

**Assessing the Atomic Structure and In Situ Detectability of
Amorphous Sulfates on the Martian Surface**

A Dissertation Presented

by

Reed Joseph Hopkins

to

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in Partial Fulfillment of the

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Abstract of the Dissertation

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Across the stratigraphy of Gale crater, Mars, the Curiosity rover has persistently detected high-abundances of amorphous materials, or materials with no long-range structural order. The composition of this amorphous component cannot be directly measured using the instruments onboard Curiosity, and is instead estimated from mass-balance calculations using data from several other instruments. These resulting estimations include significant amounts of amorphous sulfate-bearing material. In many locations, but particularly within the Layered Sulfate-Bearing Unit above the clay-sulfate transition zone, sulfates are abundant both as an amorphous material and crystalline mineral. Sulfate deposits on Mars can be indicative of a colder and dry ancient environment, and the study of these sulfates can give insight to environmental change on Mars. However, it is not well understood how sulfate crystallinity factors into these interpretations. Before implications of these amorphous sulfates can be considered, their fundamental structural characteristics must be evaluated. There are also significant assumptions made in the calculations that estimate these amorphous compositions, and it is critical to have confidence in the basic estimated abundances of these materials.

The purpose of my dissertation is to fundamentally characterize the common amorphous sulfate compositions found on Mars, including a relevant anhydrous ferric sulfate, and address the effects of amorphous coatings on the detectability of materials with the CheMin instrument onboard Curiosity. In this dissertation, I present the results of three studies: (1) a Raman and XRD analysis of amorphous ferric sulfate coatings on crystalline Ca-sulfate grains, to assess the effects of amorphous coatings and XRD technique on the detectability of Ca-sulfate, (2) a characterization of the short-range order of amorphous ferric sulfate and amorphous magnesium sulfate using pair distribution function analysis on total scattering data acquired at a synchrotron beamline, and (3) a low-temperature refinement of the crystal structure of mikasaite, an anhydrous ferric sulfate with relevance for the Martian surface, including terrestrial and laboratory analogs.

Dedication Page

For my friends and family.

Especially my parents,
whose support has carried me through many ups and downs.



Saga of the Swamp Thing #24, Page 23

“What happens in your head also happens.”

-Martian, *Absolute Martian Manhunter* (2025)

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List of Abbreviations

AFS: Amorphous ferric sulfate
AMS: Amorphous magnesium sulfate
APXS: Alpha Particle X-ray Spectrometer
BB: Bragg-Brentano
BNL: Brookhaven National Laboratory
CheMin: Chemistry & Mineralogy instrument
CIF: Crystallographic Information File
DS: Debye-Scherrer
EDS: Energy-Dispersive X-ray Spectroscopy
EGA: Evolved Gas Analysis
Gyp: Gypsum
MSL: Mars Science Laboratory
NSLS-II: National Synchrotron Light Source II
PDF: Pair Distribution Function
RH: Relative humidity
SAM: Sample Analysis at Mars instrument
SEM: Scanning Electron Microscope/Microscopy
XPD: X-ray Powder Diffraction
XRD: X-ray Diffraction/Diffractometer

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Chapter 1

Introduction & Overview

1.1 Background

1.1.1 Curiosity in Gale Crater

The Curiosity rover has been systematically exploring the stratigraphy of Mt. Sharp (Aeolis Mons) on Mars since landing in 2012. Mt. Sharp is the central peak within Gale crater, a 155 km wide impact crater hosting strata indicative of past fluvial, lacustrine, and aeolian environments (e.g., Anderson & Bell 2010; Grotzinger et al., 2012; Milliken et al., 2010). The mission of Curiosity is to explore the habitability of Mars through geological and geochemical characterization of the stratigraphic rock record, and to help interpret modern and ancient environments of Gale crater. Landing at the base of Mt. Sharp and gradually exploring up the stratigraphy, Curiosity has taken direct measurements and observations of Gale crater's mineralogy and rock record using a diverse suite of instruments. Most relevant to the studies of this dissertation, the Chemistry and Mineralogy (CheMin) instrument utilizes X-ray powder diffraction to characterize the crystallinity and mineralogy of a sediment or powdered rock (Blake et al., 2012), the Alpha Particle X-ray Spectrometer (APXS) provides bulk elemental analysis of the rocks and sediments using a combination of X-ray fluorescence and X-ray emission (Campbell et al., 2012), and the Sample Analysis on Mars (SAM) instrument provides complimentary measurements of volatiles and light isotopes using evolved gas analysis (EGA) (Mahaffy et al., 2012). Together, these instruments were meant to provide a complete and comprehensive characterization of the mineralogy of the rocks and sediments in Gale crater. However, about one

year after Curiosity landed on Mars, Bish et al. (2013) would debut what has become a common thread across Gale crater: the widespread and highly-abundant amorphous component.

1.1.2 The Amorphous Component of Gale Crater

Amorphous materials are those that show no long-range crystal structure. The ‘amorphous component’ of Gale crater is the fraction of both the sediment and rocks that appear as ‘X-ray amorphous’, and includes truly amorphous material, nanocrystalline materials, and any material present below the CheMin detection limit of ~3 wt% (Blake et al., 2012). This amorphous component is pervasive, and Curiosity has consistently detected high abundances (15-90 wt%) of amorphous material in the sediment and sedimentary rocks of Gale crater (Achilles et al., 2017; Bish et al. 2013; Blake et al. 2013; Dehouck et al. 2014; Ehlmann et al., 2017; Rampe et al., 2020a; Rampe et al., 2020b; Treiman et al., 2016; Vaniman et al. 2014; Yen et al. 2017). The composition of the amorphous component cannot be directly measured with the instruments onboard Curiosity, because the available instruments can either only characterize crystalline material (CheMin), or cannot distinguish between crystalline or amorphous materials in their bulk measurements (APXS, SAM). Thus, data from multiple instruments must be utilized to estimate the amorphous compositions. Primarily, this has been done using data from CheMin and APXS. CheMin can identify and determine the abundances of crystalline materials, as well as the sample’s amorphous percentage (Blake et al., 2012; Morrison et al., 2018a), and APXS measures bulk elemental abundances (Campbell et al., 2012; Gellert et al., 2015). By subtracting the abundances of materials attributed to the crystalline component from the bulk elemental abundance, the composition of the overall amorphous component can be estimated as the difference. The compositions from this mass-balance calculation are variable, but typically include significant amounts of SO₃, FeO, and SiO₂ (e.g., Achilles et al. 2017; Achilles et al. 2020; McAdam et al.

2020; Morris et al. 2016; Morrison et al. 2018b; Rampe et al. 2018; Rampe et al. 2020b; Smith et al. 2021; Smith et al. 2022). These mass-balance calculations have shown that the calculated amorphous component is inconsistent with any single amorphous material, which suggests that the amorphous component is a complex mixture of multiple phases. Most of the S-bearing amorphous component has been interpreted to be variable proportions of Fe-, Mg-, and Ca- sulfates (Chipera et al., 2023; Smith et al., 2022).

1.1.3 Amorphous Sulfates on Mars

This dissertation focuses specifically on the sulfate-bearing portion of the amorphous component of Gale crater. Amorphous sulfate phases are not common on Earth. The closest natural terrestrial example of an ‘X-ray amorphous’ sulfate is the nanocrystalline iron oxyhydroxysulfate schwertmannite, which has been found in environments such as acid mine drainage systems (Bigham et al., 1996; Fernandez-Martinez et al., 2010). Due in part to the lack of natural terrestrial analogs, the formation processes, stability, structural, and spectral characteristics of amorphous sulfate phases are not well understood, especially when compared to crystalline sulfate minerals. Secondary mineral assemblages that contain sulfate are commonly used to help interpret depositional and diagenetic processes, as well as ancient habitability (e.g., Magnuson et al., 2023; Moreras-Marti et al., 2022; Paul & Mormile 2020). Polyhydrated Mg-sulfates such as epsomite, hexahydrate, and starkeyite transform to an amorphous Mg-sulfate under extremely dry environments (Chipera et al., 2023; Vaniman et al., 2004; Vaniman & Chipera 2006; Wang et al., 2006; Wang et al., 2011). Amorphous Fe^{3+} -sulfates, along with minerals such as jarosite, can be used to interpret the acidity and composition of past lakes, rivers, or weathering-derived fluids, as pH strongly affects Fe mobility in a fluid (e.g., Rapin et al., 2019; Tosca et al., 2005). It is important to consider both amorphous and crystalline sulfates together as a system, as it is not well-studied

how the degree of crystallinity of these materials factors into the environmental interpretations of their diagenesis. Both amorphous sulfate phases and crystalline sulfate minerals are seemingly ubiquitous on Mars, yet there is a clear discrepancy of studies of these two sides of sulfate on Mars, with cleaner datasets and terrestrial comparisons making it much easier to study the crystalline fraction. Amorphous sulfates or S-bearing phases are also not unique to Gale crater. For example, spectra of the Dourbes target in Jezero crater support the presence of amorphous Mg-sulfate phases (Siljeström et al., 2024), and in Gusev crater, Mössbauer spectra from the Spirit rover shows nanophase ferric oxide in association with sulfur and chloride (Morris et al., 2006).

Crystalline sulfates are prevalent in the sedimentary rocks of Gale crater, and abundances of Fe-, Mg-, and Ca-, sulfates have been found in a wide range of assemblages (e.g., Vaniman et al., 2024, and references therein). Yet, it is not uncommon for many sampling locations to have substantially more amorphous sulfate than crystalline sulfate. From the base of Mt. Sharp up to just below the clay-sulfate transition zone, between ~20-90 wt% of the total SO₃ in Gale crater drill holes samples is in the amorphous component (Chipera et al., 2023; Smith et al., 2022). Amorphous Mg-sulfate in particular has become even more abundant as Curiosity explores past the clay-sulfate transition region, and up through the Layered Sulfate Unit (Chipera et al., 2023; Clark et al., 2024; Meyer et al., 2024).

Many studies since the landing of Curiosity have suggested several methods by which amorphous sulfates may form on Mars. These include induced amorphization by electrostatic discharge from Martian dust activities (Wang et al., 2020), brine-induced alteration of clays (Bristow et al., 2021; Thorpe et al., 2022), or products of brine desiccation/dehydration or cryoprecipitation (e.g., Chipera & Vaniman, 2007; Hopkins et al., 2023; Sklute et al., 2018; Smith et al., 2021; Vaniman et al., 2004; Vaniman & Chipera, 2006). Realistically, it is possible that many

of these formation mechanisms occurred throughout the history of Gale crater and contributed to the high abundance of amorphous sulfate measured in Gale crater today. It would be beneficial to any interpretation regarding these amorphous sulfates if we had a more complete understanding of their fundamental characteristics.

1.2 Dissertation Goals

The primary goal of this dissertation is to address the knowledge deficit surrounding amorphous sulfates by determining their atomic structures at Martian temperatures using laboratory analog experiments. To achieve this, I utilized pair distribution function analysis on total scattering data of amorphous Mg-sulfate and Fe^{3+} -sulfate at Mars-relevant low-temperatures. This allowed me to determine the short-range order and atomic distances within amorphous Mg-sulfate and Fe^{3+} -sulfate. Additionally, I determined the low temperature crystal structure and thermal contraction behavior of the anhydrous ferric sulfate mineral Mikasaite, which is often used in Mars laboratory analog experiments. A secondary goal is to determine how amorphous sulfates may affect the X-ray diffraction measurements of a mixed crystalline-amorphous sample, and assess any implications for the mass-balance calculations used to estimate the amorphous component composition within Gale crater.

1.3 Methods

1.3.1 Synthesis of Amorphous Sulfates

The experiments throughout this dissertation required that I follow a reliable procedure to synthesize amorphous magnesium sulfate (AMS) and amorphous ferric sulfate (AFS). I synthesized AMS based on a procedure by Vaniman et al. (2004), which showed that polyhydrated Mg-sulfates, such as epsomite and hexahydrite, will dehydrate to an amorphous $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ in

a rapidly desiccating low relative humidity (RH) atmosphere, such as a vacuum. This loss of crystal structure from dehydration occurs on timescales of about a day at ~1 torr vacuum (Vaniman et al., 2004). For the AMS used in this dissertation, I dehydrated epsomite under vacuum (~1-5 torr) for ~3 days to ensure amorphization.

The synthesis of AFS begins with the synthesis of mikasaite, i.e. anhydrous ferric sulfate. Following similar procedures to those in Xu et al. (2009), Sklute et al. (2015), and Hopkins et al. (2023), I formed mikasaite by heating hydrated ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$) at 300 °C for 24 hours, with an initial ramp up rate of 60°C every 15 minutes. To then synthesize AFS, I first allowed the mikasaite to deliquesce fully into a saturated ferric sulfate solution inside air-tight containers buffered to 92% RH. When the solution reached saturation after about 4 days under 92% RH, the solution was transferred into another air-tight container buffered to 11% RH using lithium chloride. In this low-RH atmosphere, the solution desiccates and forms an AFS ‘chip’.

1.3.2 Raman Spectroscopy

Raman spectroscopy is a non-destructive analytical technique that identifies minerals by measuring scattered light off molecular bonds when a laser is directed at a sample. This technique is based on the inelastic scattering of monochromatic light, where photons interact with the vibrational modes of molecular bonds within a material’s structure. Incident photons from a laser with a specific wavelength excite a molecule to a virtual energy state. Most photons scatter elastically at the same frequency as the incident light, or are absorbed and re-emitted at the same wavelength (i.e., Rayleigh scattering). However, some photons are scattered inelastically, and are re-emitted at shifted wavelength dependent on the molecular vibrations of the sample. These shifts in frequency (or wavelength) are known as Stokes and anti-Stokes shifts, or Raman shifts (Raman, 1928; Raman & Krishnan, 1928; Sharma & Egan, 2019). These Raman shifts are unique for

specific molecular vibrations; thus, a Raman spectrum can be used for molecular species and mineral identification. I utilize Raman spectroscopy in Chapter 2 of this dissertation for the analysis of mixed crystalline-amorphous samples.

The characterization of amorphous materials with Raman spectroscopy can be complicated due to their elusive behavior in spectral mixtures (e.g., Sklute et al. 2015; Sklute et al. 2018; Sheppard et al. 2022). It has been shown that in simple mixtures, amorphous materials can be masked by crystalline materials (e.g., Sklute et al. 2015; Sklute et al. 2018; Sheppard et al. 2022), and thus significantly underestimated in spectral data. Masking of amorphous phases in Raman spectra can be caused by sharp crystalline peaks overlaying broader features, although non-linear mixing is seen in Raman data as well due to differences in Raman cross-sections (e.g., Breitenfeld et al., 2025; Haskin et al. 1997).

1.3.3 Scanning Electron Microscopy

In this dissertation, I use scanning electron microscopy (SEM) to characterize the micro-scale textures of amorphous sulfates, and to assess the textural properties of amorphous coatings in crystalline grains. SEM works by directing a beam of electrons across the surface of a sample, and detecting the signals produced by the interaction of those electrons with the material. I also utilize energy-dispersive X-ray spectroscopy (EDS) for phase identification within crystalline-amorphous mixtures.

1.3.4 X-ray Diffraction

X-ray diffraction (XRD) is an analytical technique in which a beam of X-rays is directed at a material, and the structure of this material scatters the X-rays at specific angles governed by Bragg's Law: $n\lambda = 2d\sin\theta$, where λ is the X-ray wavelength, d is the interplanar spacing, and θ is the angle of incidence. The resulting diffraction pattern is a fingerprint of the crystal structure, with

sharp diffraction peaks corresponding to specific atomic planes. Amorphous materials cause very broad features in XRD, which are often referred to in the literature as amorphous ‘curves’ or ‘humps’. The lack of long-range structural order of amorphous materials results in a wide distribution of d-spacings, rather than the regular discrete interplanar d-spacings in crystalline materials. The less crystalline a material is, the more irregular its d-spacings become, causing wider peak widths.

I utilized three different XRD techniques throughout this dissertation, as different techniques provide various advantages and disadvantages. First, I utilized Bragg-Brentano (BB) geometry XRD. In BB geometry, the X-ray source and detector are positioned so that as the sample rotates by angle θ , the detector rotates by 2θ , collecting the diffraction data of a flat powdered sample over a range of 2θ . BB geometry XRD works extremely well for flat bulk powder samples, and typically results in excellent signal to noise and sharp angular resolution. The studies within this dissertation utilized two BB instruments, both using $\text{CuK}\alpha$ (1.5428 Å) radiation. Some disadvantages of BB geometry are its sensitivity to sample surface properties, such as roughness, displacement, or preferred orientation. In contrast to BB geometry, I also utilized Debye-Scherrer (DS) XRD. In a DS geometry XRD, the X-ray beam is passed through a powdered sample with (ideally) random orientations between two Kapton windows. The diffracted X-rays are collected on a detector plate, forming concentric rings with diameters dependent on the diffraction angle. DS XRD has the advantages of requiring less sample, and removes the sensitivity of sample surface roughness and preferred orientation that are a problem with the BB style. However, the X-ray beam passing through a thickness of sample, including sample-holder windows, can result in increased X-ray absorption and worse signal-to-noise. In the studies of this dissertation, DS geometry was used for two XRD setups are very different scales. First, a benchtop DS XRD instrument that was

used as a laboratory analog to the CheMin XRD and $\text{CoK}\alpha$ (1.7903 Å) radiation. Second, the X-ray Powder Diffraction (XPD) beamline of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory, with radiation wavelength of 0.181 Å.

The advantages of disadvantages of BB and DS techniques for the analysis of mixed crystalline-amorphous samples are discussed in Chapter 2 of this dissertation, and the results of the XPD beamline analysis of amorphous sulfates are the focus of Chapter 3.

1.4 Overview of Chapters

1.4.1 Chapter 2

In Chapter 2 of this dissertation, I examine the possibility of underrepresented crystalline phases in XRD data using mixtures of AFS and crystalline Ca-sulfate. Two compositionally equivalent mixtures were made with different morphologies: first, a simple mixture of AFS and Ca-sulfate grains and second, Ca-sulfate grains with AFS coatings. I characterized each mixture with Raman spectroscopy, and two X-ray diffractometers: a Bragg-Brentano instrument with $\text{CuK}\alpha$ radiation and a Debye-Scherrer instrument with $\text{CoK}\alpha$ radiation. Raman peaks from Ca-sulfate dominate both mixtures, but are dampened when AFS coats the Ca-sulfate grains. In XRD data, I found that AFS coatings cause an overestimation of the amorphous percentage, with a difference between the known and measured amorphous abundances of 29-34 wt%, compared to 2-2.8 wt% for the uncoated mixtures. The effects of the coatings are slightly amplified with the Debye-Scherrer XRD, primarily due to the increased scattering and absorption of the $\text{CoK}\alpha$ radiation. I discuss the implications for interpreting XRD data of mixed amorphous-crystalline samples on Mars, as any Fe-rich amorphous coating may cause an overestimation of the amorphous abundance.

1.4.2 Chapter 3

In Chapter 3 of this dissertation, I determine the local atomic structure and short-range order of AFS and AMS under Martian conditions to help distinguish the boundary between amorphous, crypto- or nanocrystalline, and crystalline sulfate phases. I acquired 2D diffraction and total scattering of AFS and AMS at twenty temperatures from 300 K to 100 K at the XPD beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory. I then determined the pair distribution function of AFS and AMS at each temperature. Both AFS and AMS show very little structural change from 300 K to 100 K. At short-range (<4 Å), I observed consistent bonds of the SO_4 tetrahedra and the first Fe^{3+}/Mg coordination shell in the pair distribution functions. I also confirm that these sulfates are amorphous, as both have consistent coherence lengths around $8.3 - 8.4$ Å, with no discernable structural order at lengths >8.5 Å.

1.4.3 Chapter 4

In Chapter 4 of this dissertation, I present the first systematic characterization of the crystal structure of trigonal mikasaite as a function of temperature, using X-ray powder diffraction and Rietveld refinement across eight temperatures from 25 °C to -114 °C. Rietveld refinement of each diffraction pattern resulted in reliable structural data of mikasaite, with weighted residuals consistently between $\sim 1.8 - 2.5\%$. I characterize the unit cell parameters, and discuss the anisotropy between the a -axis and the c -axis. I use a linear regression of $\ln(\text{Volume})$ against temperature to calculate a volumetric thermal expansion coefficient of $\alpha_V = 3.64 \pm 0.64 \times 10^{-5} \text{ K}^{-1}$, which is consistent with values reported for other anhydrous sulfates, including anhydrite ($3.66 \times 10^{-5} \text{ K}^{-1}$) and $\alpha\text{-MgSO}_4$ ($3.74 \times 10^{-5} \text{ K}^{-1}$). Lastly, I present analysis of ellipsoid fitting of

the two distinct FeO₆ coordination sites within mikasaite. Trends, or lack thereof, in the fitted ellipsoids suggest that there may be multiple factors affecting the mikasaite structural data.

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Chapter 2

Obscuration of Crystalline Ca-Sulfate in XRD and Raman Data when Coated by Amorphous Ferric Sulfate: Implications for the Amorphous Components at Gale Crater

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Abstract

Throughout Gale crater, Mars, the *Curiosity* rover has found high abundances (15-73 wt%) of X-ray amorphous materials in the rocks and sediments. The composition of this amorphous fraction is primarily calculated by subtracting crystalline abundances measured by the Chemistry & Mineralogy X-Ray Diffractometer (CheMin) from bulk elemental abundances from the Alpha Particle X-Ray Spectrometer (APXS). If any crystalline phase were underrepresented in the CheMin data, the elemental components of that phase would be overestimated in the amorphous fraction. This study examines the possibility of underrepresented crystalline phases in X-ray diffraction data using mixtures of amorphous ferric sulfate (AFS) and crystalline Ca-sulfate. Two compositionally equivalent mixtures were made with different morphologies: first, a simple mixture of AFS and Ca-sulfate grains and second, Ca-sulfate grains with AFS coatings. Each mixture was characterized with Raman spectroscopy, and two X-ray diffractometers (XRDs): a Bragg-Brentano instrument with CuK α radiation and a Debye-Scherrer instrument with CoK α radiation. Raman peaks from Ca-sulfate dominate both mixtures, but are dampened when AFS coats the Ca-sulfate grains. In XRD data, AFS coatings cause an overestimation of the amorphous percentage, with a difference between the known and refined amorphous abundances of 29-34 wt%, compared to 2-2.8 wt% for the uncoated mixtures. The effects of the coatings are slightly

amplified with the Debye-Scherrer XRD, primarily due to the increased scattering and absorption of the CoK α radiation. This has implications for interpreting XRD data of mixed amorphous-crystalline samples on Mars, as any Fe-rich amorphous coating may cause an overestimation of the amorphous abundance.

Plain Language Summary

In Gale crater on Mars, the *Curiosity* rover has consistently detected large amounts of ‘amorphous’ material, meaning material with little to no crystal structure. To determine the chemical composition of this amorphous material, observations from multiple instruments onboard *Curiosity* need to be combined. If data from one of these instruments is misinterpreted, the overall amorphous material may be misunderstood. In this study, we investigate a possible way in which this amorphous material may be overestimated. We made mixtures of amorphous and crystalline material in the lab, and analyzed these mixtures with instruments similar to those on *Curiosity*. Our main discovery is that when an iron-rich amorphous material coats the outside of a crystalline grain, X-rays that are used to characterize that grain can be scattered and absorbed, lowering the return signal of that crystalline grain. This can cause the amorphous material abundance to be overestimated. If these iron-rich coatings are a factor on Mars, then they need to be considered to properly interpret the properties of Martian rocks and soils.

