite.

Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)
Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
NWA 4502_ROM

NWA 4502_ROM slice, showing spots analyzed

Table showing parameters used to collect μXRD data on NWA 4502 ROM, scan type was omega scan

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μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.

Light Blue: Forsterite \( \text{Mg}_{1.86}\text{Fe}_{0.14}\text{SiO}_4 \), PDF 77-1025

Blue: Fassaite \( (\text{Ca}_{0.968}\text{Mg}_{0.578}\text{Fe}_{0.220}\text{Al}_{0.161}\text{Ti}_{0.059})(\text{Si}_{1.728}\text{Al}_{0.272})\text{O}_6 \), PDF 83-2083

Red: Gehlenite \( \text{Al}_2(\text{CaO})_3(\text{SiO}_2)_2 \), PDF 02-0823.
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.  
Light Blue: Forsterite (Mg$_{1.360}$Fe$_{0.640}$SiO$_4$, PDF 76-0552)  
Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)  
Red: Gehlenite (Al$_2$(CaO)$_3$(SiO$_2$)$_2$, PDF 02-0823).
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.  
Red: Gehlenite (Al$_2$(CaO)$_3$(SiO$_2$)$_2$, PDF 02-0823)  
Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.14}$SiO$_4$, PDF 77-1025)  
Blue: Clinoenstatite (MgSiO$_3$, PDF 73-1758).
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite. 
Red: Gehlenite (Al$_2$(CaO)$_3$(SiO$_2$)$_2$, PDF 02-0823) 
Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.14}$SiO$_4$, PDF 77-1025) 
Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.
Red: Gehlenite \((\text{Al}_2\text{(CaO)}_3\text{SiO}_2)_2\), PDF 02-0823
Light Blue: Forsterite \((\text{Mg}_{1.86}\text{Fe}_{0.14}\text{SiO}_4)\), PDF 77-1025
Blue: Clinoenstatite \((\text{MgSiO}_3)\), PDF 73-1758.
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.

Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.14}$SiO$_4$, PDF 77-1025)

Blue: Clinoenstatite (MgSiO$_3$, PDF 73-1758)

Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551).
NWA 4502_ROM Spot 7

μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.
Light Blue: Forsterite ($\text{Mg}_{1.86}\text{Fe}_{0.14}\text{SiO}_4$, PDF 77-1025)
Blue: Clinoenstatite ($\text{MgSiO}_3$, PDF 73-1758)
Pink: Grossular ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$, PDF 75-1551).
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.
Light Blue: Forsterite (Mg\textsubscript{1.86}Fe\textsubscript{0.17}SiO\textsubscript{4}, PDF 79-1212)
Blue: Clinoenstatite (MgSiO\textsubscript{3}, PDF 73-1758)
Pink: Grossular (Ca\textsubscript{3}Al\textsubscript{2}(SiO\textsubscript{4})\textsubscript{3}, PDF 75-1551).
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.
Light Blue: Forsterite (Mg$_{1.74}$Fe$_{0.26}$SiO$_4$, PDF 79-1198)
Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)
Red: Gehlenite (Al$_2$(CaO)$_3$(SiO$_2$)$_2$, PDF 02-0823).
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite. 
Red: Gehlenite (Al₂(CaO)₃(SiO₂)₂, PDF 02-0823) 
Light Blue: Forsterite (Mg₁.₈₆Fe₀.₁₄SiO₄, PDF 77-1025) 
Blue: Clinoenstatite (MgSiO₃, PDF 75-1404).
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.

Light Blue: Forsterite (Mg$_{1.8}$Fe$_{0.2}$SiO$_4$, PDF 74-2253)

Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)

Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$, PDF 75-1551).
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite. Light Blue: Forsterite (Mg$_{1.63}$Fe$_{0.37}$SiO$_4$, PDF 79-1210) Blue: Clinoenstatite (MgSiO$_3$, PDF 73-1758) Pink: Goethite (Fe$_2$O$_3$$\cdot$H$_2$O)$_3$, PDF 02-0272).
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.

Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.17}$SiO$_4$, PDF 79-1212)

Blue: Fassaite ((Ca$_{0.968}$Mg$_{0.578}$Fe$_{0.220}$Al$_{0.161}$Ti$_{0.059}$)(Si$_{1.728}$Al$_{0.272}$)O$_6$, PDF 83-2083).
NWA 4502_ROM Spot 14

μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite. Light Blue: Forsterite (Mg\textsubscript{1.86}Fe\textsubscript{0.17}SiO\textsubscript{4}, PDF 79-1212) Blue: Clinoenstatite (MgSiO\textsubscript{3}, PDF 73-1758).
μXRD of an inclusion in NWA 4502_ROM, containing olivine (forsterite) and fassaite.  
Light Blue: Olivine (Mg$_{1.83}$Fe$_{0.170}$SiO$_4$, PDF 83-1535)  
Blue: Clinoenstatite (MgSiO$_3$, PDF 75-1404)  
Pink: Goethite (Fe$_2$O$_3$H$_2$O)$_3$, PDF 02-0272).
Micro X-Ray
Diffraction of NWA 7678

1. NWA 7678
NWA 7678
Context Map and Parameters

Context map of NWA 7678 showing spots analyzed.

Table showing parameters used to collect μXRD data on NWA 7678, scan type was omega scan:

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μXRD of inclusion in NWA 7678 slab, containing olivine (forsterite) and fassaite and albite.

Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.14}$SiO$_4$, PDF 77-1025)

Blue: Clinoenstatite (MgSiO$_3$, PDF 73-1758).
μXRD of inclusion in NWA 7678 slab, containing olivine (forsterite) and fassaite and albite.
Light Blue: Forsterite (Mg_{1.86}Fe_{0.14}SiO_{4}, PDF 77-1025)
Blue: Diopside (CaMgSi_2O_6, PDF 03-0860).
μXRD of inclusion in NWA 7678 slab, containing olivine (forsterite) and fassaite and albite.

Light Blue: Forsterite (Mg$_{1.808}$Fe$_{0.192}$SiO$_4$, PDF 83-1536)
Blue: Clinoenstatite (MgSiO$_3$, PDF 73-1758).
μXRD of inclusion in NWA 7678 slab, containing olivine (forsterite) and fassaite and albite.

Light Blue: Forsterite (Mg$_{1.86}$Fe$_{0.14}$SiO$_4$, PDF 77-1025)
Blue: Pyroxene (Mg$_{0.89}$Fe$_{0.08}$Al$_{0.2}$Cr$_{0.04}$Ti$_{0.01}$Ca$_{0.76}$Na$_{0.10}$Si$_{1.92}$O$_{6}$, PDF 85-1827).
μXRD of inclusion in NWA 7678 slab, containing olivine (forsterite) and fassaite and albite.
Light Blue: Forsterite ($\text{Mg}_{1.360}\text{Fe}_{0.640}\text{SiO}_4$, PDF 76-0552)
Blue: Clinoenstatite ($\text{MgSiO}_3$, PDF 73-1758).
Appendix B: Micro X-ray Diffraction and Nuclear Magnetic Resonance Spectroscopy
Characterization of NMR Standards
X-Ray
Diffraction and NMR
Spectroscopy of NMR Standards

1. Spinel (Ceylon)
2. Spinel (Myanmar)
3. Gehlenite (natural)
4. Grossular (natural)
5. Grossular (synthetic)
Spinel DANA #664 (Ceylon)
Context Images and Parameters

Powder samples of Ceylon Spinel of two different colours. Rietveld quality data was collected. There were two distinct compositions of spinel showing up in the XRD pattern. This sample was not used as a standard. (the pale-pink spinel has no photo prior to crushing)

Powder X-ray Diffraction data were collected from 5 to 120° 2θ, with a 0.02 ° step size and a 5 second dwell time (October 2017).
μXRD diffraction pattern of NWA 6991 powder showing forsterite, fassaite, gehlenite, spinel and grossular.