2.1 Introduction

High abundances (15-73 wt%) of amorphous materials are pervasive in the sediment and sedimentary rocks of Gale crater, Mars (Bish et al., 2013; Blake et al., 2013; Dehouck et al., 2014; Ehlmann et al., 2017; Rampe, Blake, et al., 2020; Treiman et al., 2016; Vaniman et al., 2014; Yen et al., 2017). The amorphous compositions between samples analyzed in Gale crater are variable,

but typically includes significant amounts of FeO_T and SiO_2 , as well as an abundance of volatiles such as S, Cl, and H_2O (Achilles et al., 2017; Achilles et al., 2020; David et al., 2022; Leshin et al., 2013; McAdam et al., 2020; Morris et al., 2016; Morrison et al., 2018; Rampe, Bristow, et al., 2020; Rampe et al., 2018; Smith et al., 2021; Smith et al., 2022; Sutter et al. 2017). The amorphous composition of Gale crater materials is primarily calculated using data from two instruments onboard *Curiosity*: the Alpha Particle X-Ray Spectrometer (APXS) and the Chemistry & Mineralogy X-Ray Diffractometer (CheMin). APXS measures bulk elemental abundances (Campbell et al., 2012), and CheMin can identify and determine the abundances of crystalline materials, as well as the sample's amorphous percentage (Blake et al., 2012). By subtracting the abundances of materials attributed to the crystalline component from the bulk elemental abundance, the composition of the overall amorphous component can be determined. Once the overall amorphous composition is established, the crucial work of interpreting and extrapolating the individual phases and formation mechanisms can begin. However, calculation of the amorphous composition rests on the assumption that CheMin can accurately detect all crystalline material above the detection limit of about 3 wt% (Blake et al. 2012). If any crystalline phase were underrepresented in the data of CheMin, the elemental components of that phase would be overestimated in the calculated amorphous fraction. Using laboratory analog experiments, this study explores the mechanics and likelihood of this phenomenon using mixtures of amorphous ferric sulfate (an amorphous phase likely present in Martian surface materials) and crystalline calcium sulfate.

Amorphous sulfate phases are not found commonly on Earth. The formation processes, stability, structural, and spectral characteristics of amorphous S-bearing phases are not well understood, especially when compared to crystalline S-bearing minerals. Secondary mineral

assemblages that often contain S-bearing materials are commonly used to help interpret depositional and diagenetic processes, as well as ancient habitability (e.g., Magnuson et al., 2023; Moreras-Marti et al., 2022; Paul & Mormile 2020). Thus, it is necessary to understand the formation processes and required conditions for amorphous S-bearing materials to help distinguish ancient depositional processes and diagenetic overprinting from modern surface-atmosphere exchange processes.

X-ray amorphous or poorly-crystalline S-bearing materials have been detected or suggested at sites across Mars. For example, spectra of the Dourbes target in Jezero crater support the presence of amorphous Mg-sulfate phases (Siljeström et al., 2024), and in Gusev crater, Mössbauer spectra from the MER Spirit rover shows nanophase ferric oxide in association with sulfur and chloride (Morris et al., 2006). Crystalline S-bearing minerals are prevalent in the sedimentary rocks of Gale crater. Abundances of Fe-, Mg-, and Ca-, sulfates have been found in a wide range of assemblages, as detected by the CheMin (Blake et al., 2012) and Sample Analysis at Mars (SAM) (Mahaffy et al., 2012) instruments. However, even with the prevalent detection of crystalline sulfates, ~20-90 wt% of the total SO₃ of Gale crater drill hole samples is included within the amorphous component (Chipera et al., 2023; Smith et al., 2022). On average, these samples have ~4.1 wt% amorphous SO₃-bearing material, which includes variable mixtures of Fe-, Mg-, and Ca- sulfates or sulfites (Chipera et al., 2023; Simpson et al., 2025; Smith et al., 2022). The abundance of both crystalline and amorphous S-bearing materials, and the variability and complexity of the amorphous components across the rover traverse, suggests that there are multiple superimposed geologic processes that influence the formation and stability of these amorphous materials (Blake et al., 2024; Smith et al., 2022). For example, studies have suggested several methods to form amorphous sulfates on Mars, including induced amorphization by electrostatic

discharge from Martian dust activities (Wang et al., 2020), brine-induced alteration of clays (Bristow et al., 2021; Thorpe et al., 2022), or products of brine desiccation/dehydration/cryoprecipitation (e.g., Chipera & Vaniman, 2007; Hopkins et al., 2023; Pandey et al., 2025; Sklute et al., 2015; Sklute et al., 2018; Smith et al., 2021; Vaniman et al., 2004; Vaniman & Chipera, 2006). Some hypotheses suggest possible non-amorphous S-bearing phases that may lead to this detection, such as sulfide and other S-bearing phase inclusions (e.g., McAdam et al., 2014; Sutter et al., 2017) or adsorbed SO_4 onto nanophase minerals or other amorphous phases (e.g., Rampe et al., 2016). Realistically, it is possible that many of these formation mechanisms occurred throughout the history of Gale crater and contributed to the high abundance of amorphous sulfate measured in Gale crater today. However, to extrapolate these various processes, it is important to have confidence in the initial amorphous composition calculations.

It is useful to review the process by which speciation and abundance estimates for the sulfur-bearing amorphous and crystalline components have been determined. The SAM instrument measures volatiles releases from phases at characteristic temperatures and can detect SO_2 decomposed from phases such as Mg- and Fe- sulfates, sulfites, sulfides, and elemental sulfur to determine the abundance of SO_3 in a sample (Mahaffy et al., 2012). Importantly, SAM cannot detect Ca-sulfates, which decompose at temperatures beyond the upper limit of SAM (Mahaffy et al., 2012). Thus, Ca-sulfate phases are not included in the total SO_3 abundance measured by SAM, and the difference between the SO_3 abundances measured using APXS and SAM can be attributed to the bulk Ca-sulfate abundance (Sutter et al., 2017). The uncertainties and limitations of APXS and SAM are well-understood (Campbell et al., 2012; McAdam et al., 2014), and while there are some known matrix effects on APXS analysis (e.g., Campbell et al., 2012; Johnson et al., 1999), this calculated bulk Ca-sulfate is assumed to include both crystalline and amorphous contributions

for this mass-balance calculation (Smith et al., 2022). By subtracting the CheMin-derived crystalline Ca-sulfate abundances from this bulk Ca-sulfate abundance, the amorphous Ca-sulfate abundance can be estimated (Smith et al., 2022).

The Ca-sulfate reported within the amorphous component (Smith et al., 2022) is of particular interest, as it is not stable as an amorphous phase, except for as a very short-lived intermediate precursor in the precipitation of gypsum (e.g., Jia et al., 2020; Jia et al., 2021). This amorphous Ca-sulfate is found in three samples, ranging from 1.2-5.5 wt% (Smith et al., 2022), and a possible formation mechanism for this phase has remained elusive. Furthermore, it is unclear whether the Ca-bearing phase is truly amorphous, or whether it is a crystalline or intermediate phase that appears as X-ray amorphous due to the limitations of the instruments available onboard *Curiosity*. The inherent uncertainties of the mass-balance calculation of crystalline and amorphous Ca-sulfate have been examined extensively, and suggest that spurious identification of amorphous Ca-sulfate from instrument uncertainty is unlikely (Smith et al., 2022).

In this study, we hypothesized that the morphology of a mixture, specifically coated grains as opposed to physical mixtures of pure grains, may lead to varying detectability between instruments. Because some proposed salts for Mars are highly hygroscopic and may undergo relative humidity (RH)-induced deliquescence and efflorescence, such as amorphous ferric sulfate and perchlorates (e.g., Chevrier & Altheide 2008; Hopkins et al., 2023; Gough et al., 2011; Nuding et al., 2014; Xu & Parise 2012), it is possible that salt coatings around non-deliquescent grains could form over time during RH cycles. CheMin is particularly susceptible to sample morphology or crystallinity, as it can only determine the composition of crystalline materials that return X-ray diffraction peaks. Additionally, due to the transmission geometry specific to CheMin (**Section 3.3**), X-rays must pass through a thickness of sample and may experience a range of absorption and

scattering processes through materials of many different grain sizes, crystallinity, and composition when passing between X-ray emitter and detector.

2.2 Methods

We analyzed multiple mixtures of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and amorphous ferric sulfate. These starting components were chosen for multiple reasons. In Gale crater, gypsum is the most commonly detected Ca-sulfate mineral, before bassanite, anhydrite, and starkeyite (Chipera et al., 2023; Vaniman & Chipera 2006; Vaniman et al., 2018). Salts containing S and Fe are ubiquitous across Mars' surface (e.g., Berger et al., 2016; Burns, 1987), and would likely contribute to the brines that have been hypothesized to be involved with the formation of amorphous sulfates. The rapid desiccation of a ferric sulfate brine under low-pressure and low-relative humidity (RH) Martian conditions produces an amorphous solid (Hopkins et al., 2023; Sklute et al., 2015; Sklute et al., 2018; Xu & Parise, 2012). Ferric sulfates have been observed or suggested throughout Mars and Gale crater (Bishop et al., 2004; Burns, 1987; Lane et al., 2004; Mitra et al., 2023; Morris et al., 2006; Smith et al., 2022; Wang & Ling, 2011). The presence of various Fe^{3+} -sulfates on Mars, its ability to form an amorphous solid from solution, and the enrichment of Fe-S phases in the amorphous component in Gale crater (Smith et al., 2022) support ferric sulfate as a starting component in this study.

2.2.1 Sample Preparation

The process to synthesize amorphous ferric sulfate (hereafter 'AFS') begins with ferric sulfate hydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$). This ferric sulfate hydrate is dehydrated to anhydrous $\text{Fe}_2(\text{SO}_4)_3$ via heating at 300 °C for 24 hours, with an initial ramp up rate of 60°C every 15 minutes in small batches (8–10 g each), to ensure homogenous dehydration of each batch (Hopkins et al., 2023).

This anhydrous ferric sulfate is also known as the mineral mikasaite. Aliquots of mikasaite are placed in sample cups and transferred inside air-tight containers buffered to 92% RH with deionized water. The purpose is to allow the mikasaite to deliquesce gradually to a homogenous saturated solution. We used this deliquescence method to ensure a controlled and consistent pathway to saturation, as opposed to directly mixing the dry powders into water, which would introduce additional opportunities for measurement error. The volume of deliquesced water is monitored. When the solution stops taking on more water and all the mikasaite powder is dissolved, the solution has reached saturation. When the solution reaches saturation after about 4 days under 92% RH, the sample is transferred into another air-tight container buffered to 11% RH using lithium chloride. In this low-RH atmosphere, the solution desiccates and forms an amorphous ‘chip’. We found that 1.0 g of initial mikasaite typically yields 1.46 g of AFS after one cycle of deliquescence and desiccation. This indicates that AFS is not anhydrous and is consistent with previous work by Ling & Wang (2010), which found AFS to carry five structural waters ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$).

For our experiments, two compositionally identical sample mixtures were made, but with different morphologies. Each sample is a 50-50 wt% mixture of AFS and 25-63 μm gypsum. The gypsum was ground and sieved from a single crystal specimen from Ward’s Science. The two mixtures differ in their preparation technique, resulting in different morphologies. The first sample, hereafter referred to as the uncoated Gyp-AFS mixture, was formed as a simple mixture of AFS and gypsum, with the AFS having been formed through desiccation of a saturated ferric sulfate solution as described above. Before mixing with the gypsum, the AFS was gently ground into a powder with a mortar and pestle. The second sample, hereafter referred to as the coated Gyp-AFS mixture, was formed by adding the gypsum powder to the saturated ferric sulfate solution *before*

desiccation of the AFS, so that the resulting mixture would consist of a AFS film coating the gypsum grains. The mass of initial mikasaite required to achieve the resulting 50 wt% AFS after desiccation of the mixture was determined using the known yield of AFS using the deliquescence/desiccation formation method. After desiccating, the coated Gyp-AFS sample was gently ground with a mortar and pestle to break up the brittle chip into a powder, but without finely grinding the sample, as to preserve the AFS coatings on the grains of gypsum.

2.2 Analytical Techniques

Scanning Electron Microscope (SEM) images were acquired of each sample, along with complimentary Energy Dispersive X-ray Spectroscopy (EDS) analysis. The SEM used was a Thermo Scientific Phenom XL G3 Desktop SEM. We used the backscattered electron detector with 10 kV accelerating voltage, low beam intensity, and with the chamber set to low pressure at 10 Pa. These parameters allowed us to maximize the data quality without altering our samples.

Raman spectra were acquired using a B&W Tek i-Raman Plus, with a 532 nm laser set at 7.5 mW power (100-3800 cm^{-1} , $\sim 1.5 \text{ cm}^{-1}$ spectral sampling). During this analysis, the samples were kept in glass containers buffered to 11% RH, which included a 1.5 mm thick polished quartz window transparent to the Raman laser.

Before X-ray Diffraction (XRD) analysis, a small amount of silicon powder (NIST Standard Reference Material 640d) was added to each sample as a normalization standard when refining the samples composition and crystallinity. The uncoated and coated AFS-Gyp samples had 5.6 wt% and 3.7 wt% silicon, respectively. XRD analysis was performed on each sample using two separate instruments. First, the samples were analyzed with an Olympus BTX-II. With this instrument, a small amount of powder sample is sandwiched between two vertical Kapton windows. The spacing between these windows is $\sim 200 \text{ }\mu\text{m}$. An actuator on the sample holder

vibrates and agitates the powder throughout the analysis to ensure that the sample is well mixed. X-rays from a $\text{CoK}\alpha$ (1.7903 Å) source pass through the sample in a Debye-Scherrer geometric setup. Importantly, this transmission geometry and radiation source is identical to that used in the CheMin instrument onboard MSL *Curiosity*. The second instrument we used was a Rigaku Miniflex that uses a $\text{CuK}\alpha$ (1.5428 Å) radiation source in a Bragg-Brentano geometric setup. To suppress Fe-fluorescence from the $\text{CuK}\alpha$ radiation, the baseline of the pulse-height analyzer was set to 45 and the window narrowed to 7, improving the peak-to-background of the diffraction data. For this instrument, the powdered sample was placed on a glass sample holder with a shallow well. Hereafter, these two instruments will be referred to by their geometric setups, Debye-Scherrer (DS) and Bragg-Brentano (BB).

Rietveld refinement was performed on each diffraction pattern acquired of both samples by each instrument. The open access software GSAS-II was used for all Rietveld refinements (Toby & Von Dreele, 2013). During this refinement, any signal from the instrument, the sample holder, and any amorphous phases were included as the background signal, which was not used in the amorphous percentage calculation as to not introduce scaling bias of different diffraction geometries and detector responses. The background was refined as a Chebyshev polynomial, with the number of coefficients ranging from 14 to 18 depending on the sample. Structure refinements were performed using the default analytical Hessian method in GSAS-II, which utilizes a least-squares minimizer that uses a singular-value decomposition to reduce the errors caused by correlated variables, as well as the Levenberg-Marquardt algorithm (Toby & Von Dreele, 2013). A pseudo-Voigt powder peak profile function was used for peak fitting, as is the default in GSAS-II (Toby & Von Dreele, 2013; Thompson et al., 1987). Refined variables for each diffraction pattern from both BB and DS instruments include zero-point shift, U-V-W Gaussian and X-Y Lorentzian

peak shape coefficients, and unit cell parameters for gypsum. For diffraction data taken with the BB instrument, sample displacement and roughness parameters were also refined, as well as the March-Dollase ratio for the preferred orientation of gypsum along the (010) planes. For the diffraction data taken with the DS instrument, sample displacement both parallel and perpendicular to the beam were refined separately. Not every diffraction pattern required all of these parameters to be refined. Each additional refined variable was added incrementally as the decreasing weighted residuals stalled. The weight fractions for gypsum and silicon were determined from the refined scale factors, based on the crystalline peaks. Then, the wt% abundances of these phases were normalized to the known wt% of the added silicon standard. Any outstanding wt% was assigned as X-ray amorphous. With this method, we can compare the measured values from each instrument to the known abundances of AFS and gypsum in our samples and determine how instrument parameters and AFS-coating affect the accuracy of these measurements.

2.3 Results

2.3.1 SEM-EDS Analysis

The first step in the analysis of the uncoated and coated Gyp-AFS samples is to compare their physical nature, and to confirm their uncoated and coated morphologies. Figure 2.1 shows an SEM image of the uncoated Gyp-AFS sample. In this sample, we see discrete grains of both gypsum and AFS. The gypsum grains are the clumped acicular needle-like grains in Figure 2.1 and are slightly darker in backscatter than the AFS grains. Points #2 and #3 in Figure 2.1 are placed on two of these gypsum crystals. Points #1 and #4 are placed on grains of AFS, which exhibits a smoother surface texture than the gypsum, with more rounded conchoidal fracturing. While there are wide variations in grain size and an abundance of fines as result of the grinding before analysis, this SEM image shows that the uncoated Gyp-AFS sample is a simple physical mixture of discrete

grains. Table 2.1 shows the relevant elemental concentrations of the four EDS point spectra from Figure 2.1. From these EDS elemental concentrations, we can clearly see that the gypsum crystals (#2 and #3) are very chemically homogeneous, as there was no detectable Fe in either grain. There was a small amount of Ca detected in the analysis of the AFS grains (#1 and #4), which we attribute to surface fines of gypsum scattered across the AFS. Overall, EDS spectra show clear distinction between Ca-bearing and Fe-bearing materials, with no mixing within individual grains.

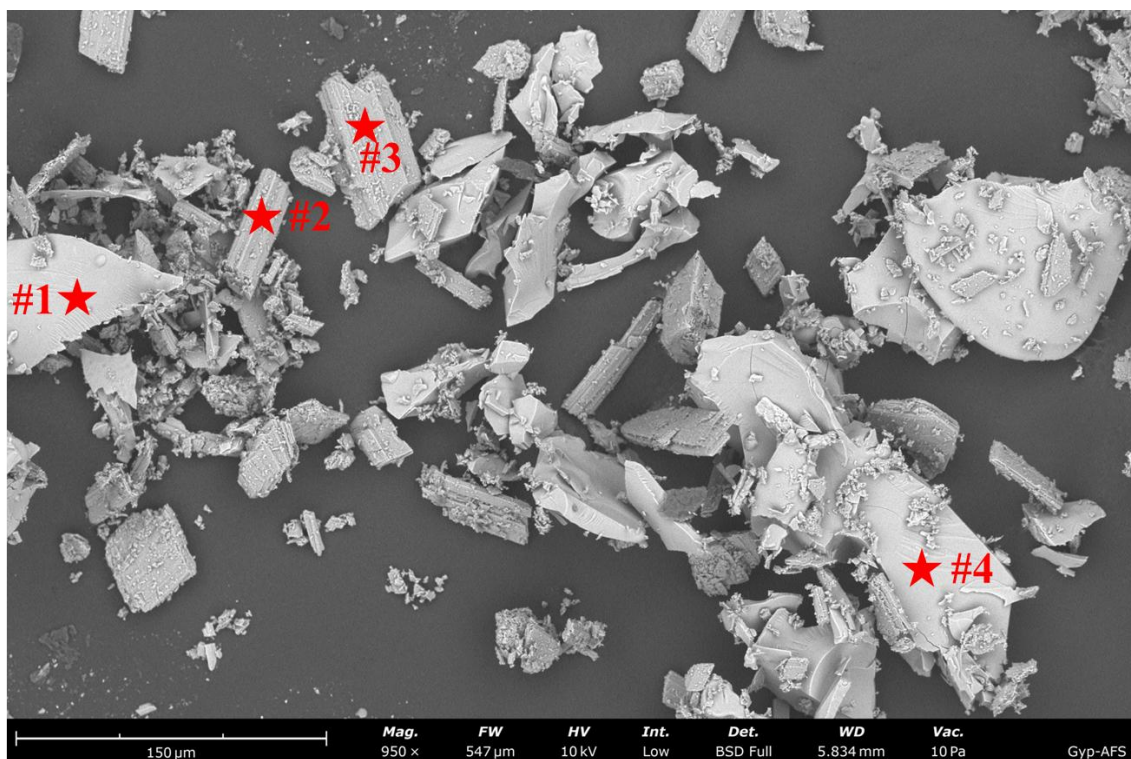


Figure 2.1. SEM image of the uncoated Gyp-AFS sample. Scale bar is 150 μm. Numbered red stars are locations where spot EDS spectra were acquired, with results shown in Table 2.1. Points #1 and #4 are on irregular grains of AFS, and points #2 and #3 are on crystalline grains of gypsum.

Table 2.1. Weight concentrations of Fe, Ca, S, and O from semi-quantitative analysis of the four EDS point spectra (red stars) taken of the uncoated Gyp-AFS sample grains, shown in Figure 2.1. EDS point spectra were acquired over a 60 second integration with a 10 kV beam. Full semi-quantitative EDS analysis of all point spectra is provided in the Zenodo repository (10.5281/zenodo.17575248).

Star #	Weight Concentration (wt%)			
	Fe	Ca	S	O
1	7.79	1.39	42.95	26.87
2	0.00	30.73	23.12	36.74
3	0.00	19.40	15.30	56.60
4	13.01	2.00	26.63	41.94

Figure 2.2 shows a SEM image of the coated Gyp-AFS sample. In contrast to the uncoated sample, the coated sample does not show discrete grains of gypsum or AFS. Each grain is a cemented mixture of gypsum grains with an AFS matrix. The surface of these grains is rough due to irregular surface or near surface expressions of the gypsum grains with varying orientations. These cemented gypsum grains also break up the smooth conchoidal fracturing the AFS would normally exhibit. Nowhere in the sample could we find clean grains of gypsum that are not clumped together in a larger grain with AFS. An EDS line scan from points A to B in Figure 2.2 confirms that these grains are a mixture of gypsum and AFS, as we see both Ca and Fe across the heterogeneous grain. The concentrations of Ca and Fe across the grain are anticorrelated, as the contributions from both AFS and gypsum depend on how much or little AFS is covering a particular gypsum grain at each pixel. These SEM and EDS analyses from Figures 1 and 2 confirm that “uncoated” and “coated” Gyp-AFS samples are indeed uncoated and coated. Additional SEM images and full EDS analyses of both samples can be found in the Zenodo repository (10.5281/zenodo.17575248).

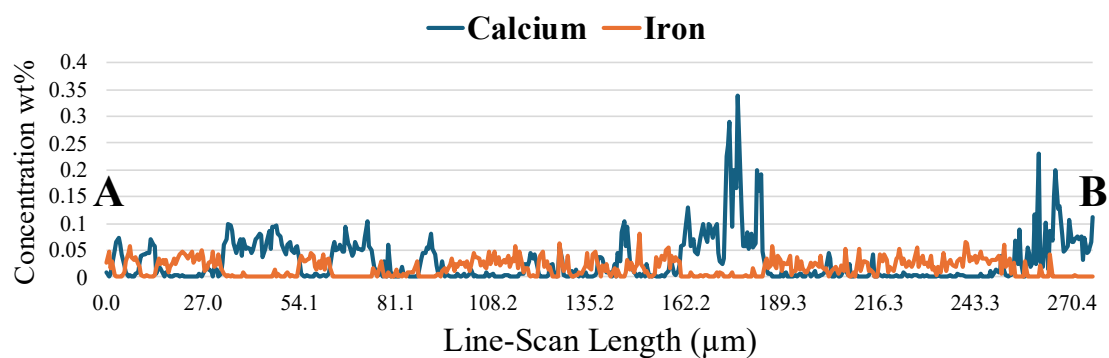
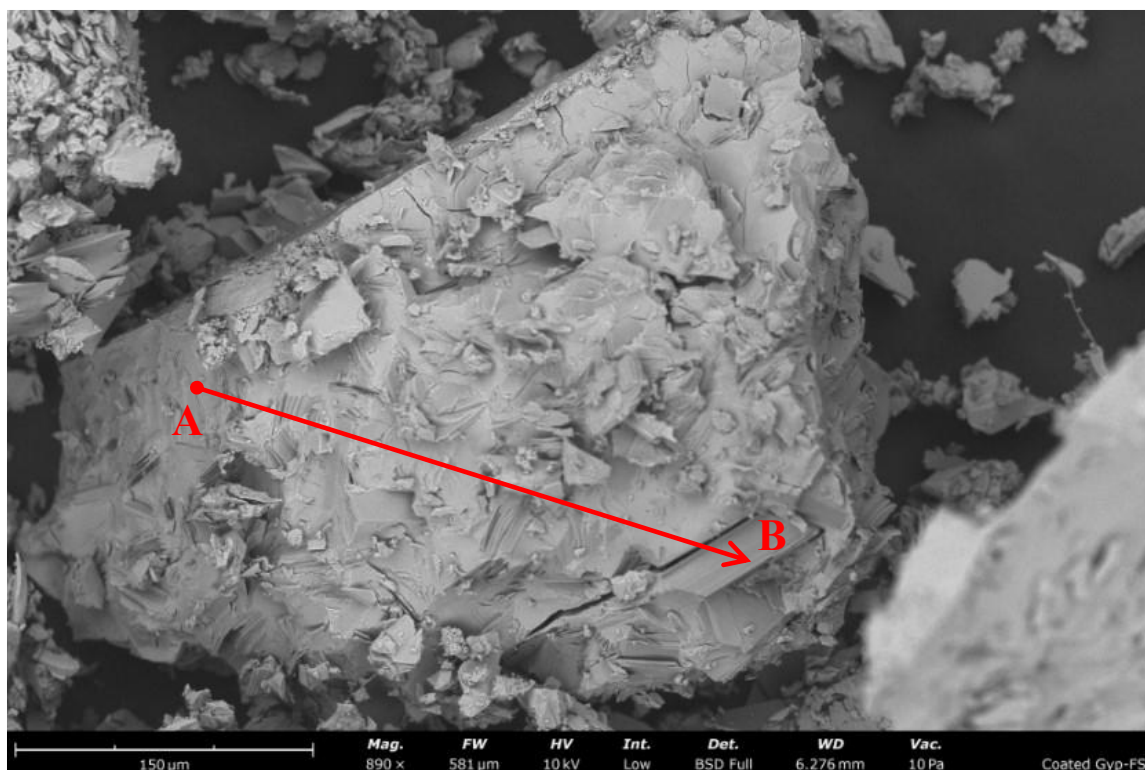


Figure 2.2. (Top) SEM image of the coated Gyp-AFS sample. Scale bar is 150 μm . Line A-B is a $\sim 277 \mu\text{m}$ length EDS line scan with 512-pixel resolution, with a 1 second hold time on each pixel. (Bottom) Weight percent concentrations of Ca and Fe along the EDS line scan from A to B.

2.3.2 Raman Spectra

Figure 2.3 shows the Raman spectra of each experimental sample, in addition to the spectra of their starting components. Raman band assignments were made based on Hopkins et al. (2023) and references therein. The Raman spectrum of synthesized anhydrous $\text{Fe}_2(\text{SO}_4)_3$, also known as mikasaite, has two distinct groupings of peaks. First is a doublet at 442 cm^{-1} and 460 cm^{-1} due to the SO_4 ν_2 symmetric bending vibrational mode. Second, we see SO_4 ν_1 symmetric stretching modes at 1073 cm^{-1} and 1094 cm^{-1} , and a SO_4 ν_3 asymmetric stretching mode at 1120 cm^{-1} . There are no features at greater wavenumbers, confirming that our $\text{Fe}_2(\text{SO}_4)_3$ is anhydrous. We see clear changes to the Raman spectra as the $\text{Fe}_2(\text{SO}_4)_3$ is transformed into AFS through the deliquescence/desiccation cycling. The signal-to-noise is decreased due to the amorphous nature of the sample, although there are still sharp Raman peaks. Starting at low Raman shift, we see a weak SO_4 ν_2 symmetric bending peak at $\sim 470\text{ cm}^{-1}$, a SO_4 ν_4 asymmetric bending at 616 cm^{-1} , two SO_4 ν_1 symmetric stretching peaks at 998 and 1026 cm^{-1} , a H_2O bending peak at 1602 cm^{-1} , and a H_2O stretching peak at $\sim 3050\text{ cm}^{-1}$. The Raman spectrum of our starting gypsum sample has two SO_4 ν_1 peaks at 1004 and 1034 cm^{-1} , and H_2O stretching features at ~ 3404 and $\sim 3490\text{ cm}^{-1}$.

The uncoated and coated Gyp-AFS samples both show more noise compared to gypsum, likely due in part to their partially amorphous nature. These two samples should share the same Raman peaks. First, the silicon standard 640d that was added to the sample shows a peak at 515 cm^{-1} . The gypsum in these two samples contributes two SO_4 ν_1 peaks at 1004 and 1034 cm^{-1} , and a H_2O feature at $\sim 3490\text{ cm}^{-1}$. The water feature in gypsum at $\sim 3404\text{ cm}^{-1}$ is indistinguishable from the noise in both the uncoated and coated Gyp-AFS samples. A significant difference between the uncoated and coated Gyp-AFS samples is the spectral contributions from the AFS. There are no identifiable Raman peaks of AFS in the uncoated Gyp-AFS sample. However, the coated sample

shows broadened features between ~ 1000 and 1075 cm^{-1} due to additional SO_4 vibrations, including a distinct shoulder at 1026 cm^{-1} , which is a $\text{SO}_4\text{ } \nu_1$ peak seen in the spectrum of AFS.

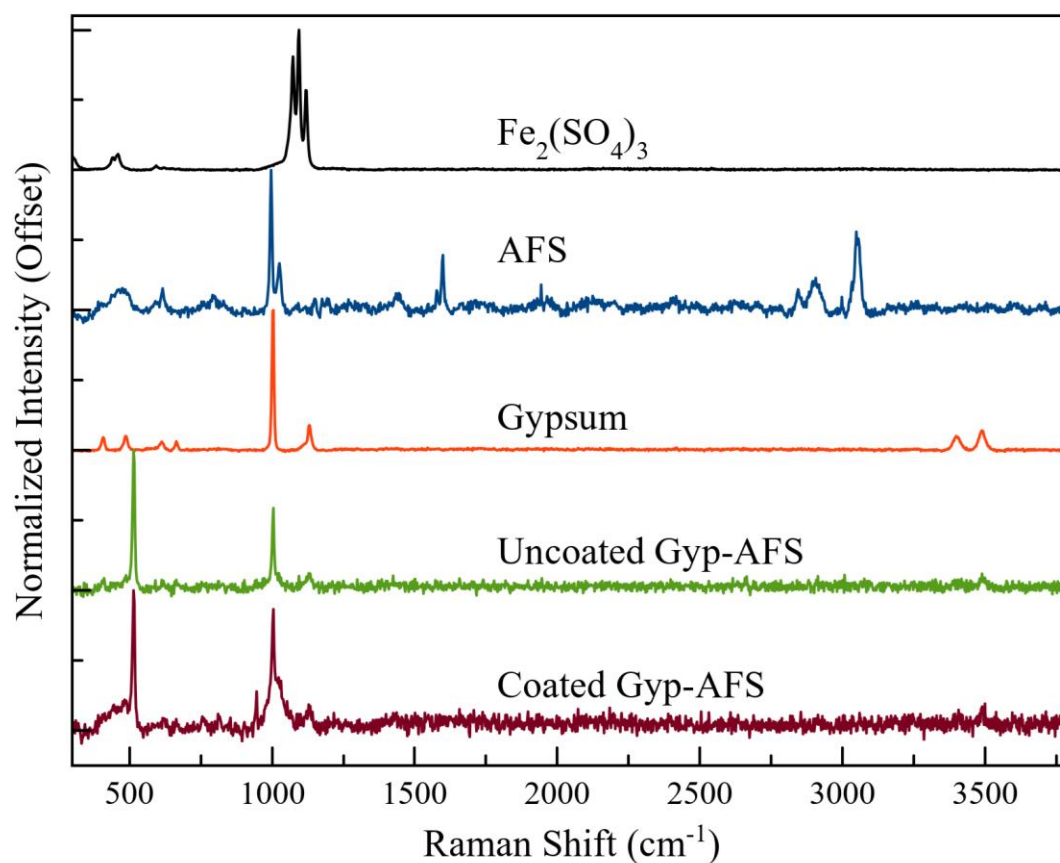


Figure 2.3. Raman spectra of the uncoated and coated Gyp-AFS samples, along with reference spectra of their individual components. Spectra are normalized to their maximum intensity and offset on the y-axis for clarity. All spectra were taken using a B&W Tek i-Raman Plus (532 nm, 7.5 mW, 100-3800 cm⁻¹, ~1.5 cm⁻¹ sampling).

2.3.3 X-Ray Diffraction

Figure 2.4 shows the coated and uncoated Gyp-AFS diffraction patterns for the BB instrument, with the modeled pattern from Rietveld refinement. The coated samples have a lower peak to background ratio, and the overall intensity of the diffraction peaks of the uncoated sample is significantly higher. Both diffraction patterns clearly show crystalline gypsum and the internal silicon standard. Any broad curve due to the amorphous component or the sample holder was simply treated as a background during the refinement process. Once the crystalline component weight percents were refined, the added silicon internal standard was used to normalize the crystalline gypsum component abundances, and the remaining unallocated wt% was attributed to the AFS component.

The coated Gyp-AFS modeled refinement resulted in a weighted residuals percentage of 4.64%, showing a good fit to the diffraction data. After normalizing the refined phase abundances to our silicon internal standard set to 3.7 wt%, refinement found that the coated Gyp-AFS sample is 19.1 wt% gypsum and 77.2 wt% amorphous (Table 2.2). Taking into account the silicon internal standard, we prepared the sample so that the gypsum and AFS would be in equal abundance at ~48.15 wt%. This means that the BB instrument inaccurately characterized the abundances of crystalline gypsum and AFS in the coated Gyp-AFS sample by about 29 wt%.

For the uncoated Gyp-AFS sample, the overall weighted residual percentage was limited to 13.50% due to the BB instrument alignment with the sample holder causing a slight shift in 2θ values. After normalizing the refined abundances to the 5.6 wt% abundance of the silicon internal standard, the crystalline gypsum of the uncoated sample was measured at 44.3 wt%, and AFS was calculated to be 50.0 wt%. With an absolute difference of about 2.9 wt%, this is an improvement in the difference between the actual and normalized refined values, compared to the coated sample.

Table 2.2. Weight percents of the materials comprising the coated and uncoated Gyp-AFS samples from both the Rigaku Miniflex (BB) and Olympus BTX-II (DS) XRDs. All values shown are weight percents (wt%) of the bulk samples. Refined values are normalized to the known wt% of the silicon 640d internal standard. Both the refined and normalized values are reported. The difference is a measure of the inaccuracy between the actual wt% values of each sample set during sample preparation, and the normalized wt% values after Rietveld Refinement.

		Gypsum	Silicon	Amorphous
Uncoated	Actual wt%	<i>47.20</i>	<i>5.60</i>	<i>47.20</i>
	Refined BB wt%	88.70	11.30	0.00
	Normalized BB wt%	44.30	5.60	50.04
	BB Difference ($\pm$ wt%)	-2.90	0.00	+2.84
	Refined DS wt%	89.70	10.30	0.00
	Normalized DS wt%	49.20	5.60	45.20
	DS Difference ($\pm$ wt%)	+2.00	0.00	-2.00
Coated	Actual wt%	<i>48.15</i>	<i>3.70</i>	<i>48.14</i>
	Refined BB wt%	83.60	16.40	0.00
	Normalized BB wt%	19.10	3.70	77.20
	BB Difference ($\pm$ wt%)	-29.05	0.00	+29.06
	Refined DS wt%	78.80	21.20	0.00
	Normalized DS wt%	13.90	3.70	82.40
	DS Difference ($\pm$ wt%)	-34.25	0.00	+34.26

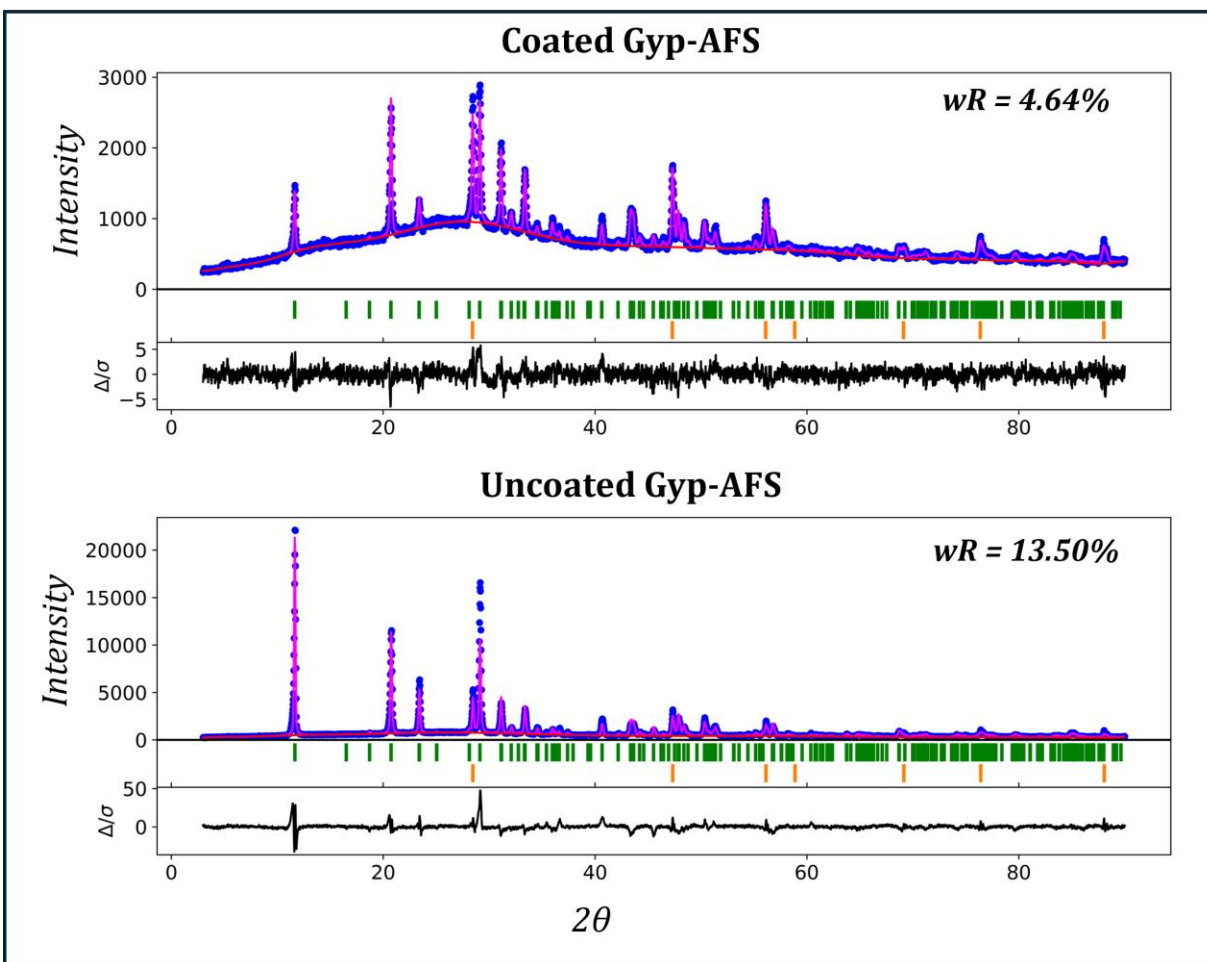


Figure 2.4. Rietveld refinement plots of the coated (top) and uncoated (bottom) Gyp-AFS diffraction patterns taken with the Rigaku Miniflex instrument, utilizing Bragg-Brentano (BB) geometry and $\text{CuK}\alpha$ radiation. The blue dots are the diffraction data, the pink plots are the refined profiles, and the red curve is the background profile. Green and orange ticks show the peak locations of gypsum and silicon standard, respectively. The black Δ/σ plot is the weighted difference curve of the refined profile vs the diffraction data. Weighted residuals (wR) of the calculated fit are shown in the top right of each plot. GSAS-II was used for this Rietveld refinement (Toby & Von Dreele, 2013).

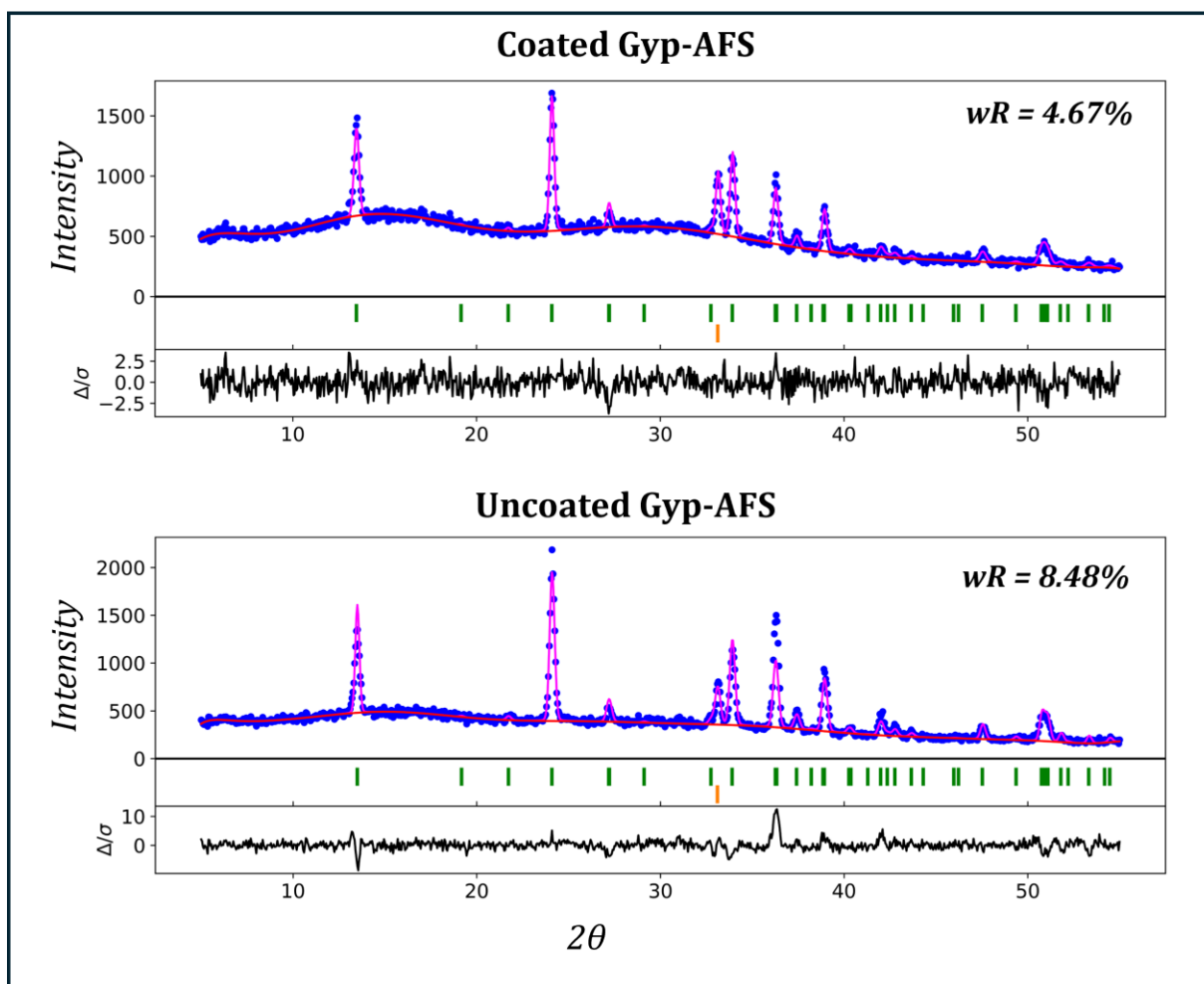


Figure 2.5. Rietveld refinement plots of the coated (top) and uncoated (bottom) Gyp-AFS diffraction patterns taken with the Olympus BTX-II instrument, utilizing Debye-Scherrer (DS) geometry and CoK α radiation. The blue dots are the diffraction data, the pink plots are the refined profiles, and the red curve is the background profile. Green and orange ticks show the peak locations of gypsum and silicon standard, respectively. The black Δ/σ plot is the weighted difference curve of the refined profile vs the diffraction data. Weighted residuals (wR) of the calculated fit are shown in the top right of each plot. GSAS-II was used for this Rietveld refinement (Toby & Von Dreele, 2013).

Figure 2.5 shows the diffraction data and Rietveld refinement profiles for the coated and uncoated Gyp-AFS samples taken with the DS instrument. Both diffraction patterns have similar overall peak intensities and elevated background, although the coated sample shows a more distinct broad amorphous curve. This amorphous curve appears to have two general broad peaks, centered at $\sim 16^\circ$ and $\sim 29^\circ$ 2θ . These two broad maxima represent the contributions of the structure factor of AFS to the diffraction pattern. Generally, the structure factor of an amorphous material shows multiple broad diffraction maxima as a function of scattering angle, representing the local and intermediate range atomic structure (Billinge & Kanatzidis, 2004; Egami & Billinge, 2012). It is likely that there are more than these two maxima within our data (3rd order, etc.), but these do not have the necessary intensity to be distinguishable from the background and noise. Both modeled diffraction patterns fit the respective data well, with a weighted residual percentage of 4.67% for the coated Gyp-AFS sample and 8.48% for the uncoated Gyp-AFS sample. Normalization of the refined abundances determined that the coated Gyp-AFS sample had a gypsum abundance of 13.9 wt% and an AFS abundance of 82.4 wt% (Table 2.2). Thus, the modeled difference for this sample is 34.3 wt%, which is worse than the result of the same sample with the BB instrument. For the uncoated Gyp-AFS sample, normalization of the refined abundances yielded a gypsum abundance of 49.2 wt% and an AFS abundance of 45.2 wt%, with an inaccuracy of ± 2 wt%.

For both instruments, the normalized abundances of gypsum and AFS in the coated samples show a substantial difference after Rietveld refinement. In both cases, the abundance of crystalline gypsum was underestimated, causing an over estimation in the amorphous abundance.

Despite having the same bulk composition as the uncoated sample, the AFS dominates the XRD patterns when it is in the form of a coating rather than discrete particles.

2.4 Discussion

In the Raman spectra, the peaks associated with gypsum dominate both the coated and uncoated samples, as gypsum has a stronger Raman cross section than AFS. However, the gypsum peaks are slightly weakened when the gypsum grains are coated with AFS. We interpret this difference to be caused by sample bias, where the Raman laser is more likely to interact with the AFS coating rather than the coated gypsum grains. Though we do not make any abundance estimations using Raman spectroscopy, the differences in the spectra due to coatings could lead to misinterpretation. If these two samples were unknown and analyzed in-situ on Mars via Raman spectroscopy, they would likely be interpreted as having two different bulk compositions. These observations demonstrate the importance of considering coatings when interpreting spectra.