Green: Spinel (Mg$_{0.995}$Mn$_{0.013}$Al$_{1.992}$O$_{4}$, PDF 04-016-2494)

Dark Green: Spinel (Mg$_{0.80}$Al$_{0.18}$) (Al$_{1.86}$Mg$_{0.14}$)O$_{4}$, PDF 01-070-6979

Purple: Quartz (SiO$_{2}$, PDF 05-0490)
μXRD diffraction pattern of NWA 4502 Slice A spot 1 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Green: Spinel (Mg$_{0.751}$Fe$_{0.036}$Mn$_{0.002}$Zn$_{0.003}$Al$_{0.207}$) (Al$_{1.769}$Fe$_{0.001}$Ti$_{0.002}$Mg$_{0.228}$) O$_4$, PDF 01-079-5994

Dark Green: Spinel (Mg$_{0.80}$Al$_{0.18}$) (Al$_{1.86}$Mg$_{0.14}$) O$_4$, PDF 01-070-6979

Purple: Quartz (SiO$_2$, PDF 01-0649)
Spinel Standard (DANA #4502)
Context Map and Parameters

Image of spinel standard prior to crushing.

Table showing parameters used to collect μXRD data on spinel standard, scan type was omega scan

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Spinel Standards (Myanmar), colourless

μXRD diffraction pattern of NWA 6991 powder showing forsterite, fassaite, gehlenite, spinel and grossular.

Green: Spinel (MgAl₂O₄, PDF 05-0672)
$^{27}\text{Al MAS NMR of colourless spinel standard}$
(DANA #4305)

$\n\n= \text{spinning side bands}$
$^{27}$Al 3Q MAS NMR of colourless spinel standard (DANA #4305)
Spinel Standards (Myanmar), pink

μXRD diffraction pattern of NWA 6991 powder showing forsterite, fassaite, gehlenite, spinel and grossular.
Green: Spinel (MgAl₂O₄, PDF 05-0672)
$^{27}$Al MAS NMR of pink spinel standard (DANA #4305)

= spinning side bands
$^{27}$Al 3Q MAS NMR of pink spinel standard
(DANA #4305)
Gehlenite Standard DANA #3461 (natural)
Photo and Parameters

Image of the gehlenite standard prior to crushing, and some hand separation of certain grains (examined here by XRD).

Table showing parameters used to collect μXRD data on NWA 4502 Slice A, scan type was omega scan

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Gehlenite spot 1

μXRD diffraction pattern of NWA 4502 Slice A spot 3 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

- Orange: Monticellite Ca(Mg$_{0.88}$Fe$_{0.12}$) (SiO$_4$), PDF 77-1025
- Pink: Gehlenite (Ca$_2$Al$_4$Si$_7$O$_{20}$, PDF 35-0755)
- Dark Blue: Calcite CaCO$_3$, PDF 01-0982
μXRD diffraction pattern of NWA 4502 Slice A spot 3 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Orange: Monticelte Ca(Mg$_{0.88}$Fe$_{0.12}$) (SiO$_4$), PDF 83-0695
Pink: Gehlenite (Ca$_2$Al$_4$Si$_7$O$_{22}$, PDF 02-0982)
Dark Blue: Calcite CaCO$_3$, PDF 01-0623)
Gehlenite spot 3

μXRD diffraction pattern of NWA 4502 Slice A spot 3 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Pink: Gehlenite (Ca$_2$Al$_2$SiO$_7$, PDF 35-0755)
Dark Blue: Calcite (CaCO$_3$, PDF 01-0623)
Pink: Grossular (Ca$_3$Al$_2$(SiO$_4$)$_2$OH$_4$, PDF 42-0570)
Gehlenite spot 4

μXRD diffraction pattern of NWA 4502 Slice A spot 3 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Pink: Gehlenite (Ca$_2$Al$_2$SiO$_7$, PDF 35-0755)
Dark Blue: Calcite (CaCO$_3$, PDF 01-0837)
Pink: Grossular Ca$_3$Al$_2$(SiO$_4$)$_2$(OH)$_4$, PDF 31-0250)
\(^{27}\)Al MAS NMR of natural gehlenite (DANA #3461)

\[ \text{ppm} \]

\[\begin{align*}
0.00 & \quad 7.27 \\
14.53 & \quad 21.80 \\
29.06 & \quad -
\end{align*}\]

= spinning side bands
\(^{27}\)Al 3Q MAS NMR of natural gehlenite (DANA #3461)
Grossular DANA #3209 (natural)
Photo and Parameters

Image of the grossular natural standard prior to crushing.

Table showing parameters used to collect μXRD data on Grossular DANA #3209, scan type was coupled scan

<table>
<thead>
<tr>
<th>Date Collected</th>
<th>Theta1 $\theta_1$</th>
<th>Theta2 $\theta_2$</th>
<th>Width $\omega$</th>
<th>Time (min)</th>
<th>Oscillation</th>
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<tr>
<td>March 2018 Coupled</td>
<td>14.5</td>
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<td>10</td>
<td>60</td>
<td>XY, 3 mm</td>
</tr>
<tr>
<td></td>
<td>2 Frames</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>
Grossular DANA #3209

μXRD diffraction pattern of NWA 4502 Slice A spot 2 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Pink: Grossular \((\text{Ca}_{2.87}\text{Fe}_{0.13})(\text{Al}_{1.61}\text{Ti}_{0.07}\text{Fe}_{0.28})\text{Si}_3\text{O}_{12}\), PDF 75-1681)
$^{27}$Al MAS NMR of natural grossular (DANA #3209)

= spinning side bands
$^{27}\text{Al}$ 3Q MAS NMR of natural grossular (DANA #3209)
Grossular (synthetic)
Context and Parameters

Image of synthetic grossular powder (RM 003A).

Table showing parameters used to collect μXRD data on synthetic grossular powder, scan type was omega scan

<table>
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<th>Date Collected</th>
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<th>Theta2 ($\theta_2$)</th>
<th>Width ($\omega$)</th>
<th>Time (min)</th>
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</table>
Grossular (synthetic) spot 1

μXRD diffraction pattern of NWA 4502 Slice A spot 3 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Pink: Grossular ($Al_2Ca_3(SiO_4)_3$, PDF 74-1088)
Grossular (synthetic) spot 2

\[ \mu XRD \text{ diffraction pattern of NWA 4502 Slice A spot 3 showing forsterite and diopside.} \]
\[ \text{This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.} \]
\[ \text{Pink: Grossular (Ca}_{3}\text{Al}_{2}(\text{SiO}_{4})_{3}, \text{ PDF 88-2208)} \]
Grossular (synthetic) spot 3

μXRD diffraction pattern of NWA 4502 Slice A spot 3 showing forsterite and diopside. This spot was a large and irregular inclusion seen in CT scans, but is almost indistinguishable from the matrix visibly.

Pink: Grossular (Ca$_3$Al$_2$Si$_3$O$_{12}$, PDF 83-2207)
$^{27}$Al MAS NMR of Synthetic Grossular (RM 003A)

= spinning side bands
$^{27}$Al 3Q MAS NMR of Synthetic Grossular (RM 003A)
Appendix C: Nuclear Magnetic Resonance Spectroscopy of Meteorite Samples
$^{27}$Al MAS NMR Spectroscopy
of Meteorite Samples

1. NWA 6603
2. NWA 6991 (white)
3. NWA 2364
4. Allende 3529
5. Allende TS62b
NWA 6603 1-92

CAI in NWA 6603 after extraction of some material for NMR.
$^{27}\text{Al MAS NMR NWA 6603}$

$^{27}\text{Al 3Q MAS NMR NWA 6603}$
Table of peak fitting parameters for one-dimensional $^{27}$Al MAS NMR fit of NWA 6603