The XRD data shows that coatings can obscure or weaken the intensity of diffraction peaks from the enclosed coated materials. In this particular example, AFS coatings obscure the diffraction contribution from gypsum. There are several factors which contribute to this phenomenon. AFS coatings on the gypsum grains increases the likelihood of the X-rays being scattered and/or absorbed before ever interacting with a gypsum lattice. Additionally, for an X-ray to interact with a coated gypsum grain and diffract back to the detector, it must pass through multiple amorphous layers. As seen in the SEM images of the coated Gyp-AFS sample (Figure 2.2), the coated grains are comprised of smaller gypsum crystals cemented together with AFS,

with each individual gypsum crystal coated with a variable thickness of AFS. A gypsum crystal at the center of these cemented grains would effectually be coated with several layers of AFS.

The more amorphous material an X-ray must pass through, the greater the opportunity for the X-ray to be scattered and/or absorbed before interacting with the coated grain. Additionally, the DS instrument in this study uses a Co (6.93 keV) radiation source, which has a lower energy than the Cu (8.04 keV) radiation source used in the BB instrument. For Fe-bearing samples, such as AFS coatings, CoK α X-rays are substantially more absorbed and scattered than CuK α X-rays, which lowers the effective penetration depth of the X-ray. These factors can dramatically decrease the intensity of crystalline diffraction peaks, and as these X-rays must pass through multiple layers of a Fe-bearing coating to reach the detector, the peak to background ratio of the diffraction data is decreased.

When coatings are absent, as with our uncoated Gyp-AFS sample, both the BB and DS instruments perform adequately to provide diffraction data that accurately represents the sample after a Rietveld refinement. However, with the coated Gyp-AFS sample, the DS instrument results in a ~5% greater difference from the actual wt% when compared to the BB instrument. In a Bragg-Brentano geometry, the X-rays only interact with the top layers of a flat-laying sample, so while the effects of the coatings on those layers are still significant, the amorphous coatings throughout the bulk sample contribute to the scattering and/or absorption less, slightly minimizing the effect compared to the DS instrument.

2.5 Conclusions

We have found that the AFS coatings are the primary cause of the differences in the practical interpretation of both Raman and XRD data of our mixed crystalline-amorphous samples. In the Raman spectra, the coatings cause a sampling bias, as the laser is more likely to interact

with an AFS coating rather than a clean gypsum surface, which could lead to misinterpretation if the sample morphology and bulk chemistry are unknown. For XRD data, these coatings cause a major difference between the known weight percentages and normalized weight percentages of the coated and uncoated samples. These coatings cause these differences because of two key factors: X-ray scattering/absorption, and X-ray path-length through the sample. For an X-ray to interact with a coated crystalline grain and diffract back to the detector, it must pass through the amorphous layer multiple times. The iron in the AFS coatings can scatter and/or absorb these X-rays before and after the X-rays interact with each crystalline grain. With a greater volume of sample for the X-rays to pass through, the more opportunity for scattering to increase the X-ray path-length and absorption to decrease the peak-to-background ratio. Because of these key factors, our AFS coatings have a strong effect on the diffraction data of both the BB and DS instruments, with the DS instrument being affected more due to the increased path length through the sample, and the CoK α radiation being more easily absorbed by the iron in the coatings than the CuK α radiation of the BB instrument.

These findings have significant implications for interpreting X-ray diffraction data acquired of mixed amorphous-crystalline samples on Mars. The CheMin XRD instrument onboard Curiosity uses a Debye-Scherrer geometry with CoK α radiation and is thus particularly susceptible to the effects of Fe-rich amorphous coatings. If the samples analyzed in this study were analyzed by the instruments available on Curiosity, a significant percentage of the crystalline Ca-sulfate would be overlooked or underrepresented. An underestimation of crystalline Ca-sulfate by CheMin would propagate through the mass-balance calculations used to determine the amorphous compositions. Underestimation of crystalline Ca-Sulfate would lead to the overallocation of Ca-

sulfate to the amorphous component. This could be a potential explanation for the unaccountable ‘amorphous’ Ca-sulfate found in Gale crater.

While there is no direct morphological evidence that the Fe-rich amorphous component found in Gale crater takes the form of a coating, any amorphous material that forms through brine desiccation, brine-rock interaction, or other post-depositional processes such as RH fluctuations, could lead to enclosure and coating of crystalline grains, particularly in a sediment or porous sedimentary rock. These Fe-rich amorphous coatings would have the same effects on the diffraction data of the bulk sample that are outlined in this study, and may result in an overestimation of the overall amorphous fraction in Martian surface materials.

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Open Research

All data from this study are available at <https://doi.org/10.5281/zenodo.17575248> (Hopkins et al., 2025).

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Chapter 3

Structural Characterization of Mars-Relevant Amorphous Sulfates at Low-Temperatures with Pair Distribution Function Analysis

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Abstract

Throughout the sediment and sedimentary rocks of Gale crater, Mars, there is a pervasive amorphous component that is often enriched in sulfur, which suggests an abundance of amorphous sulfate materials. Although secondary minerals such as sulfates are often used to help interpret past environmental conditions, it is not well understood how the varying sulfate crystallinity factors into the interpretations of Martian sediments and rocks. Determining the local atomic structure and short-range order of these amorphous sulfates under Martian conditions will help to distinguish the boundary between amorphous, crypto- or nanocrystalline, and crystalline sulfate phases, and aid with the interpretation of these sulfates in the Martian surface/subsurface. In this study, we acquired 2D diffraction and total scattering of amorphous Fe^{3+} and Mg sulfates at twenty temperatures from 300 K to 100 K at the XPD beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory, and determined the pair distribution function of amorphous Fe^{3+} and Mg sulfate at each temperature. Both amorphous Fe^{3+} and Mg sulfate show very little structural change from 300 K to 100 K. At short-range ($<4 \text{ \AA}$), we see clear and consistent bonds of the SO_4 tetrahedra and the first Fe^{3+}/Mg coordination shell in the pair distribution functions. We also confirm that these sulfates are amorphous, as both have consistent coherence lengths around $8.3 - 8.4 \text{ \AA}$, with no discernable structural order at lengths $>8.5 \text{ \AA}$.

3.1 Introduction

The Mars Science Laboratory (MSL) Curiosity rover has been exploring the geology and geochemistry of Gale Crater, Mars, since 2012. Onboard Curiosity, instruments such as CheMin (Chemistry & Mineralogy), SAM (Sample Analysis at Mars), and APXS (Alpha Particle X-ray Spectrometer) have been used to characterize the complex mineralogy of Gale Crater, an ancient lake system with hundreds of meters of stratigraphy along Mt. Sharp (e.g. Blake et al., 2012; Cabrol et al., 1999; Campbell et al., 2012; Clark et al., 2024; Grotzinger et al., 2015; Hurowitz et al., 2017; Mahaffy et al., 2012). Throughout this traverse up Mt. Sharp, the Curiosity team has consistently found high abundances of X-ray amorphous material throughout the sediment and sedimentary rocks (Achilles et al., 2017; Bish et al., 2013; Blake et al., 2013; Dehouck et al., 2014; Ehlmann et al., 2017; Rampe et al., 2020a; Rampe et al., 2020b; Treiman et al., 2016; Vaniman et al., 2014; Yen et al., 2017). Truly amorphous materials are those that have no long-range crystal structure, and ‘X-ray amorphous’ materials include truly amorphous material, crypto- or nano-crystalline materials with a coherence length < 50 nm, as well as any material present below the detection limit for a given X-ray Diffractometer (XRD). For the CheMin XRD onboard Curiosity, this detection limit is about 3 wt% (Blake et al., 2012).

The composition of amorphous phases detected in Gale crater is variable, but typically includes significant amounts of FeO and SiO₂, as well as an abundance of volatiles such as S, Cl, and H₂O (e.g., Achilles et al., 2017; Achilles et al., 2020; David et al., 2022; Leshin et al., 2013; McAdam et al., 2020; Morris et al., 2016; Morrison et al., 2018; Rampe et al., 2020a; Rampe et al., 2020b; Rampe et al., 2018; Smith et al., 2021; Smith et al., 2022; Sutter et al. 2017). S-bearing phases are abundant in Gale crater as both crystalline and amorphous phases. There are many examples of detections of various crystalline sulfate minerals in Gale crater and across Mars, and

sulfate phases such as gypsum, bassanite, anhydrite, Fe-sulfates (e.g. jarosite), and Mg-sulfates (e.g. starkeyite) are common across Mars' surface (e.g., Blake et al., 2024; Chipera et al., 2023; Nachon et al., 2014; Rampe et al., 2017; Rapin et al., 2019; Vaniman et al., 2014). Smith et al., 2021 and Smith et al., 2022 characterized and summarized the amorphous S-bearing abundances of 19 drill samples from various formations below the clay-sulfate transition zone, and not only identified abundant S-bearing amorphous material throughout the stratigraphy, but also found that up to ~90 wt% of the bulk SO₃ in many samples is in an amorphous phase. More recently, the Curiosity rover has explored the clay-sulfate transition zone, and the overlying 'Layered Sulfate-bearing' unit of Mt. Sharp (Clark et al., 2024; Grotzinger et al., 2012; Milliken et al., 2010). These regions were initially characterized via orbital remote sensing (e.g., Fraeman et al., 2016; Milliken et al., 2010; Sheppard et al., 2022) as the stratigraphy transitions from mineralogy dominated by both clay and sulfate to assemblages dominated by sulfate and oxides. This change in mineralogy likely reflects a transition from wetter to dryer depositional environments (e.g., Meyer et al., 2024). Clark et al., (2024) used SAM evolved gas analysis to characterize drill samples spanning from the top of the clay-rich Glen Torridon region to the clay-sulfate transition zone, up through the Marker Band Valley, which marks the beginning of the layered sulfate unit as defined from orbit. That study, along with Seeger & Grotzinger (2024), showed the decrease in abundance of clay minerals, and an increase in the abundance of both crystalline and amorphous Mg-sulfates, along with variable amounts Ca-, and Fe- sulfates (Clark et al., 2024; Seeger & Grotzinger, 2024). Overall, Mg-, Fe-, and Ca- are the primary cations associated with sulfate throughout the stratigraphy of Gale crater. The overall ~20-90 wt% amorphous fraction of the total SO₃ in Gale crater drill hole has been calculated to include variable mixtures of Fe-, Mg-, and Ca-sulfate (Chipera et al., 2023; Smith et al., 2022). However, there are major considerations to make

regarding the seemingly ‘amorphous’ Ca-sulfate, which is possibly an error originating from the detection bias of Fe-rich amorphous coatings surrounding crystalline gypsum, bassanite, or anhydrite (Hopkins et al., 2026). Thus, for this study, we focus only on amorphous Mg- and Fe³⁺-sulfate.

Many studies since the landing of Curiosity have suggested several methods by which amorphous sulfates may form on Mars. These include induced amorphization by electrostatic discharge from Martian dust activities (Wang et al., 2020), brine-induced alteration of clays (Bristow et al., 2021; Thorpe et al., 2022), or products of brine desiccation/dehydration or cryoprecipitation (e.g., Chipera & Vaniman, 2007; Hopkins et al., 2023; Sklute et al., 2015; Sklute et al., 2018; Smith et al., 2021; Vaniman et al., 2004; Vaniman & Chipera, 2006), and polyhydrated Mg-sulfates such as epsomite, hexahydrite, and starkeyite transform to an amorphous Mg-sulfate under extremely dry environments (Chipera et al., 2023; Vaniman et al., 2004; Vaniman & Chipera 2006; Wang et al., 2006; Wang et al., 2011). Realistically, it is possible that many of these formation mechanisms occurred throughout the history of Gale crater and contributed to the high abundance of amorphous sulfate measured in Gale crater today.

Sulfates are often used to help interpret past environmental conditions, but it is not well understood how the varying sulfate crystallinity factors into the interpretations of Martian sediments and rocks. It is important for the interpretation of the geologic history of Gale crater to understand a clear distinction between amorphous sulfates and their crystalline counterparts, independent of the detection limits and interpretive lens of instruments onboard Curiosity. In this study, we approach this with three goals in mind: (1) determine the short-order atomic structure of amorphous Mg- and Fe³⁺-sulfate, (2) determine the coherence length of amorphous Mg- and Fe³⁺-sulfate, or the atomic distance where we can no longer distinguish ordered structure, and (3) if and

how the short-range structural order and coherence length change with temperature from 300 K to 100 K. To accomplish this, we acquired 2D diffraction and total scattering data of amorphous Mg- and Fe^{3+} -sulfates from 300 K to 100 K at the X-ray Powder Diffraction (XPD) beamline of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory (BNL). Using these data, we performed a Pair Distribution Function (PDF) analysis of amorphous magnesium sulfate (AMS) and amorphous ferric sulfate (AFS) at temperatures from 300 K to 100 K. A PDF plot describes the probability of finding a pair of atoms at a specific distance r , and can be used to characterize the short-range order of AMS and AFS, as well as their coherence lengths.

3.2 Methods

3.2.1 Sample Synthesis & Preparation

We synthesized both amorphous Mg- and Fe^{3+} -sulfate for this study. Our AMS was synthesized based on Vaniman et al. (2004), which showed that the polyhydrated Mg-sulfates epsomite and hexahydrite will dehydrate to an amorphous $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ in a rapidly desiccating low-RH atmosphere, such as a vacuum. For our AMS, we started with about ~25g of epsomite, which we desiccated in a vacuum bell jar at room temperature for about 3 days. After desiccation, the vial was sealed with parafilm. To synthesize our AFS, we followed a similar procedure based on Hopkins et al. (2023), Hopkins et al. (2026), and Xu et al. (2009). First, we made anhydrous ferric sulfate by heating hydrated ferric sulfate at 300 °C for 24 hours, with an initial ramp up rate of 60°C every 15 minutes in small batches (8–10 g each). This anhydrous ferric sulfate is also known as the mineral mikasaite. We allowed the mikasaite to deliquesce fully into a saturated ferric sulfate solution inside air-tight containers buffered to 92% RH. When the solution reached saturation after about 4 days under 92% RH, the solution was transferred into another air-tight container buffered to 11% RH using lithium chloride. In this low-RH atmosphere, the solution

desiccates and forms an amorphous ‘chip’. In a low-RH atmosphere lab, this chip of AFS was ground into a powder, and stored inside an airtight vial.

3.2.2 XPD Beamline Experiments

In preparation for XPD beamline analysis at NSLS-II, both the AMS and AFS samples were ground into fine powders, and placed inside 0.5 mm Kapton capillaries, sealed with air-tight clay. This step of the sample preparation was completed inside a controlled laboratory facility at BNL. Total scattering of each sample was collected at the XPD beamline. The wavelength of the synchrotron beam was 0.181 Å, and we acquired the diffraction data from 0-53° 2 θ . We also acquired data of the empty 0.5 mm Kapton capillaries, and a CeO₂ calibration standard. A nitrogen cryostream was used to cool the capillaries, and we attempted to make measurements of each sample from 300 K to 100 K with a measurement every 5 K. We were able to achieve all of these measurements with the AFS sample, but with the AMS sample, we encountered issues with water ice condensing on the outside of the Kapton capillaries once the temperature reached below ~180 K. Thus, we acquired data at every 5 K from 300-180 K, and every 10 K from 180-100 K for the AMS sample, which decreased the overall cooling time at cryo-temperatures, allowing for less time for ice to form and more time to clear any ice between measurements. We acquired data of the CeO₂ standard at 300, 200, and 100 K. Before each measurement step, we held the sample for 4 minutes at the specified temperature to allow the sample to homogenously equilibrate with the cryostream. After equilibrating, diffraction data was collected over a 4-minute scan, along with an associated 4-minute dark scan at each temperature step. Each measurement of the empty Kapton capillaries and CeO₂ were also 4-minute scans.

3.2.3 Data Reduction & Pair Distribution Function Analysis

The raw total scattering data was first processed using the software Dioptas (Prescher & Prakapenka, 2015). The diffraction data of CeO₂ was used to calibrate parameters used to integrate the diffraction data of our AMS and AFS. The resulting calibration parameters can be found in Table B1 in Appendix B. Once the calibration parameters were determined, each individual 2D pattern of AMS and AFS at each temperature step was visually inspected. Masks were applied to remove any shadows caused by the sample holder and post, and to remove any spurious scattering from external water ice crystals. After sufficient masking, the 2D diffraction rings were integrated, and the resulting data was exported for the next step in the analysis. PDF analysis was completed using the python program ‘PDFgetX3’ (Juhás et al., 2013). Example configuration parameters used for these analyses can be seen in Appendix B. ‘PDFgetX3’ calculates the PDF $G(r)$ through a pipeline of equations, starting with the diffraction intensities $I(Q)$ in Q -space ($\text{\AA}^{-1}$), which are corrected by a polynomial fit and normalized by scattering factors to the total scattering structure function $S(Q)$. The reduced structure function $F(Q)$ is then calculated as equal to $Q(S(Q) - 1)$, and the PDF $G(r)$ is calculated as the sine Fourier transformation of the reduced structure function:

$$G(r) = \frac{2}{\pi} \sum_{Q_{min}}^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ$$

or

$$G(r) = \frac{2}{\pi} \sum_{Q_{min}}^{Q_{max}} F(Q) \sin(Qr) dQ \quad (1)$$

For amorphous samples, the PDF $G(r)$ should oscillate around and converge to 0 with increasing distance r . Further explanations and derivations of these equations can be found in Egami and Billinge (2012), Keen (2001), Neder and Proffen (2020), and Terban and Billinge (2022).

3.3 Results

3.3.1 Diffraction Patterns

Figure 3.1 shows the 2D diffraction patterns and 1D integrated diffraction plots for AFS at 300, 200, and 100 K. Both samples were confirmed to be amorphous from this initial data, as the diffraction patterns show no sharp concentric rings at any temperature. For AFS, we see two bright but broad features at ~ 1 and $2.5^\circ 2\theta$, with additional broad peaks at $\sim 6^\circ$ and $\sim 9.5^\circ$. These features remain consistent throughout all temperatures in this study. There is a slight increase in noise due to ice crystals condensing on the outside of the capillaries, as seen around $4.5 - 5^\circ 2\theta$. For AMS, we see one significant broad feature at $\sim 2.6^\circ 2\theta$, with a series of weaker broad features from $\sim 5 - 10^\circ 2\theta$, as seen in Figure 3.2. As with the AFS, we do not see any significant changes in the diffraction pattern of AMS from 300 K to 100 K. All integrated diffraction patterns of AFS and AMS at all temperatures are available in Appendix C.

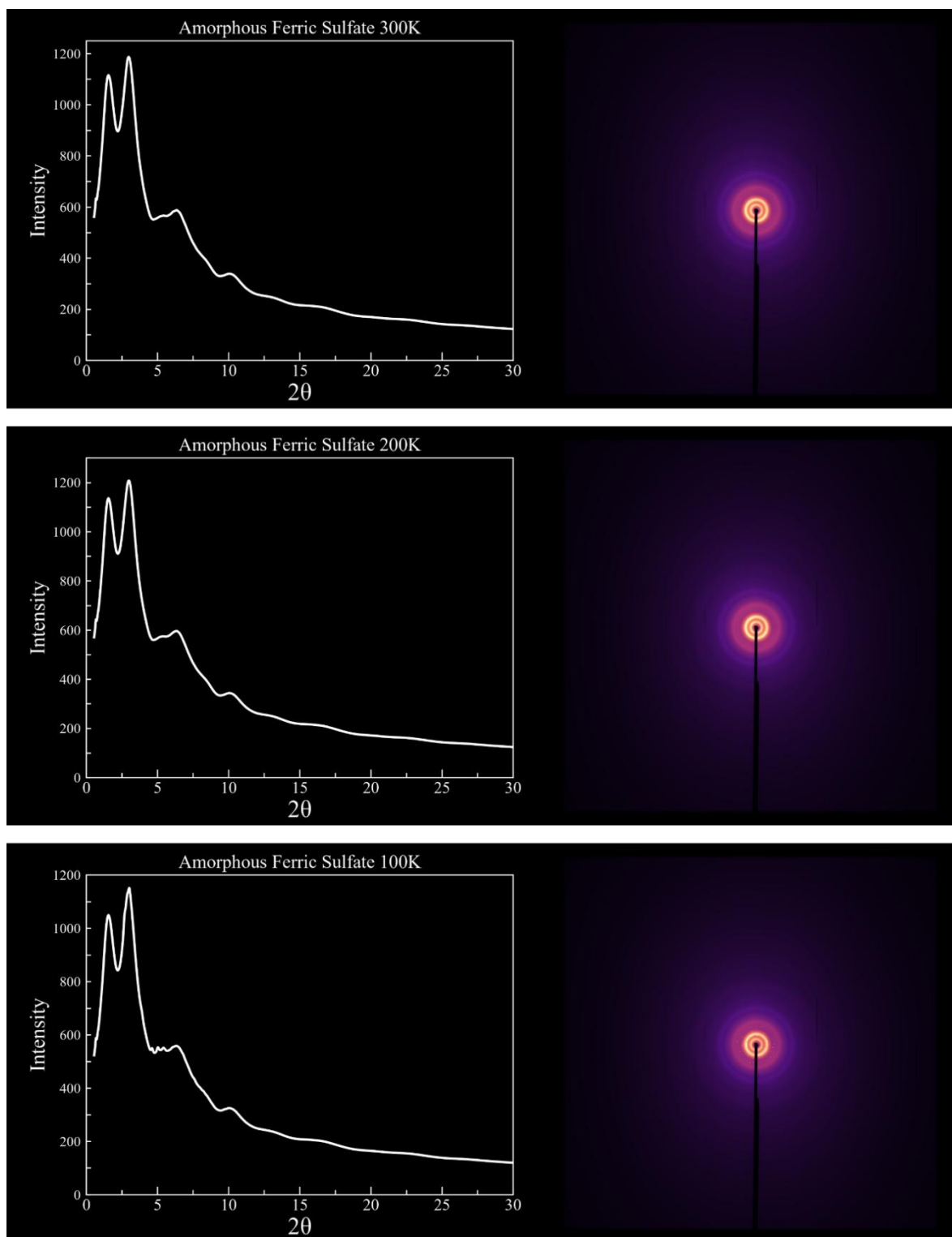


Figure 3.1 (Left) Integrated diffraction pattern of Amorphous Ferric Sulfate at three representative temperatures of 300 (top), 200 (middle), and 100 K (bottom) from 0-30° 2θ. (Right) Images of the raw data diffraction rings of Amorphous Ferric Sulfate at the three representative temperatures. Raw diffraction data integration and visualization was completed using the software Dioptas (Prescher & Prakapenka, 2015).