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Position</th>
<th>$\delta_{m}$ (Hz)</th>
<th>$\delta_{Q}$ (kHz)</th>
<th>$\eta_{Q}$</th>
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<tbody>
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<td>spinel tetrahedral</td>
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<td>76.35</td>
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<td>4978.51</td>
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<td>Q mas 1/2</td>
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<td>Q mas 1/2</td>
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<td>grossular octahedral</td>
<td>Q mas 1/2</td>
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<td>650.94</td>
<td>3565.68</td>
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<tr>
<td>fassaite octahedral</td>
<td>Q mas 1/2</td>
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<td>2.9</td>
<td>4613.47</td>
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NWA 6991
$^{27}\text{Al} \text{ MAS NMR NWA 6991 (white), fitted}$

Table of peak fitting parameters for DMfit $^{27}\text{Al} \text{ MAS NMR fit of NWA 6991 (white fraction)}$

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<th>Position (ppm)</th>
<th>Em (Hz)</th>
<th>CQ (KHz)</th>
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$^{27}\text{Al MAS NMR NWA 6991 (black)}$

![Diagram showing $^{27}\text{Al MAS NMR NWA 6991 (black)}$ with spinning side bands marked by triangular symbols at 0 and 181.65 ppm.](image)
$^{27}$Al MAS NMR NWA 6991 (black), fitted

![Graph showing $^{27}$Al MAS NMR spectra with peaks labeled for spinel, gehlenite, fassaite, and grossular.]

Table of peak fitting parameters for one-dimensional $^{27}$Al MAS NMR fit of NWA 6991 (black fraction)

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<th>Peak</th>
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<th>Position (ppm)</th>
<th>Em (Hz)</th>
<th>CQ (KHz)</th>
<th>$\eta$</th>
<th>$Q$</th>
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NWA 2364
$^{27}$Al MAS NMR NWA 2364

= spinning side bands

$^{27}$Al 3Q MAS NMR NWA 2364
Table of peak fitting parameters for one-dimensional $^{27}$Al MAS NMR fit of NWA 2364

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<tr>
<th>Peak</th>
<th>Type</th>
<th>Amp</th>
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<th>$CQ$ (KHz)</th>
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Allende 3529
$^{27}$Al MAS NMR Allende 3529

$^{27}$Al 3Q MAS NMR Allende 3529

= spinning side bands
Allende TS62b
$^{27}$Al 3Q MAS NMR Allende TS62b
Appendix D: Temperature Calculations
## Summary of Calculated Temperatures

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<th>Minimum (K)</th>
<th>Maximum (K)</th>
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# Temperature Calculations based on Calibration Curves in the Literature

## NWA 6603

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<th>x  *</th>
<th>B  **</th>
<th>alpha</th>
<th>beta</th>
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<th>x^2/(1-x)(2-x)</th>
<th>ln(prev)</th>
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<th>Andreozzi (oxygen parameter)</th>
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**Equations:**
- O'Neill and Navrotsky 1983 (K)
  \[ T(K) = (\alpha + 2\text{Betax})/[-R*(\ln(x^2/(1-x)(2-x)))] \]
- Princivalle (K)
  \[ T(K) = (B * 6440) + 273.15 \]
- Andreozzi (oxygen parameter)
  \[ u = (21.396 - x)/80.714 \]

* \( x = 2/(1+(\text{sp oct}/\text{sp tet})) \)

** \( B = \text{sp tet}/(\text{sp tet} - \text{sp oct}) \)
# Temperature Calculations based on Calibration Curves in the Literature - Higher Baseline for Error Calculation

**NWA 6603**

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**Equations shown below**

- O'Neill and Navrotsky 1983 (K)
  \[ T(K) = \alpha + 2B\text{Betax}/[-R\times \ln(\frac{x^2}{(1-x)(2-x)})] \]
  \[ x = \frac{2}{1+(\text{sp oct}/\text{sp tet})} \]
- Princivalle (K)
  \[ T(K) = (B \times 6440) + 273.15 \]
- Andreozzi (oxygen parameter)
  \[ u = \frac{21.396 - x}{80.714} \]
## Temperature Calculations based on Calibration Curves in the Literature - Lower Baseline for Error Calculation