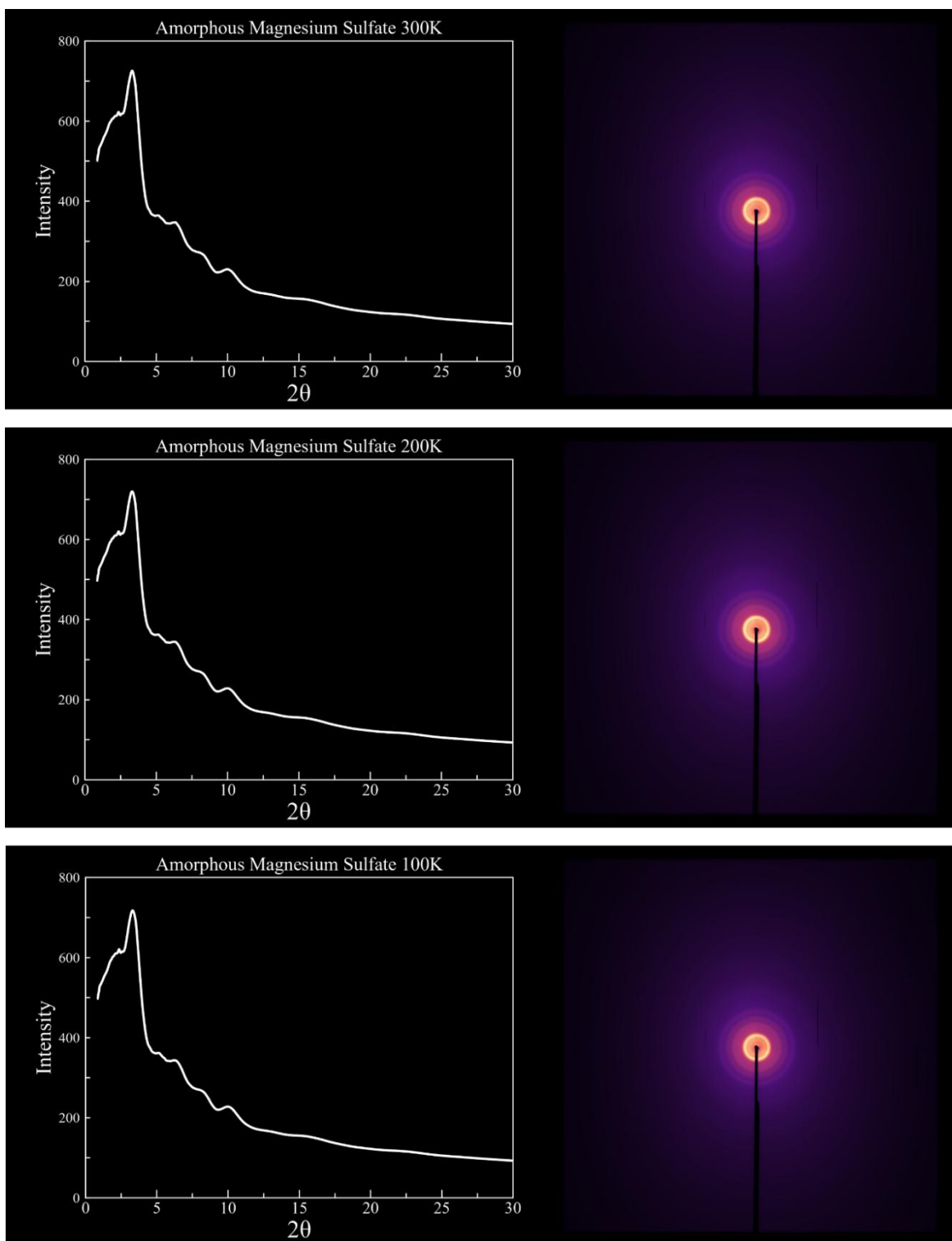


Figure 3.2 (Left) Integrated diffraction pattern of Amorphous Magnesium Sulfate at three representative temperatures of 300 (top), 200 (middle), and 100 K (bottom) from 0-30° 2θ. (Right) Images of the raw data diffraction rings of Amorphous Magnesium Sulfate at the three representative temperatures. Raw diffraction data integration and visualization was completed using the software Dioptas (Prescher & Prakapenka, 2015).

3.3.2 Pair Distribution Function

Starting with the integrated diffraction patterns of AFS and AMS from Dioplas, we calculate the PDF, $G(r)$, of each sample at each temperature using 'PDFgetx3' (Juhás et al., 2013). Importantly, we had to set an upper Q cutoff (Q_{max}) for the sine Fourier transformation (Equation 1). To do this, we first assessed the optimal Q value, just below where we see significantly increased noise and anomalies in the structure function $S(Q)$ and in the atomic form factor, or reduced structure function, $F(Q)$, which may cause the $S(Q)$ and $F(Q)$ to not converge cleanly to 1 and 0, respectively. Example $S(Q)$ and $F(Q)$ plots with an unoptimized Q_{max} of $30 \text{ \AA}^{-1}$ can be seen in Figure 3.3 for AFS and Figure 3.4 for AMS. From both samples, we determined an optimal value of $Q_{max} = 17 \text{ \AA}^{-1}$, which resulted in clean structure function plots and $G(r)$ plots with very good signal-to-noise.

Figure 3.5 shows the resulting PDF $G(r)$ plots of AFS for all measured temperatures. The striking result from this PDF analysis was that there was no significant change in the PDF from 300 K to 100 K. The peak positions, width, and relative intensities remained consistent throughout the cooling. This includes the coherence length, which we interpret to be at $\sim 8.3 \text{ \AA}$ for AFS. After this coherence length, there is no discernable structure information from the PDF, and so our AFS sample is confirmed to be amorphous at all temperatures. Figure 3.7 gives a more detailed view of the PDF of AFS at three representative temperatures of 300, 200, and 100 K, with peaks in the PDF assigned to atomic pairs. Sharper peaks from 1 – 3.5 $\text{\AA}$ are due to specific atomic pairs. We see the S-O bonds that make up the SO_4 tetrahedra at 1.49 $\text{\AA}$, with the O-O pair at 2.43 $\text{\AA}$ showing neighboring oxygen within these tetrahedra. At 1.99 $\text{\AA}$, we see the Fe-O bonds within the FeO_6 octahedra, with O-O pairs at 2.79 $\text{\AA}$ showing the neighboring oxygen within these octahedra. Finally, we have the Fe-S pair distances showing a peak at 3.25 $\text{\AA}$, representing the distance between the two closest O-sharing SO_4 and FeO_4 centers within the AFS. The complete first shell

S and Fe coordination environments are represented within ~ 3.5 Å. Above 3.5 Å, we begin to see 2nd order shells and higher, describing the mid-range connectivity of multiple SO₄ and FeO₆ polyhedra, with features combining to form broader PDF peaks. The longer the distance r , the more difficult it becomes to interpret the specific atomic pairs contributing to the broad combined peaks. The last structurally significant feature we see is at 8.33 Å, but this feature is a combination of many indistinguishable atomic pairs.

Figure 3.6 shows the resulting PDF $G(r)$ plots of AMS for all measured temperatures. Note again that from 180 K to 100 K, we measured every 10 K rather than 5 K due to issues with external ice on the capillaries. The AMS follows the same trend as the AFS, and we do not see any significant changes in the PDF from 300 K to 100 K. We interpret a coherence length for AMS at ~ 8.4 Å, slightly longer than that of AFS, but still consistent across all measured temperatures. Figure 3.8 shows the PDF of AMS at 300, 200, and 100 K in more detail. Again, we see the S-O bonds of the SO₄ tetrahedra represented as a PDF peak at 1.48 Å. We see the Mg-O bonds of the octahedra coordination site at 2.01 Å. We see the two O-O features at 2.38 Å and 2.79 Å from within the SO₄ and MgO₆ coordination sites, respectively. At 3.33 Å, we see the feature associated with the distance between the S and Mg site centers. After this feature, we begin to see 2nd order and higher coordination shells features combining to form broader PDF peaks. The longest discernable feature we see in AMS is a weak combination feature at 8.42 Å.

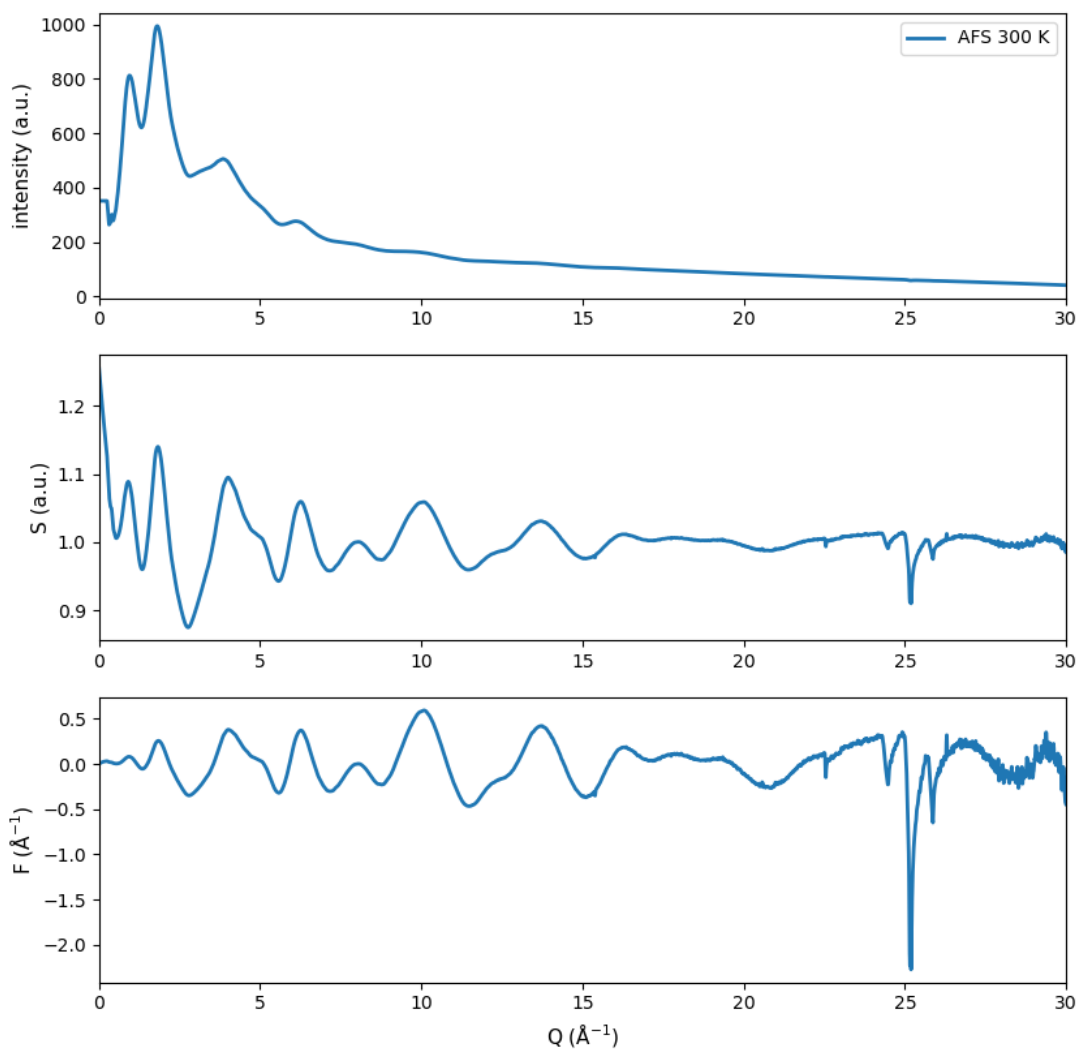


Figure 3.3 (Top) Diffraction intensity profile, $I(Q)$, of AFS at 300 K from 0-30 $\text{\AA}^{-1}$. (Middle) The total scattering structure function, $S(Q)$ with $Q_{\text{max}} = 30 \text{ \AA}^{-1}$. (Bottom) The reduced structure function, $F(Q)$, with $Q_{\text{max}} = 30 \text{ \AA}^{-1}$. The software PDFgetX3 was used for these calculations (Juhás et al., 2013).

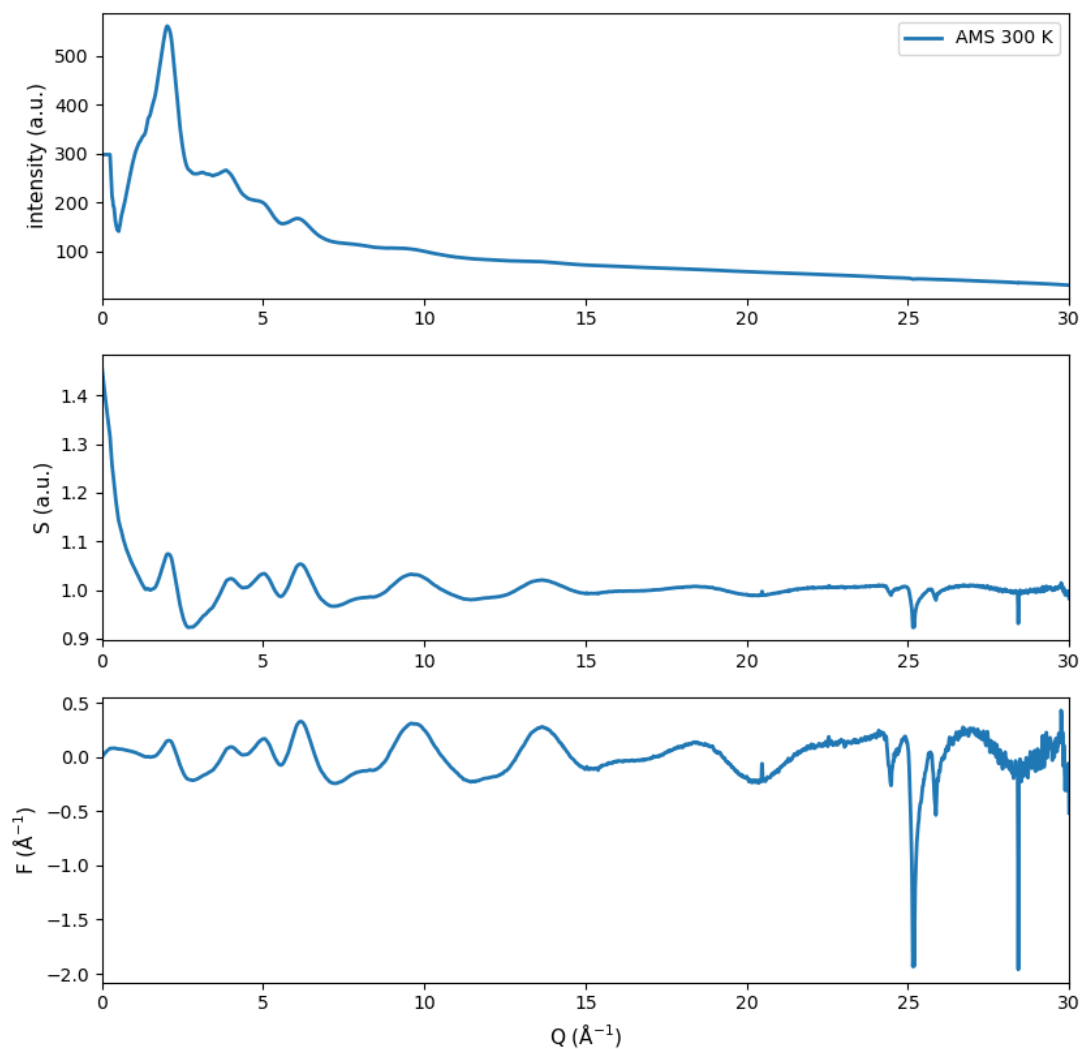


Figure 3.4 (Top) Diffraction intensity profile, $I(Q)$, of AMS at 300 K from 0-30 $\text{\AA}^{-1}$. (Middle) The total scattering structure function, $S(Q)$ with $Q_{\text{max}} = 30 \text{ \AA}^{-1}$. (Bottom) The reduced structure function, $F(Q)$, with $Q_{\text{max}} = 30 \text{ \AA}^{-1}$. The software PDFgetX3 was used for these calculations (Juhás et al., 2013).

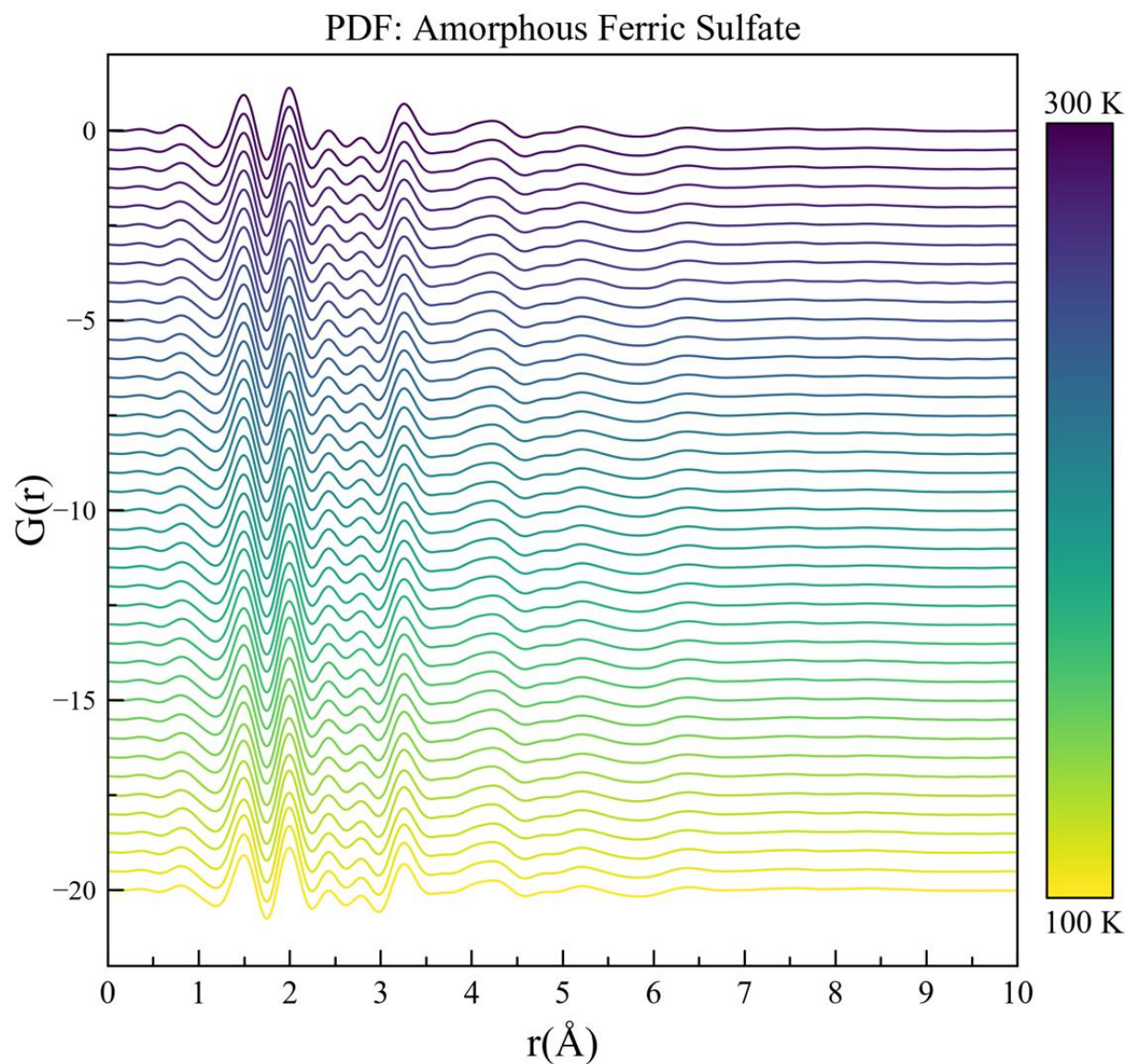


Figure 3.5 Pair Distribution Function plots of our Amorphous Ferric Sulfate samples from 0-10 $\text{\AA}$ at all measured temperatures, with patterns offset for visual clarity. The software PDFgetX3 was used for these calculations (Juhás et al., 2013).

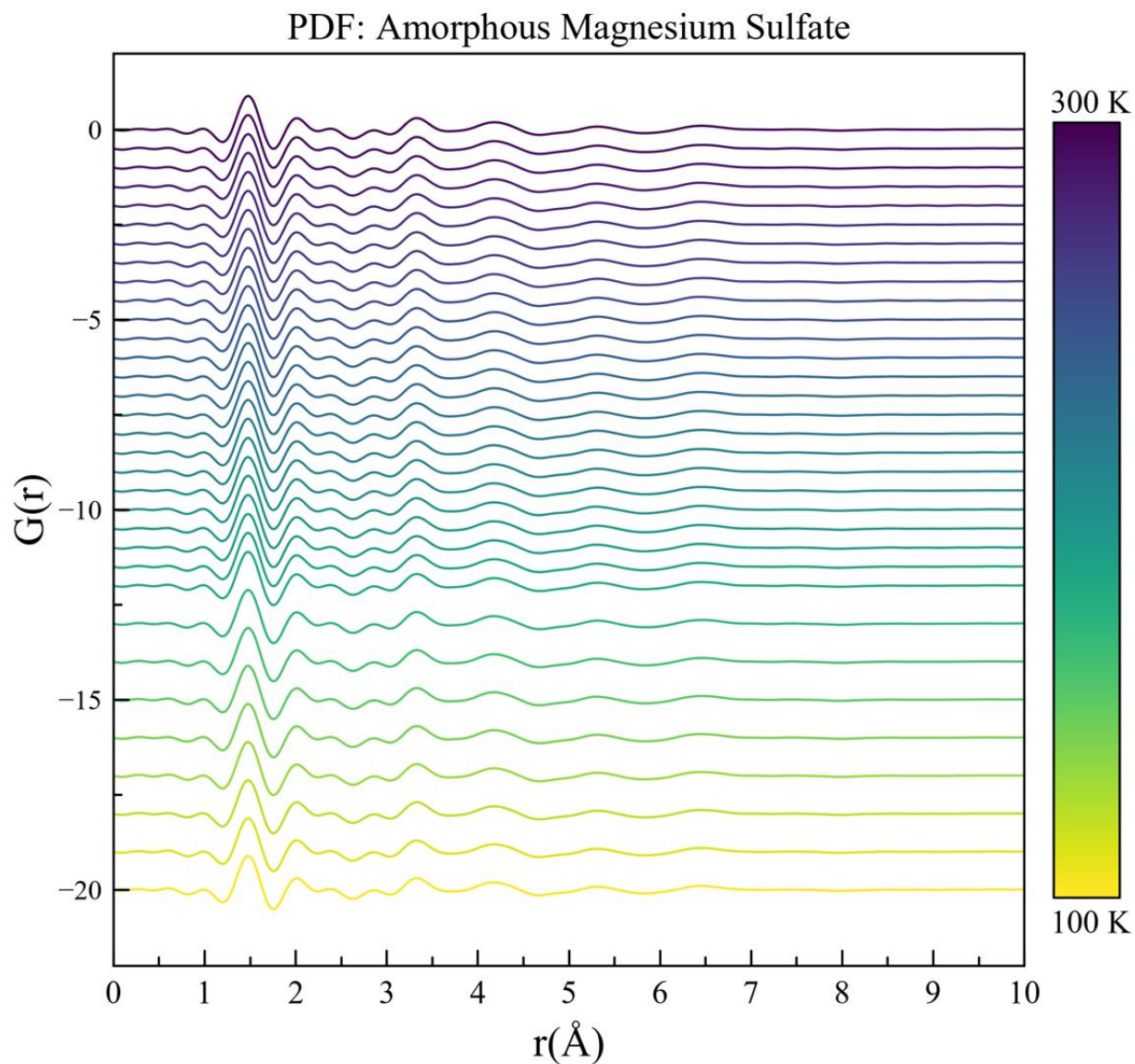


Figure 3.6 Pair Distribution Function plots of our Amorphous Magnesium Sulfate samples from 0-10 $\text{\AA}$ at all measured temperatures, with patterns offset for visual clarity. The software PDFgetX3 was used for these calculations (Juhás et al., 2013).

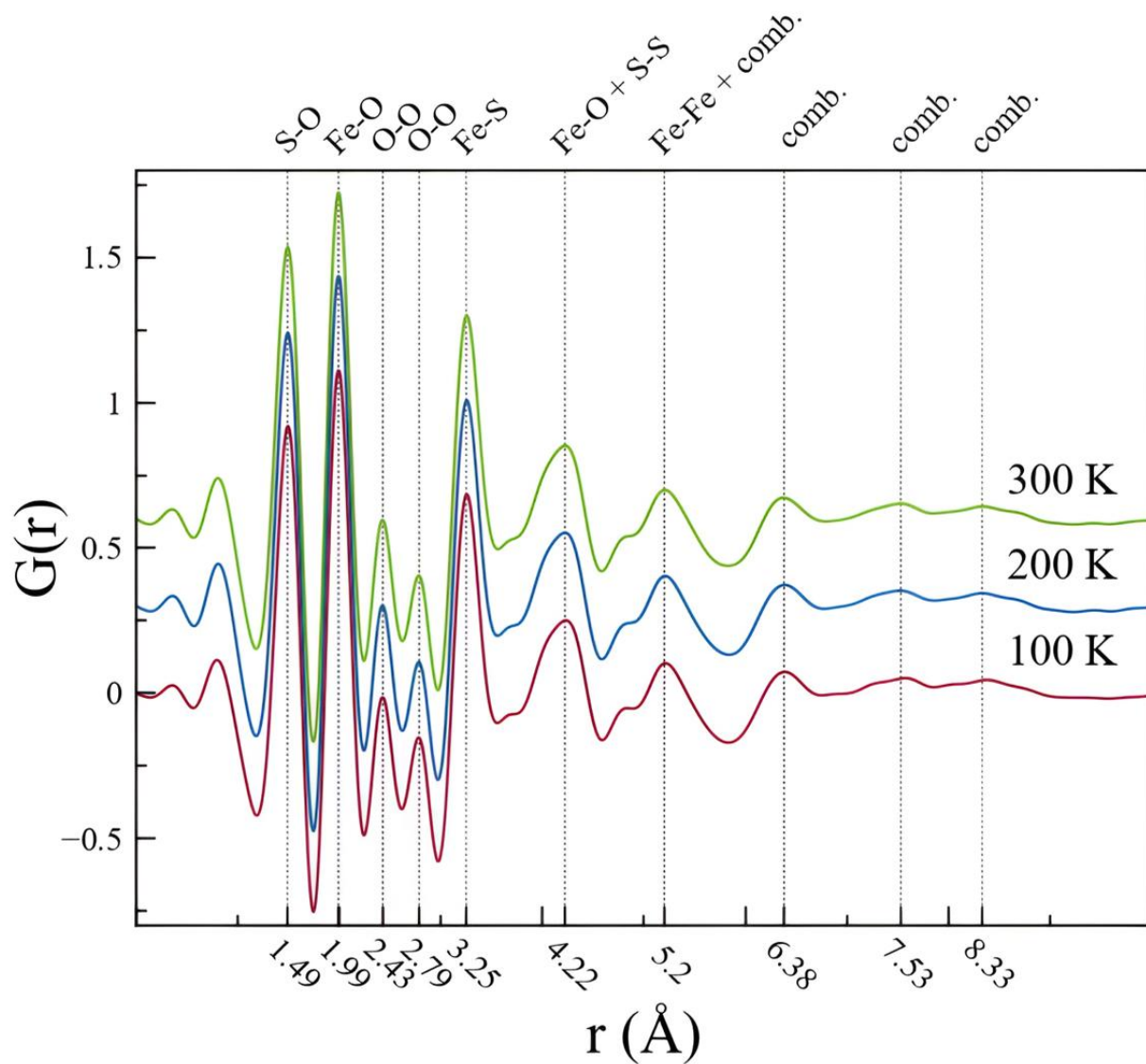


Figure 3.7 Pair Distribution Function plots of our Amorphous Ferric Sulfate samples from 0-10 Å at three representative temperatures of 300, 200, and 100 K, with patterns offset for visual clarity. Vertical lines indicate the radius at which specific atomic pairs cause a peak in the PDF plot. ‘comb’ refers to multiple combinations of pairs that cannot be individually distinguished. The software ‘PDFgetX3’ was used for these calculations (Juhás et al., 2013).

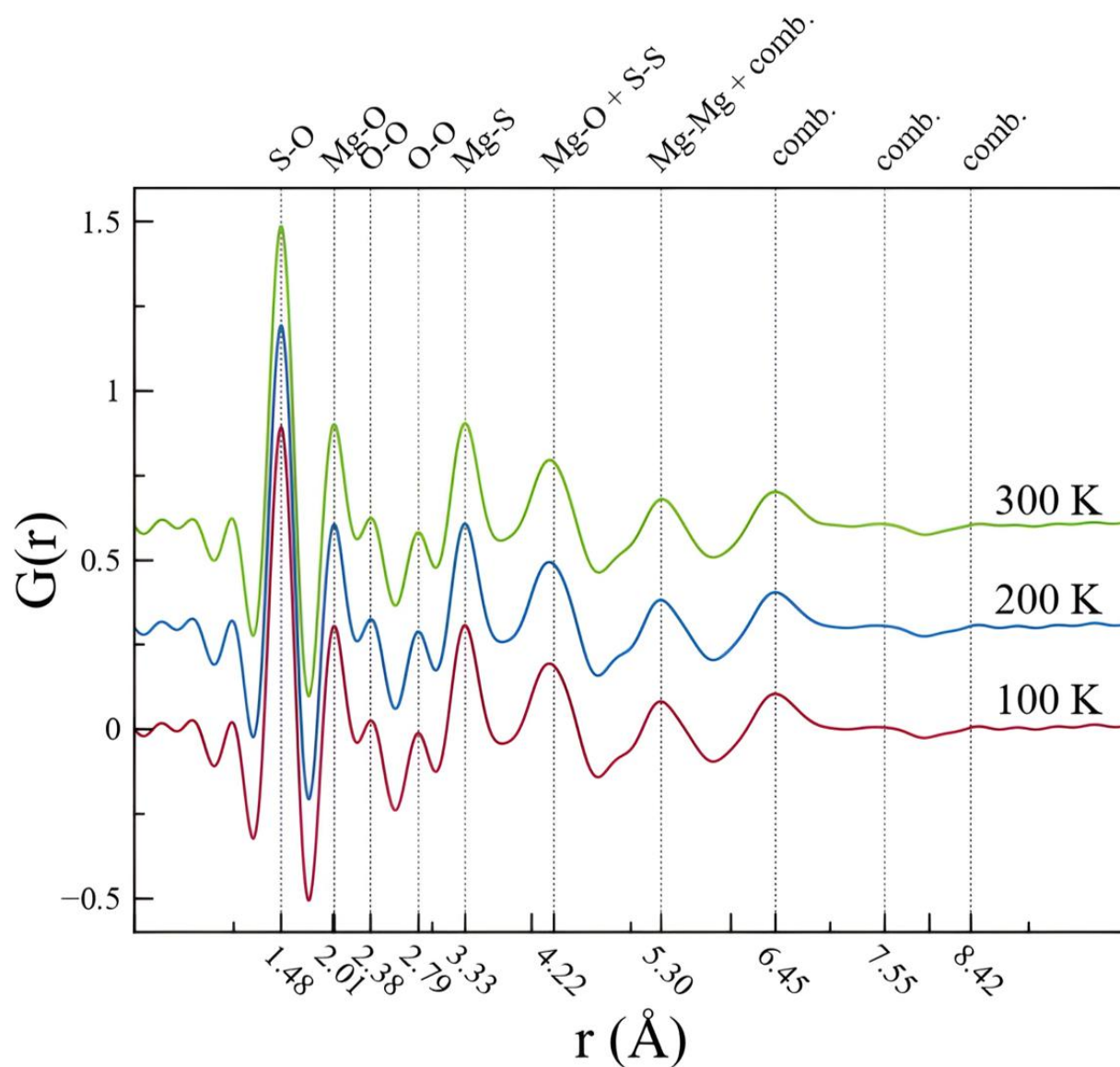


Figure 3.8 Pair Distribution Function plots of our Amorphous Magnesium Sulfate samples from 0-10 Å at three representative temperatures of 300, 200, and 100 K, with patterns offset for visual clarity. Vertical lines indicate the radius at which specific atomic pairs cause a peak in the PDF plot. ‘comb’ refers to multiple combinations of pairs that cannot be individually distinguished. The software ‘PDFgetX3’ was used for these calculations (Juhás et al., 2013).

3.4 Discussion

3.4.1 Thermal Behavior of AFS and AMS

We were surprised that for both AFS and AMS, there were no noticeable differences in the diffraction patterns or PDF patterns with decreasing temperature. There are no available published values for the thermal expansion coefficient for AFS or AMS, but we still expect to see some change in the structure from 300 K to 100 K. Both AFS and AMS are hydrated phases (David et al., 2022; Vaniman et al., 2004; Wang et al., 2006), and we expected to see thermal contraction with decreasing temperatures due to these structural waters. While our AMS was dehydrated in its amorphization process, it still maintains some hydration, with around two structural H₂O likely (Vaniman et al., 2004; Wang et al., 2006). The stable crystalline material most similar to our AMS is the monohydrated Mg-sulfate mineral kieserite, MgSO₄·H₂O. Kieserite shows significant structural changes with decreasing temperature, including a complex negative thermal expansion along the *b*-axis, and anisotropic expansion perpendicular to the *b*-axis (Wildner et al., 2022). Our AFS retains around five structural H₂O after desiccation (Hopkins et al., 2026; Ling & Wang, 2010). While it is less similar, the best available published thermal expansion comparison for AFS is for the mineral jarosite, KFe₃(SO₄)₂(OH)₆. Jarosite's structure exhibits complex thermal behavior with strong anisotropy, as the *c*-axis expands at a rate ten times greater than that of the *a*-axis (Xu et al., 2010). While these are not direct comparisons, we did expect to see at least some change in the diffraction patterns and PDF patterns.

One possible explanation relates to the scale at which we are measuring these atomic distances. Our cleanest and most well-resolved data comes from within the first-shell coordination sites, where we may not expect to see drastic changes with rigid structures, such as the SO₄ tetrahedra. Sklute et al. (2015) showed that at room temperature, the first-shell S-O and Fe-O

features in the PDF of multiple different crystalline and amorphous ferric sulfate phases are nearly identical, and that structures under ~ 3 Å are fairly rigid. Any thermal contraction may be most likely apparent as changes to the distance between the SO_4 and Fe/Mg octahedral site centers, or at greater distances into and above the 2nd shell. However, it is at these longer distances, past the first coordination shell, where we start to see broadening of our PDF features due to the combination of multiple peaks. The Δr resolution for our PDF data can be calculated as $\Delta r \approx 2\pi/Q_{\text{max}}$, which results in a Δr resolution of ~ 0.37 Å for our PDF data. It is likely that any small thermal contractions are shorter than our PDF resolution and are therefore unseen in our data, especially at mid-range among the broader combination features. For comparison, we can briefly look ahead to Chapter 4, where we determine the thermal contractions within the anhydrous ferric sulfate mikasaite ($\text{Fe}_2(\text{SO}_4)_3$). The Fe-S distances in mikasaite, or the distances between the first O-sharing tetrahedra and octahedra site centers, at most only changes by ~ 0.25 Å, well below the Δr resolution of ~ 0.37 Å for our PDF data. While AFS is not anhydrous and may behave differently, its small-scale structure would likely be comparable to that of mikasaite.

3.4.2 Short-Range Order & Coherence Length

While we do not see noticeable difference within AFS and AMS from 300 K to 100 K, we can still compare differences in the short-range order between AFS and AMS. The SO_4 tetrahedra show slight differences between AFS and AMS. For AFS (Figure 3.7), we see a most probable S-O distance of 1.49 Å, and intra-tetrahedral O-O distances show a distance of 2.43 Å, which is consistent with the room temperature PDF analysis of AFS by Sklute et al. (2015). The SO_4 tetrahedra of our AMS shows a S-O distance of 1.48 Å, but a 0.01 Å difference is just one pixel with our measurement resolution, so this is within error (Figure 3.8). We see a bigger difference with the intra-tetrahedral O-O distances, with AMS showing first shell SO_4 O-O distances of 2.38

Å, slightly shorter than in AFS. These shorter intra-tetrahedral O-O distances in AMS are interesting, given that our S-O distance is about the same as in AFS, and we would normally expect the SO_4 tetrahedra shape to be maintained with equidistant O-O pairs. One clue is the width of the O-O features at 2.43/2.38 Å. This feature appears wider in the PDF of AMS than for AFS, which could mean that the SO_4 tetrahedra shape is less consistent and may have variable levels of distortion.

Next, we look at the first shell Fe-S and Mg-S distances, or the distances between the oxygen-sharing SO_4 tetrahedra and $(\text{Fe/Mg})\text{O}_6$ octahedra centers. For AFS, we see a sharp strong PDF feature at 3.25 Å. This feature is also consistent with the room temperature PDF measurement of AFS by Sklute et al. (2015). The Mg-S feature of AMS is centered at 3.33 Å, but is again slightly broader than the Fe-S feature of AFS. This may indicate more variable distortions in the MgO_6 octahedra than the FeO_6 octahedra. We see a similar difference in the intra-octahedral O-O distances. These O-O distances for both AFS and AMS are at 2.79 Å, but this feature is broader for AMS. This trend of slightly broader features in the PDF of AMS than AFS may be due to the differences in the synthesis of these materials. AMS was synthesized from the dehydration of solid crystalline polyhydrated magnesium sulfate. This initial hydrated magnesium sulfate was likely a mixture of hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), with unknown proportions. This initial uncertain mixture of hydration states of the starting material may have led to slightly variable degrees of hydration, or minor structural variability, in the final AMS. Contrastly, AFS was synthesized via rapid desiccation of a homogenous ferric sulfate solution, and the resulting AFS should also be homogenous.

The exact coherence length can be subjective, depending on what length in the PDF one interprets the loss of significant structural features. We estimated the coherence length of AFS and

AMS by denoting the center position of the last PDF feature that appeared significantly more intense than the normal noise and oscillation around zero. This last feature, and our interpretation of the coherence length, occurs at 8.33 Å for AFS and at 8.42 Å for AMS. As with other features, this coherence length does not appear to change with temperature.

3.5 Conclusions

We successfully acquired total scattering data of AFS and AMS from 300 K to 100 K at the XPD beamline of NSLS-II. Our initial diffraction patterns confirmed the amorphous nature of both AFS and AMS, at all measured temperatures, however, we did not see any changes in the diffraction patterns with decreasing temperature. We used PDF analysis to characterize the short-range order of AFS and AMS, and identified the most probable atomic distances within and between the first shell SO_4 tetrahedra and $(\text{Fe/Mg})\text{O}_6$ octahedra. Using the last discernable PDF feature, we interpreted the coherence length of AFS to be 8.33 Å and the coherence length of AMS to be 8.42 Å. We do not see any noticeable differences in any of the PDF patterns of AFS and AMS with decreasing temperature. A potential cause of this lack of differences with temperature could be due to broad combination features of the second and third shells masking any small distance thermal contractions in the PDF, and the structures in the first shell being too rigid to noticeably contract with decreasing temperature. Any small thermal contractions that occur in these 2nd and higher order shells are likely smaller than our Δr PDF resolution can discern (~ 0.37 Å). This study provides valuable low temperature diffraction data of AFS and AMS, but further work is required to fully characterize these structures. This further work includes more detailed modelling of the structure of these amorphous sulfates, to determine overall orientation of the sulfate tetrahedra and Fe/Mg octahedra, including any differences in bond angles with temperature.

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Chapter 4

Refinement of the Crystal Structure of Trigonal Mikasaite $\text{Fe}_2(\text{SO}_4)_3$ at Mars-Relevant Low Temperatures

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Abstract

Mikasaite, $\text{Fe}_2^{3+}(\text{SO}_4)_3$, is a rare anhydrous ferric sulfate mineral, and the anhydrous endmember of an environmentally significant series of hydrated ferric sulfate phases. Mikasaite has applications as a Mars-analog material and is relevant to acid mine drainage mineralogy. Despite this, no crystallographic study of mikasaite at low temperatures has previously been published. Here we present the first systematic characterization of the crystal structure of trigonal mikasaite as a function of temperature, using X-ray powder diffraction and Rietveld refinement across eight temperatures from 25 °C to -114 °C.

Rietveld refinement of each diffraction pattern resulted in reliable structural data of mikasaite, with weighted residuals consistently between ~1.8 - 2.5%. All patterns contained a mixture of naturally occurring trigonal (~79 wt%) and synthetic monoclinic (~21 wt%) mikasaite. This study focuses on trigonal mikasaite. No evidence of a phase transition was observed across the full temperature range. The unit cell contracts with decreasing temperature, driven predominantly by shortening of the a -axis from 8.267(6) Å at 25 °C to 8.245(5) Å at -114 °C. In contrast, the c -axis shows no clear systematic trend within uncertainty, indicating that thermal contraction in mikasaite is strongly concentrated along the a -axis. A volumetric thermal expansion coefficient of $\alpha_V = 3.64 \pm 0.64 \times 10^{-5} \text{ K}^{-1}$ was determined by linear regression of $\ln(V)$ against temperature, consistent with values reported for other anhydrous sulfates including anhydrite (3.66

$\times 10^{-5} \text{ K}^{-1}$) and $\alpha\text{-MgSO}_4$ ($3.74 \times 10^{-5} \text{ K}^{-1}$). Ellipsoid fitting of the two distinct FeO_6 coordination sites reveals that the Fe1 site is primarily oblate and the Fe2 site prolate across the temperature range. Trends, or lack thereof, in the fitted ellipsoids suggest that there may be multiple factors affecting the mikasaite structural data.

4.1 Introduction

Mikasaite is a rare secondary anhydrous ferric sulfate mineral with formula $\text{Fe}_2^{3+}(\text{SO}_4)_3$. It is the Fe analogue of millosevichite, $\text{Al}_2(\text{SO}_4)_3$, and was discovered as a sublimation mineral around coal-gas escape seams in Ikushunbetsu, Mikasa City, Hokkaido, Japan (Miura et al., 1994). At room temperature, mikasaite crystallizes in a trigonal lattice, with space group $R\bar{3}$, and unit cell parameters of $a = 8.14(1) \text{ \AA}$, $c = 21.99(8) \text{ \AA}$, $Z = 6$ (Masse et al., 1973; Miura et al., 1994; Rentzeperis & Christidis, 1976). There also exists a synthetic monoclinic polymorph of mikasaite, with space group $P2_1/n$ and cell parameters of $a = 8.2966(5)$, $b = 8.5353(6)$, $c = 11.6242(5)$, $\beta = 90.729(3)^\circ$, $Z = 4$. (Christidis & Rentzeperis, 1975; Majzlan et al., 2005). Mikasaite has only been found in nature in its trigonal form (Miura et al., 1994), thus, in this study we refer to the trigonal form of mikasaite, unless otherwise stated.

Although rare, mikasaite is recognized as a signature mineral of fumarole encrustations and burning coal-dumps, typically alongside minerals such as millosevichite, efremovite, godovikovite, sabieite, and steklite. (Košek et al., 2018; Parafiniuk & Kruszewski, 2009). It is generally more common for ferric sulfates to form as hydrates, but the higher temperatures ($\geq 300^\circ\text{C}$) around environments such fumaroles or burning coal pits results in the precipitation of anhydrous ferric sulfate (Fang & Robinson 1970; Miura et al., 1994; Robinson & Fang, 1971, 1973). In general, mikasaite is the anhydrous endmember of a series of important hydrated sulfates, including kornelite ($\text{Fe}_2(\text{SO}_4)_3 \cdot \sim 7\text{-}8\text{H}_2\text{O}$), coquimbite/paracoquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$), and

rhomboclase ($\text{H}_5\text{FeO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$) (Majzlan et al., 2005). These sulfates are environmentally significant because they can store metals in a highly soluble form, for example, in the context of acid mine drainage (e.g. Nordstrom & Alpers, 2000), and their stability is typically sensitive to both temperature and relative humidity (RH). Mikasaite is substantially deliquescent and easily dissolves from absorbing atmospheric water. This is one reason why it is not particularly common on Earth, as it requires RH of less than ~10-15% to remain solid and anhydrous (e.g. Hopkins et al., 2023; Xu et al., 2009; Xu & Parise, 2012). Xu et al. (2009) found that both monoclinic and trigonal $\text{Fe}_2(\text{SO}_4)_3$ remain anhydrous at 11% RH or below, and then hydrates sequentially from ferricopiapite, rhomboclase, and kornelite, to paracoquimbite at RH between 33% and 53%. Mikasaite's simple stoichiometry and deliquescent nature has made it useful as a baseline for studying the formation and stability of ferric sulfate minerals in dry environments, such as Mars, where many ferric sulfate minerals have been identified (e.g., Berger et al., 2016; Bishop et al., 2004; Burns, 1987; Lane et al. 2004; Morris et al., 2006; Smith et al., 2022). Mikasaite has also been used for several laboratory-based Mars-analog studies as a consistent precursor to form a Fe^{3+} -rich sulfate solution via deliquescence, used to synthesize a range of Mars-analog materials, such as amorphous ferric sulfate (e.g., Hopkins et al., 2023, 2026; Sklute et al., 2015, 2018; Xu et al., 2009; Xu & Parise, 2012). Although mikasaite has relevance in the mineralogy of cold environments like Mars, its thermal behavior at low temperatures is not well understood, and has not been published. For comparison, thermal expansion has been investigated for several other minerals which mikasaite is structurally related through its trigonal framework of corner-sharing FeO_6 octahedra and SO_4 tetrahedra. Xu et al. (2010) investigated the thermal expansion and decomposition of deuterated jarosite using neutron diffraction, finding that the *c*-axis expands about ten times greater than the *a*-axis, attributing this anisotropy to the differential thermal

response of the octahedral-tetrahedral sheets stacked along [001]. Zema et al. (2012) traced thermal expansion of alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, through de-hydroxylation and structural collapse. At low temperatures, a single-crystal XRD study of synthetic $\text{Na-H}_3\text{O}$ jarosite at 102 K revealed anisotropic unit cell contraction, with the *c*-axis contracting by 0.45% compared to only 0.03% along the *a*-axis (Najorka et al., 2016). In a study on the thermal behavior of römerite over a range of Mars-relevant temperatures, Borisov et al. (2025) found that the thermal expansion coefficient α_{33} is negative throughout the range from -173 °C up to the decomposition of römerite, which undergoes amorphization around 60 °C. Further heating resulted in the crystallization of mikasaite between 250 and 525 °C (Borisov et al., 2025).

Despite its common use in current Mars-analog studies, environmental relevance in the context of both acid mine drainage and Martian iron sulfate mineralogy, and overall importance as the anhydrous endmember for ferric sulfate mineralogy, there are no published crystallographic studies of mikasaite at low temperatures. This study aims to fill this knowledge gap directly with a systematic characterization of the crystal structure of mikasaite as a function of temperature using X-ray powder diffraction, including the determination of mikasaite's thermal expansion coefficient over low-temperatures.