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### Equations:

- **O'Neill and Navrotsky 1983 (K)**
  \[
  T(K) = \frac{\alpha + 2\beta x}{-R \cdot \ln(x^2/(1-x)(2-x))}
  \]

- **Princivalle (K)**
  \[
  T(K) = (B \cdot 6440) + 273.15
  \]

- **Andreozzi (oxygen parameter)**
  \[
  u = \frac{21.396 - x}{80.714}
  \]

\* \(x = 2/(1+(sp\ oct/sp\ tet))\)

\**B = sp\ tet/(sp\ tet + sp\ oct)\)
## Temperature Calculations based on Calibration Curves in the Literature

NWA 6991 (white fraction)

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**Equations:**

O'Neill and Navrotsky 1983 (K)  
T(K) = (alpha + 2Betax) / (-R * (ln(x^2/(1-x)(2-x))))  

Princivalle (K)  
T(K) = (B * 6440) + 273.15  

Andreozzi (oxygen parameter)  
u = (21.396 - x) / 80.714  

* x = 2 / (1 + (sp oct / sp tet))  
** B = sp tet / (sp tet + sp oct)
Temperature Calculations based on Calibration Curves in the Literature - Higher Baseline for Error Calculation
NWA 6991 (white fraction)

Baseline = +1  
SDEV = 3.4923

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**Equations shown below**

**Equations:**

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<td>O'Neill and Navrotsky 1983 (K)</td>
<td>( T(K) = \frac{\alpha + 2\beta x}{-R \ln(x^2/(1-x)(2-x))} )</td>
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<td>( T(K) = (B \times 6440) + 273.15 )</td>
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<td>( u = (21.396 - x) / 80.714 )</td>
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\( x = 2/(1+(sp\ octave/sp\ tet)) \)

\( B = sp\ tet/(sp\ tet + sp\ octave) \)
Temperature Calculations based on Calibration Curves in the Literature - Lower Baseline for Error Calculation

**NWA 6991 (white fraction)**

| Paper                  | Base Calc | High Error | Low Error | Base Calc | High Error | Low Error | Base Calc | High Error | Low Error | Base Calc | High Error | Low Error | Base Calc | High Error | Low Error | Base Calc | High Error | Low Error |
|------------------------|-----------|------------|-----------|-----------|------------|-----------|-----------|-----------|------------|-----------|-----------|------------|-----------|-----------|------------|-----------|-----------|------------|-----------|
| Peterson               | 5791.45   | 406477.6   | 0.008314  | 0.028095  | 31         | -10       | -0.56191  | 0.000412  | -7.79479   | 469.68069 | 5791.45   | 406477.6   | 0.008314  | 0.028095  | 32         | -7        | -0.39334  | 0.000412  | -7.79479   | 487.71257 |
| Maekawa                | 5791.45   | 406477.6   | 0.008314  | 0.028095  | 35         | -32       | -1.79811  | 0.000412  | -7.79479   | 512.328   | 5791.45   | 406477.6   | 0.008314  | 0.028095  | 40         | -27       | -1.51716  | 0.000412  | -7.79479   | 593.81677 |
| Millard                | 5791.45   | 406477.6   | 0.008314  | 0.028095  | 30         | -37       | -2.07907  | 0.000412  | -7.79479   | 430.83923 | 5791.45   | 406477.6   | 0.008314  | 0.028095  | 20         | -13       | -0.73048  | 0.000412  | -7.79479   | 451.64888 |
| Redfern                | 5791.45   | 406477.6   | 0.008314  | 0.028095  | 32.8       | 4.7       | 0.264098  | 0.000412  | -7.79479   | 510.20179 | 5791.45   | 406477.6   | 0.008314  | 0.028095  | 33.7       | 6.7       | 0.37648   | 0.000412  | -7.79479   | 525.82354 |
| Princivalle            | 5791.45   | 406477.6   | 0.008314  | 0.028095  | 31.9       | 2.7       | 0.151716  | 0.000412  | -7.79479   | 494.58004 | 5791.45   | 406477.6   | 0.008314  | 0.028095  | 32.8       | 4.7       | 0.264098  | 0.000412  | -7.79479   | 494.58004 |