4.2 Methods

4.2.1 Sample Preparation

Mikasaite was prepared by first grinding hydrated ferric sulfate $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ into a fine powder, and heating the ferric sulfate at 300 °C for 24 hr in an oven, dehydrating the materials to form mikasaite (Hopkins et al., 2023; Hopkins et al., 2026; Xu et al., 2009). This analysis, and all subsequent analyses, were completed within rooms that had their relative humidity monitored. The relative humidity in these rooms remained below the threshold for deliquescence (~33% RH), and

was mostly below ~10% RH, thus there was no concern of our mikasaite rehydrating (Xu et al., 2009). Regardless, the mikasaite was kept inside a glass vial sealed with parafilm, and its diffraction pattern was checked throughout this analysis, and no evidence for rehydration was seen. During the initial heating, the mikasaite did form some clumps, which were manually broken apart in a mortar and pestle, but no further grinding was required.

4.2.2 X-ray Diffraction

We used a Rigaku Ultima IV with CuK α radiation (1.5428 Å) to acquire diffraction data of our mikasaite. To collect low-temperature diffraction data, we used the low/medium-temperature R300 attachment, a Rigaku liquid nitrogen flow controller, and a programmable temperature controller, allowing for precise temperature ramping and holding. The sample holder was a copper-alloy plate with a high thermal conductivity, allowing for efficient cooling of our mikasaite. The sample holder was placed inside Rigaku's airtight sample attachment, featuring an airtight polyimide window with an aluminum coating. The mikasaite was measured under vacuum in this airtight chamber attachment, to minimize X-ray attenuation and prevent any opportunity for the mikasaite to rehydrate or adsorb atmospheric water. The windows of this chamber result in a large diffraction peak at 45.7° 2 θ , which is excluded from our analysis.

We acquired diffraction data from 5-80° 2 θ , with a step size of 0.02° (0.3°/min), at 8 temperatures between 25 °C and -114 °C. The mikasaite was cooled gradually to each temperature, and then held for at least 15 minutes before each measurement, to ensure that the entire sample reached thermal equilibrium with the sample holder and chamber. All measurements were made of mikasaite from the same synthesized batch, stored in the same glass vial. Due to time constraints, the mikasaite sample had to be switched out multiple times during the 8-temperature acquisition sequence. All measured aliquots came from the same batch, and once an aliquot was

removed from the air-tight sample holder, it was disposed of, to prevent any chance of rehydration. This process resulted in consistent mikasaite purity and composition, but inconsistent sample displacement within the airtight chamber, which we address throughout our subsequent Rietveld refinement.

4.2.3 Rietveld Refinement & Analysis

Rietveld refinement was completed using GSAS-II (Toby & Von Dreele, 2013). Structure refinements were performed using the default analytical Hessian method in GSAS-II, which utilizes a least-squares minimizer that uses a singular-value decomposition to reduce the errors caused by correlated variables, as well as the Levenberg-Marquardt algorithm (Toby & Von Dreele, 2013). A Thompson-Cox-Hastings modified pseudo-Voigt peak profile function was used for peak fitting (Toby & Von Dreele, 2013; Thompson et al., 1987). Rietveld refinements were performed iteratively from the diffraction pattern taken at 25 °C to the coldest temperature at -114 °C. The initial refinement of the 25 °C used the crystallographic structure parameters of mikasaite from Christidis & Rentzeperis (1975) and Rentzeperis & Christidis (1976) as the starting point for the refinement. The final refined parameters of the 25 °C sample were then used as the starting point for the refinement of 0 °C diffraction pattern, and so on with decreasing temperature. The only stipulation was that the sample displacement of each pattern was refined foremost, before other instrument, sample, and unit cell parameters, as we were experimentally unable to keep this displacement consistent between each diffraction pattern acquisition. The background of each diffraction pattern was refined as a Chebyshev polynomial, with the number of coefficients ranging from 15 to 19 depending on the sample. For improved refinement, the 2θ range was limited from 10-80°, and the ranges from 45 - 46.7° and 43.08 - 43.5° were excluded from the refinement, as these regions included peaks associated with the airtight sample chamber and sample holder.

Refined instrument parameters include Y, V, and W coefficients of the Caglioti formula, which describes the peak widths as a function of angle. We could not exclude the possibility that our synthesized mikasaite was not entirely composed of the trigonal polymorph. Thus, each refinement included both the trigonal and monoclinic forms of mikasaite as phases, and the phase fraction of each was refined. The unit cell parameters of both the trigonal and monoclinic forms of mikasaite were refined, however these were the only other parameters of the monoclinic mikasaite to be refined, as the focus of this study was to refine the structure of the trigonal form of mikasaite. We included a standard SO_4 tetrahedra as a rigid body to the refinement at each temperature, with equidistant S-O bond lengths at 1.474 Å, allowing the center position and tetrahedra orientation to freely refine. Additionally, the fractional position of the two Fe sites in mikasaite were refined for each pattern.

After Rietveld refinement, the trends in the changing unit cell parameters, atom fractional positions, bond lengths, and bond angles with temperature were analyzed. The thermal expansion coefficient was calculated by using a linear regression model, with the natural log of the mikasaite unit cell volume (V) as the dependent variable, and the temperature as the independent variable. The distortion of the two Fe coordination sites in mikasaite were also analyzed using the PIEFACE program, which analyzes the distortion of a chemical coordination polyhedron by fitting the smallest volume ellipsoid around the polyhedron (Cumby & Attfield, 2017).

4.3 Results

4.3.1 Diffraction Patterns

Figures 4.1, 4.2, and 4.3 show the final diffraction pattern, and modeled fit from Rietveld refinement, with tick marks for diffractions peaks of trigonal mikasaite. We were able to achieve good modeled fits to the diffraction data at each temperature, with weighted residuals (wR)

between ~1.8% and ~2.5% across all eight temperatures. We found that our mikasaite did contain a mixture of the monoclinic and trigonal polymorphs, with each sample containing on average 78(2) % trigonal mikasaite. There was no trend in the phase fraction of either polymorph with temperature. The differences in the diffraction patterns themselves are minor, and to see possible trends with temperature, structural information was extracted from these data. We created a standard crystallographic information file (CIF) for our mikasaite at each temperature in this study, which are available in a Zenodo repository in Appendix D (doi.org/10.5281/zenodo.19748183).

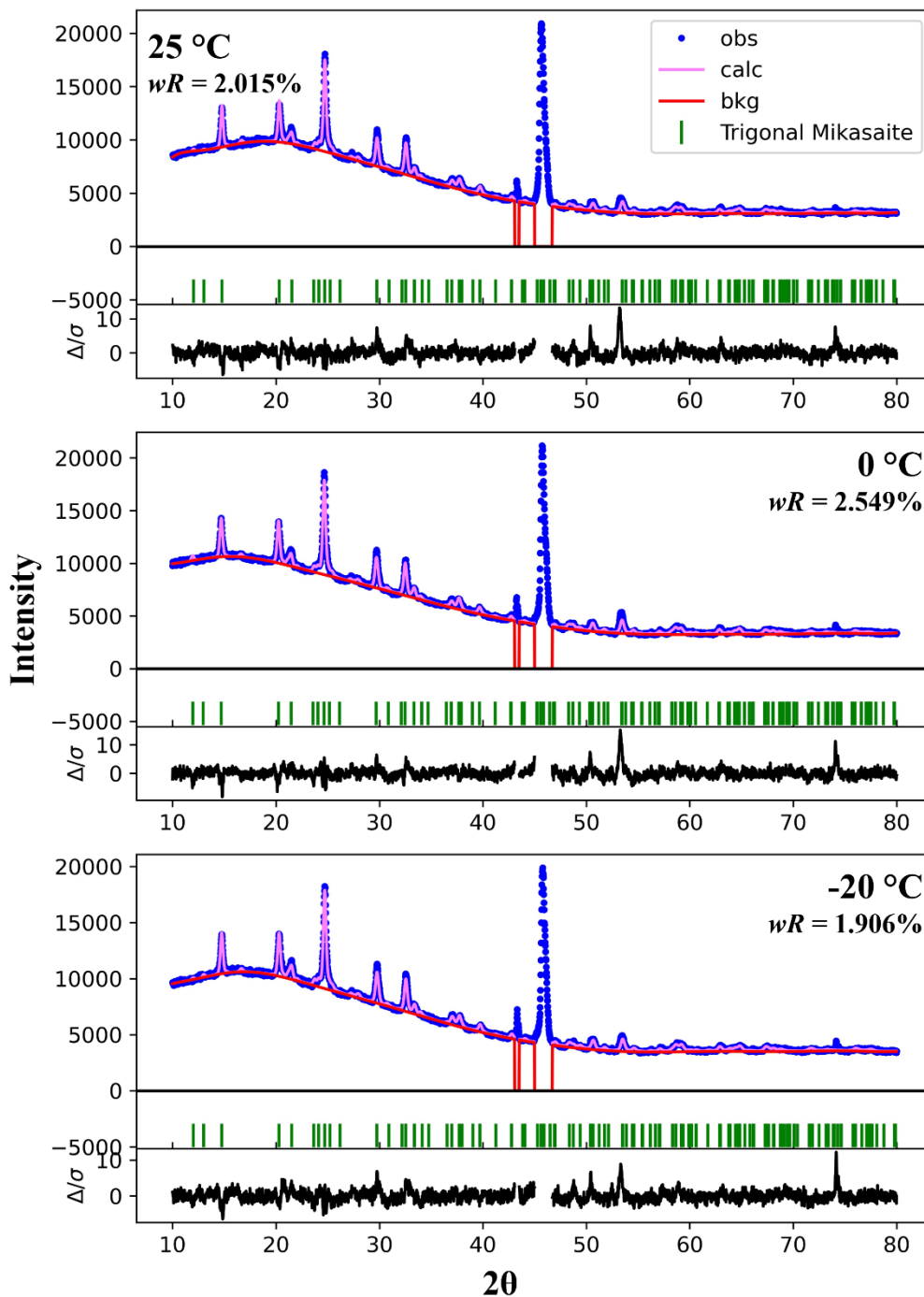


Figure 4.1. Rietveld refinement plots of the mikasaite sample at 25 °C (top), 0 °C (middle), and -20 °C (bottom). The blue dots are the diffraction data, the pink plots are the refined profiles, and the red curves are the background profile. Green ticks show the peak locations of our refined trigonal mikasaite. The black Δ/σ plot is the weighted difference curve of the refined profile vs the diffraction data. Weighted residuals (wR) of the calculated fit are shown in the top of each plot.

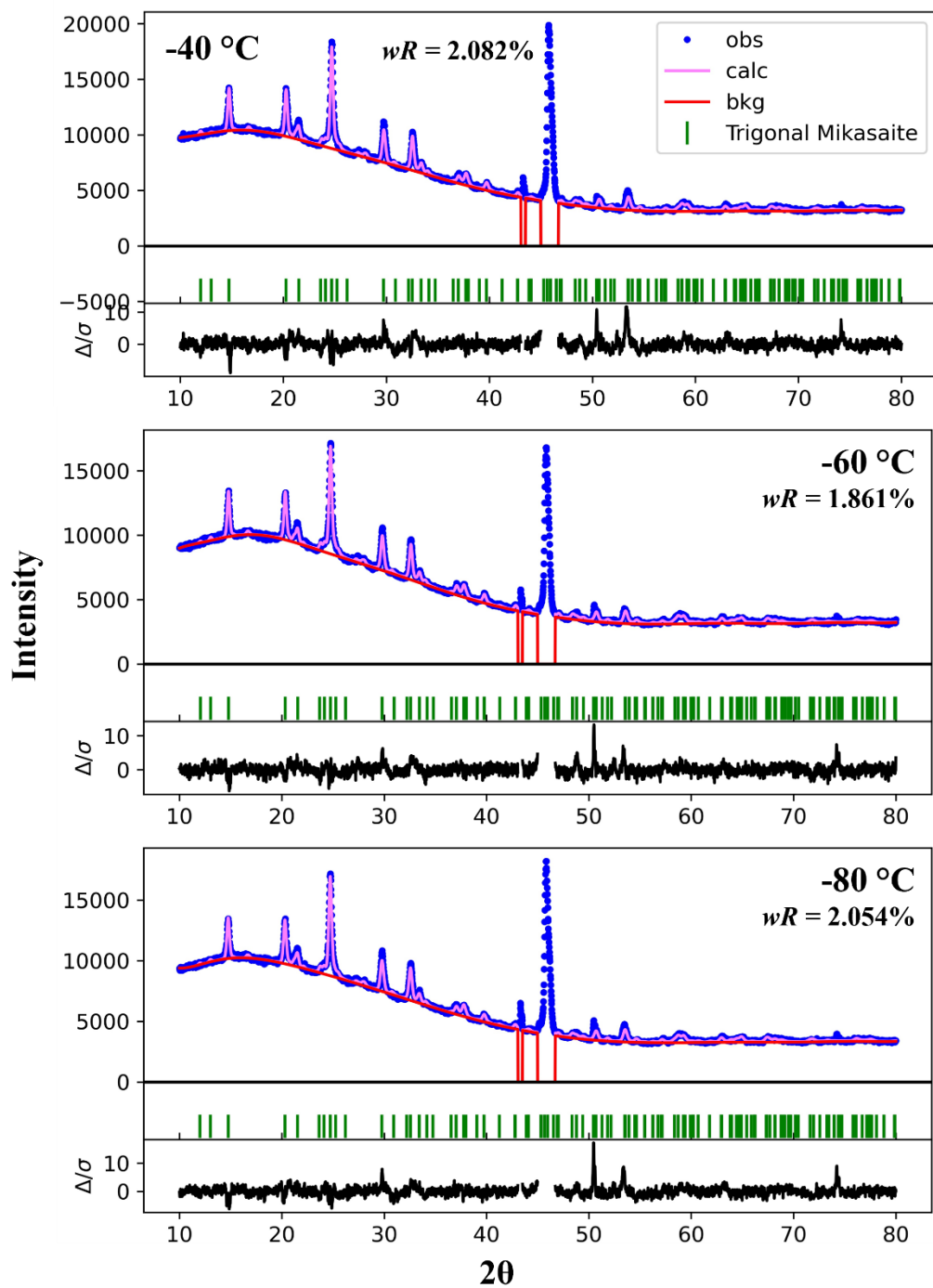


Figure 4.2. Rietveld refinement plots of the mikasaite sample at -40 °C (top), -60 °C (middle), and -80 °C (bottom). The blue dots are the diffraction data, the pink plots are the refined profiles, and the red curves are the background profile. Green ticks show the peak locations of our refined trigonal mikasaite. The black Δ/σ plot is the weighted difference curve of the refined profile vs the diffraction data. Weighted residuals (wR) of the calculated fit are shown in the top of each plot.

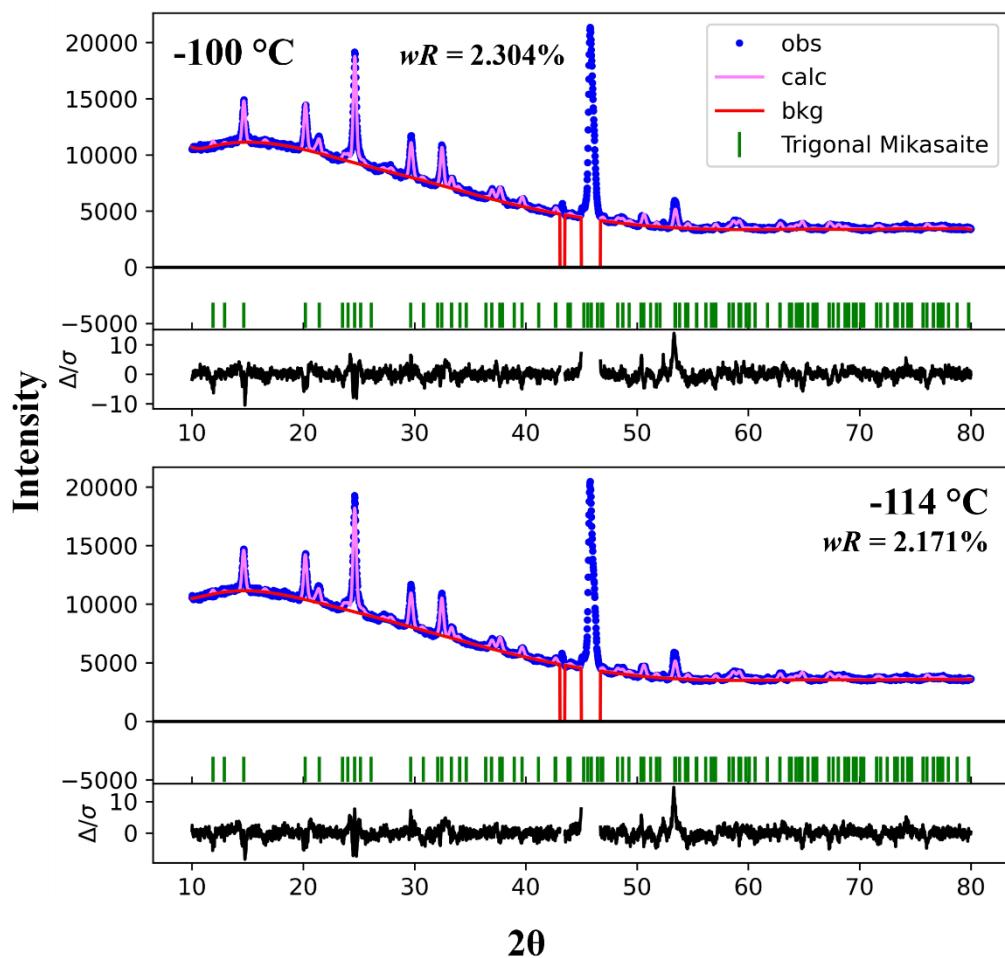


Figure 4.3. Rietveld refinement plots of the mikasaite sample at -100 °C (top), and -114 °C (bottom). The blue dots are the diffraction data, the pink plots are the refined profiles, and the red curves are the background profile. Green ticks show the peak locations of our refined trigonal mikasaite. The black Δ/σ plot is the weighted difference curve of the refined profile vs the diffraction data. Weighted residuals (wR) of the calculated fit are shown in the top of each plot.

4.3.2 Crystal Structure Evolution

The crystal structure of mikasaite contains one S tetrahedral site forming SO₄ tetrahedra, corner-sharing with two distinct FeO₆ octahedra, formed from two inequivalent Fe³⁺ sites (Fe1 and Fe2). At the starting temperature of 25 °C, using the original structure data from Rentzeperis & Christidis (1976), we refined mikasaite in the $R\bar{3}$ space group with unit-cell dimensions $a = 8.267(6)$ Å, $c = 22.143(12)$ Å, and $V = 1310.4(1.6)$ Å³ (Table 4.1). All three unit-cell parameters varied with decreasing temperature, although we only observe a clear trend of shortening along the a -axis (Figure 4.4), and a decreasing cell volume (Figure 4.6). The c -axis appears to shorten from 22.143(12) Å at 25 °C, to 22.110(12) Å at -60 °C, before increasing again to 22.137(10) Å at -114 °C (Figure 4.5), although all values for the c -axis are reasonably close considering the 4 σ error associated with each measurement. We have a 4 σ uncertainty in the unit cell parameters calculated with Rietveld refinement (Bérar & Lelann, 1991). Figure 4.7 shows the mikasaite structure graphically, using a portion of the calculated unit cell at -80 °C as a representation of the cold temperature structure. Due to setting the SO₄ tetrahedra as rigid bodies, the S-O bond lengths and O-S-O bond angles are consistent across all temperatures, and the further crystal structure information includes the various Fe-O bond lengths, O-Fe-O bond angles, and relative orientation of the SO₄ tetrahedra and FeO₆ octahedra, including changes in Fe-S site center-distances. These values for our mikasaite at each temperature can be found in Table 4.2. Fe1-O1 and Fe2-O2 distances are generally consistent with lowering temperature (Figures 4.8, 4.9). There are some slight changes to Fe1-O3, with a slight decrease from ~1.92 Å to ~1.84 Å under -20 °C, although with average uncertainty of $\pm\sim 0.06$ Å (Figure 4.10). In contrast, Fe2-O4 bonds are shortest near 0 °C, although this one measurement may be an outlier (Figure 4.11). The distances between the O1-sharing and O2-sharing S and Fe centers are generally consistent with lowering temperature

(Figures 4.12, 4.13). The distances between the O3-sharing and O4-sharing S and Fe centers (Figures 4.14, 4.15) both show distortion under 0 °C, reflecting the same trend with the Fe1-O3 and Fe2-O4 bond lengths. We see more variations in the Fe-O-S bond angles, but inconsistent trends with temperature. Fe1-O1-S1 angles range from ~152° to ~162°, while Fe1-O3-S1 angles range from ~138° to ~142° (Figures 4.16, 4.17). Fe2-S angles show slightly less variance, with Fe2-O2-S1 angles ranging from ~138° to ~145°, and Fe2-O4-S1 angles ranging from ~138° to ~142° (Figures 4.18, 4.19).

4.3.3 Thermal Expansion Coefficient

We do observe a consistent contraction of the mikasaite unit-cell volume with decreasing temperature (Figure 4.6). By using a linear regression model, with the natural log of the mikasaite unit cell volume, $\ln(V)$, as the dependent variable, and the eight temperatures (T) from 298.15 K to 159.15 K as the independent variable, we calculated the thermal expansion coefficient of our mikasaite. We determined a volumetric thermal expansion coefficient of $3.64 \times 10^{-5} \text{ K}^{-1}$ with an uncertainty of $0.64 \times 10^{-5} \text{ K}^{-1}$. Our relatively large uncertainty is due to the scatter of our eight unit-cell volumes, causing a linear regression $R^2 = 0.8457$ (Figure 4.6).

Table 4.1 Unit-cell parameters a and c , and the unit-cell volume for the refined mikasaite structure at each temperature. Temperatures are listed in degrees Celsius and Kelvin for convenience. All errors are 4 standard deviations.

Mikasaite Unit-Cell Parameters				
T (°C)	T (K)	a (Å)	c (Å)	$Vol.$ (Å ³)
25	298.15	8.267(6)	22.143(12)	1310.4(1.6)
0	273.15	8.257(6)	22.138(12)	1307.1(1.2)
-20	253.15	8.256(6)	22.123(12)	1306.0(1.2)
-40	233.15	8.252(6)	22.133(12)	1305.2(1.2)
-60	213.15	8.250(6)	22.110(12)	1303.4(1.2)
-80	193.15	8.248(6)	22.123(12)	1303.4(1.6)
-100	173.15	8.246(4)	22.133(10)	1303.4(1.0)
-114	159.15	8.245(5)	22.137(10)	1303.2(1.0)

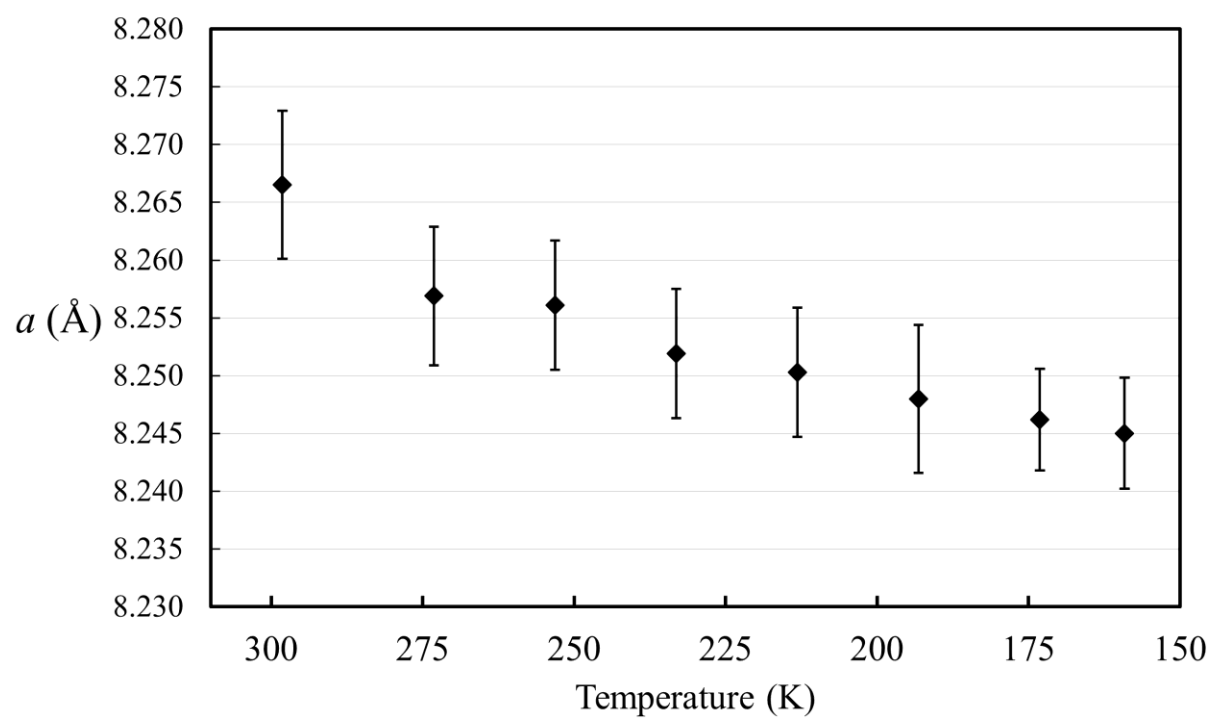


Figure 4.4. Plot of the a -axis cell length for mikasaite at each measured temperature. Error bars are $\pm 4\sigma$.