Equations:

- **O'Neill and Navrotsky 1983 (K)**
  \[ T(K) = \frac{\alpha + 2B \text{tax}}{-R \left( \ln(x^2/(1-x)(2-x)) \right) \ln(\text{prev})} \]

- **Princivalle (K)**
  \[ T(K) = B \cdot 6440 + 273.15 \]

- **Andreozzi (oxygen parameter)**
  \[ u = \frac{21.396 - x}{80.714} \]

* \( x = 2/(1+\text{sp oct/sp tet}) \)
** \( B = \text{sp tet/sp tet+sp oct} \)
Temperature Calculations based on Calibration Curves in the Literature

**NWA 6991 (black fraction)**

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Equations:
- O'Neill and Navrotsky 1983 (K) \(T(K)=(\alpha + 2\beta x)/(R \* (ln(\frac{x^2}{1-x}(2-x))))\)
- Princivalle (K) \(T(K)=(B \* 6440) + 273.15\)
- Andreozzi (oxygen parameter) \(u=(21.396 - x)/80.714\)

* \(x=2/(1+(sp \ oct/sp \ tet))\)

** \(B=sp \ tet/(sp \ tet+sp \ oct)\)
Temperature Calculations based on Calibration Curves in the Literature - Higher Baseline for Error Calculation

NWA 6991 (black fraction)

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Equations:

- **O'Neill and Navrotsky 1983 (K)**
  
  \[ T(K) = \frac{\alpha + 2\beta x}{-R \ln(x^2/(1-x)(2-x))} \]

- **Princivalle (K)**
  
  \[ T(K) = B \times 6440 + 273.15 \]

- **Anderozi (oxygen parameter)**
  
  \[ u = \frac{21.396 - x}{80.714} \]
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Equations:

- **Equations shown below**

- **O'Neill and Navrotsky 1983 (K)**
  \[ T(K) = \frac{(\alpha + 2Bx)}{(-Rx^2/(1-x)(2-x))] \]
  \[ x = 2/(1+(sp\ oct/sp\ tet)) \]

- **Princivalle (K)**
  \[ T(K) = (B * 6440) + 273.15 \]

- **Andreozzi (oxygen parameter)**
  \[ u = (21.396 - x)/80.714 \]
## Temperature Calculations based on Calibration Curves in the Literature

### NWA 2364

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### Equations:

- **O'Neill and Navrotsky 1983 (K)**
  \[ T(K) = (\alpha + 2\beta x)/(-R \times \ln(x^2/(1-x)(2-x))) \]

- **Princivalle (K)**
  \[ T(K) = (B \times 6440) + 273.15 \]

- **Andreozzi (oxygen parameter)**
  \[ u = (21.396 - x)/80.714 \]

### Values:

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**Equations shown below**

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**Appendix D**

529
### Temperature Calculations based on Calibration Curves in the Literature - Higher Baseline for Error Calculation

NWA 2364

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**Equations:**

- **O'Neill and Navrotsky 1983 (K)**
  \[ T(K) = \frac{(\alpha + 2\beta x)}{-R \cdot \ln(x^2/(1-x)(2-x))} \]

- **Princivalle (K)**
  \[ T(K) = (B \cdot 6440) + 273.15 \]

- **Andreozzi (oxygen parameter)**
  \[ u = \frac{21.396 - x}{80.714} \]

---

**Note:**
- x = \frac{2}{1 + (sp oct/sp tet)}
- B = \frac{sp tet}{sp tet + sp oct}
### Temperature Calculations based on Calibration Curves in the Literature - Lower Baseline for Error Calculation

#### NWA 2364

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  \[ u = \frac{21.396 - x}{80.714} \]
Curriculum Vitae

Victoria Houde

The University of Western Ontario

Degrees

MSc Geology with Specialization in Planetary Science
2016/09 – 2018/08 University of Western Ontario
Supervisor: Dr. Roberta Flemming

BSc Honours Specialization Geology, Minor Biology
2012/09 – 2016/05 University of Western Ontario
Supervisors: Dr. Roberta Flemming, Dr. Elizabeth Webb

Scholarships and Awards

Mineralogical Association of Canada Student Travel Grant
Awarded by: Mineralogical Association of Canada  Value: $800  Date: 2018
Description: Funding to support travel for presentation of research at the 49th Lunar and Planetary Science Conference in Texas.

Queen Elizabeth II Graduate Scholarship in Science and Technology
Awarded by: Province of Ontario  Value: $15,000  Date Held: 2017/09 – 2018/08
Description: Merit-based scholarship (competitive) for domestic graduate students in science and technology

Queen Elizabeth II Graduate Scholarship in Science and Technology
Awarded by: Province of Ontario  Value: $15,000  Date Held: 2016/09 – 2017/08
Description: Merit-based scholarship (competitive) for domestic graduate students in science and technology

The University of Western Ontario Gold Medal, Honors Specialization in Geology
Awarded by: University of Western Ontario  Date Awarded: 2016/06
Description: Awarded to undergraduate with the highest graduating average in their module, who must also be in the top 10% of all graduating students in the department

Dean's Honor List

Awarded by: University of Western Ontario  Date Held: 2013/09 - 2016/04

Description: Higher than 80% cumulative average

Mineralogical Association of Canada University of Western Ontario Undergraduate Student Award

Awarded by: Mineralogical Association of Canada  Date Held: 2013/09 - 2014/05

Description: Student who has finished second year and demonstrated excellence in mineralogy, crystallography, geochemistry, petrology, or mineral deposits

Western Scholarship of Excellence

Awarded by: University of Western Ontario  Value: $2,000  Date: 2012/09 - 2013/04

Description: 90.0 - 94.9% average in high school, entering undergraduate studies at the University of Western Ontario

Employment

Graduate Teaching Assistant for Mineral Systems, Crystallography, and Optics

(Earth Sciences 2206)
2017/09 - 2017/12
Earth Sciences, University of Western Ontario (Part-time)

Graduate Teaching Assistant for Structure and Chemistry of Minerals and Materials

(Earth Sciences 3310)
2017/01 - 2017/04
Earth Sciences, University of Western Ontario (Part-time)

Undergraduate Student Researcher (NSERC USRA)

2016/05 - 2016/08
Earth Sciences, University of Western Ontario (Full-time)
MicroXRD Lab Assistant, phase ID with XRD, and mineral separation

Undergraduate Student Researcher (NSERC USRA)
2015/05 - 2015/08
Earth Sciences, University of Western Ontario (Full-time)
MicroXRD Lab Assistant, quantifying strain in meteorites

**Undergraduate Student Researcher (ASTRO USRA)**
2014/05 - 2014/08
Earth Sciences, University of Western Ontario (Full-time)
Using microXRD to determine type of strain in minerals (earth and planetary materials)

**Publications**

**Conference Publications**

*Conference Date: 03/2018*  
*Type of Publication: Abstract for Oral Presentation*

*Conference Date: 03/2018*  
*Type of Publication: Abstract*

*Conference Date: 2018/02*  
*Type of Publication: Abstract for Oral Presentation*

*Type of Publication: Poster and Abstract*
NWA 8171 by In Situ Micro X-ray Diffraction and Micro Raman Spectroscopy. 48th Lunar and Planetary Science Conference  Type of Publication: Poster and Abstract