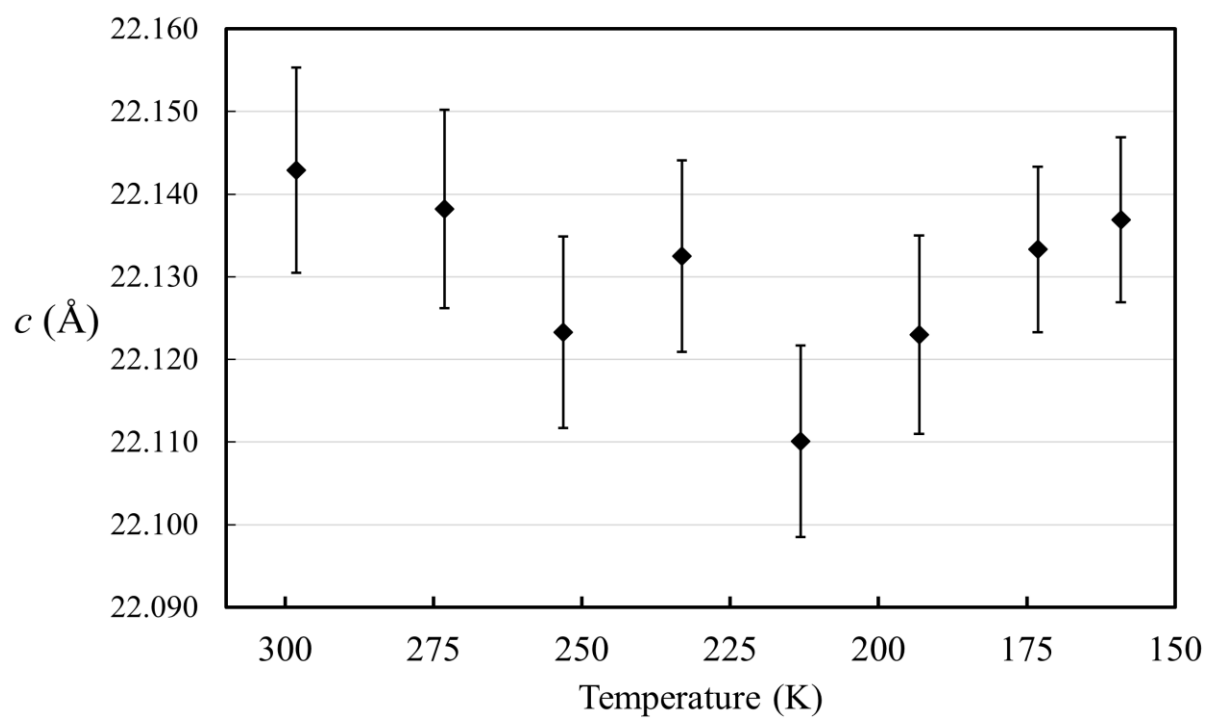


Figure 4.5. Plot of the c -axis cell length for mikasaite at each measured temperature. Error bars are $\pm 4\sigma$.

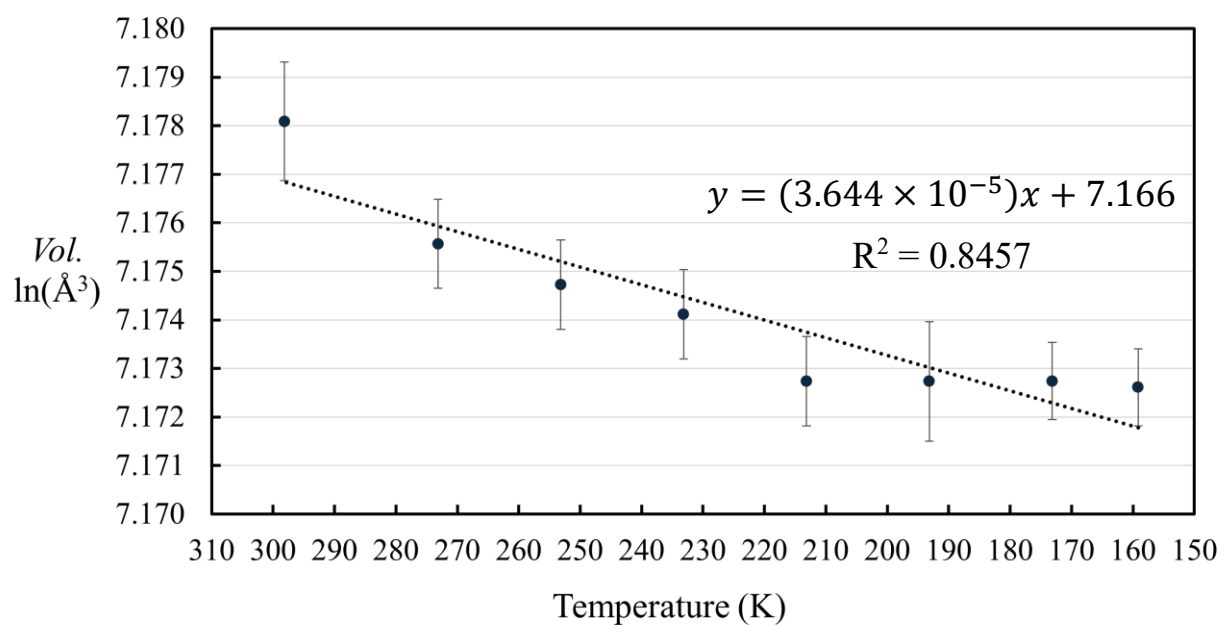


Figure 4.6. Plot of the natural log of the cell volume for mikasaite at each measured temperature. Error bars are $\pm 4\sigma$.

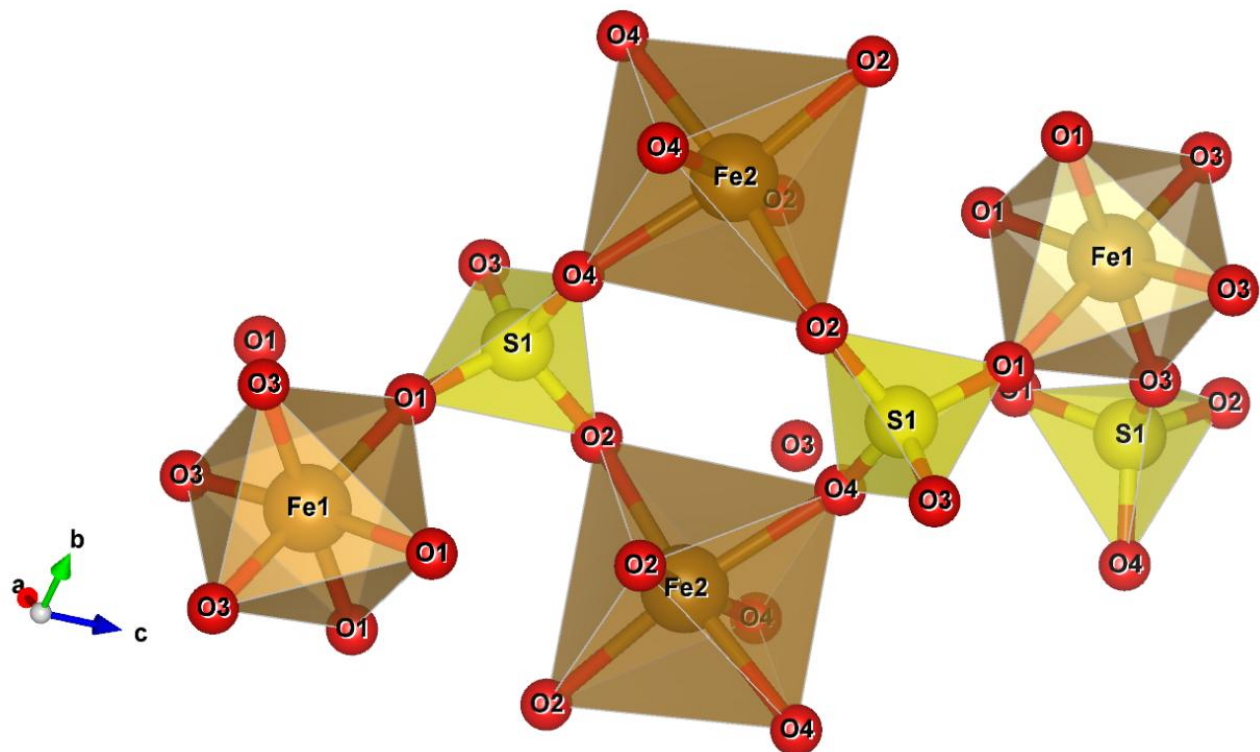


Figure 4.7. 3-D visualization of a crystal structure segment of trigonal mikasaite. For visual clarity, only a portion of the full calculated unit cell is shown, with fraction coordinates ranges limited to: $(0 < x < 0.5)$, $(0 < y < 0.7)$, and $(0.1 < z < 0.6)$. The crystal visualization software VESTA was used to make this render (Momma & Izumi, 2011).

Table 4.2 Bond lengths, atomic distances, and bond angles for each Fe-S-O bonding trio in the unit-cell of mikasaite. For each Fe–O...S trio at each temperature, the top number is the bond length of the Fe–O bond, the middle number is the distance between the O-sharing Fe and S, and the bottom number is the angle created by the Fe–O...S trio. All error values are 4σ .

Fe–O...S	Fe–O distances (Å), Fe...S distance (Å), and Fe–O...S angles (θ)							
	25 °C	0 °C	-20 °C	-40 °C	-60 °C	-80 °C	-100 °C	-114 °C
Fe1–O1...S1	1.896(56)	1.887(36)	1.898(68)	1.913(60)	1.884(52)	1.905(76)	1.913(40)	1.907(40)
	3.297(68)	3.267(44)	3.315(84)	3.325(72)	3.316(60)	3.336(92)	3.292(52)	3.290(52)
	155.9(2.8)	152.6(2.0)	158.6(3.2)	157.8(2.8)	161.8(2.0)	161.6(3.2)	152.5(2.0)	153.0(2.0)
Fe1–O3...S1	1.916(60)	1.919(40)	1.843(72)	1.850(60)	1.846(52)	1.827(76)	1.847(44)	1.862(44)
	3.169(44)	3.202(28)	3.120(52)	3.137(44)	3.126(36)	3.119(52)	3.116(28)	3.192(32)
	138.0(1.6)	140.9(1.0)	140.1(2.0)	141.1(1.6)	140.3(1.2)	141.5(2.0)	139.3(1.2)	139.1(1.2)
Fe2–O2...S1	2.100(60)	2.114(44)	2.077(64)	2.096(60)	2.123(44)	2.084(68)	2.077(44)	2.073(48)
	3.386(72)	3.432(52)	3.365(80)	3.373(72)	3.371(60)	3.349(88)	3.395(52)	3.390(56)
	142.0(1.6)	145.5(0.9)	142.1(2.0)	141.2(1.6)	138.5(1.6)	139.9(2.4)	145.3(1.0)	145.3(1.1)
Fe2–O4...S1	2.060(64)	1.984(48)	2.101(76)	2.057(68)	2.100(56)	2.100(84)	2.088(48)	2.075(52)
	3.327(48)	3.279(36)	3.367(52)	3.338(52)	3.348(40)	3.357(60)	3.365(36)	3.353(36)
	140.0(1.6)	142.5(1.0)	140.1(1.6)	141.4(1.6)	138.3(1.2)	139.1(2.0)	141.0(1.1)	141.1(1.1)

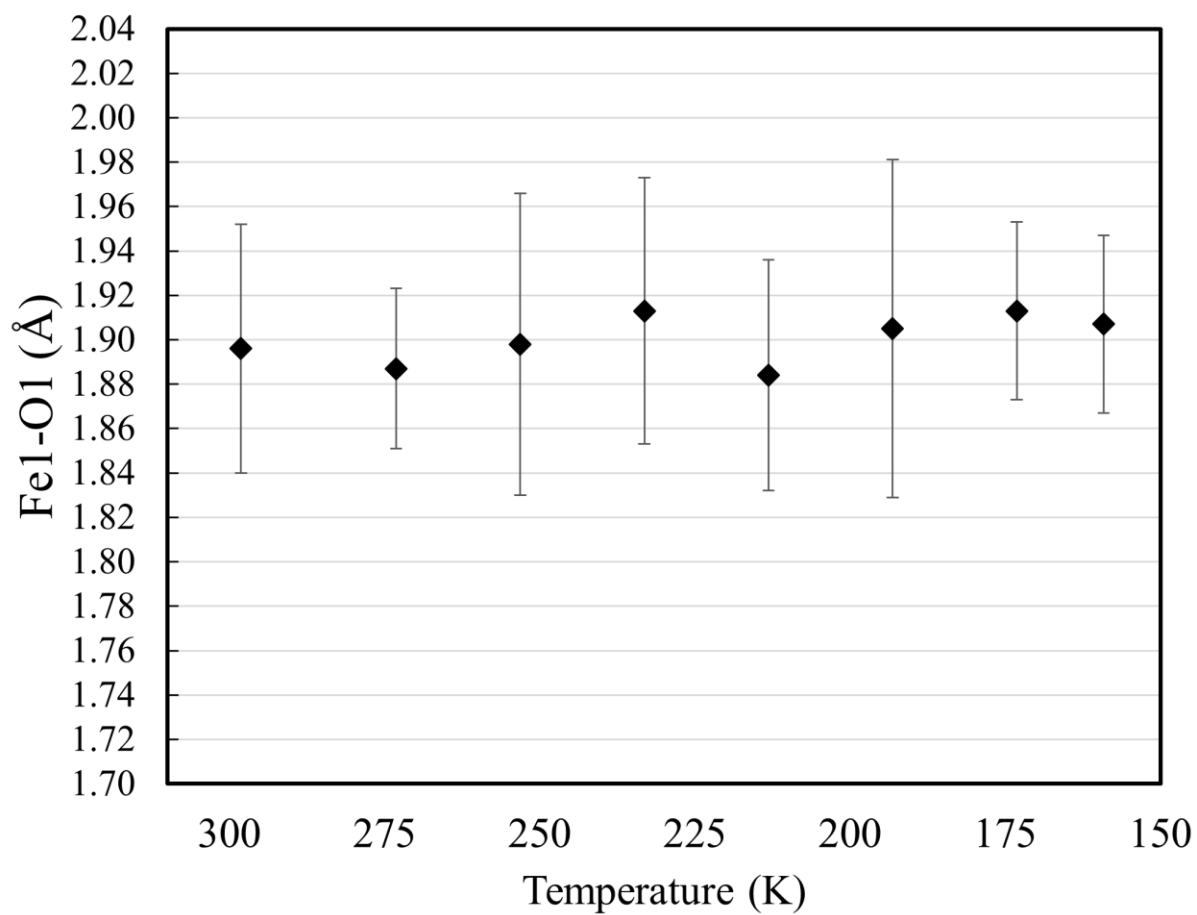


Figure 4.8. Fe1-O1 bond lengths within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

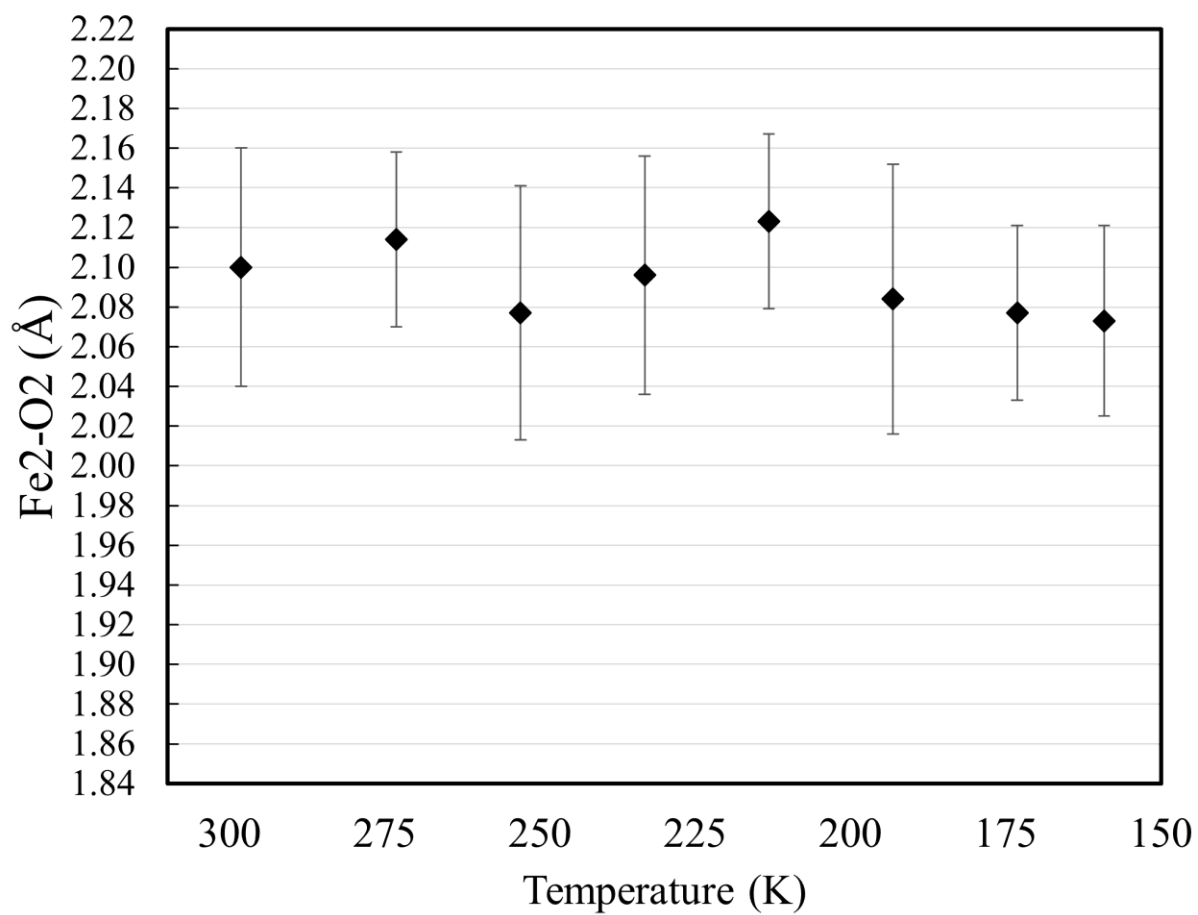


Figure 4.9. Fe2-O2 bond lengths within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

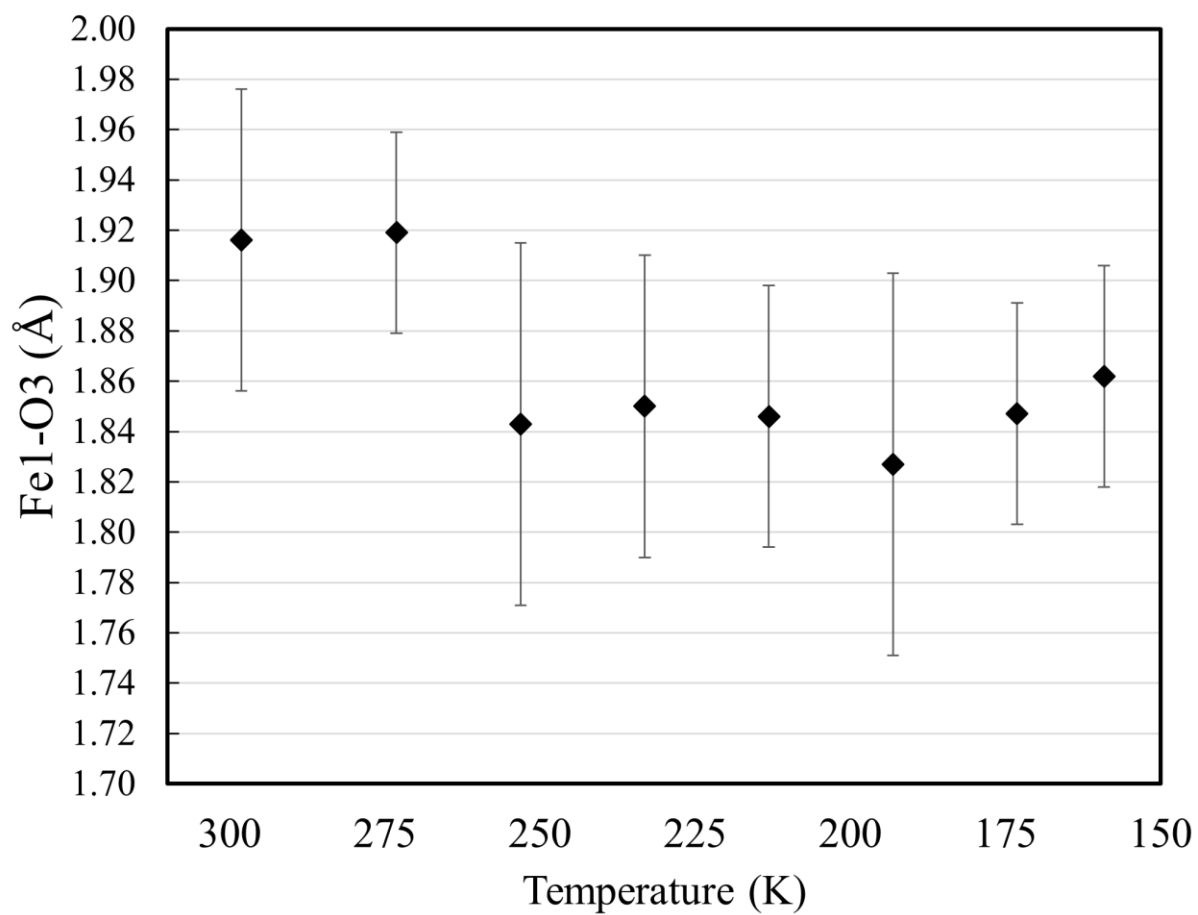


Figure 4.10. Fe1-O3 bond lengths within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

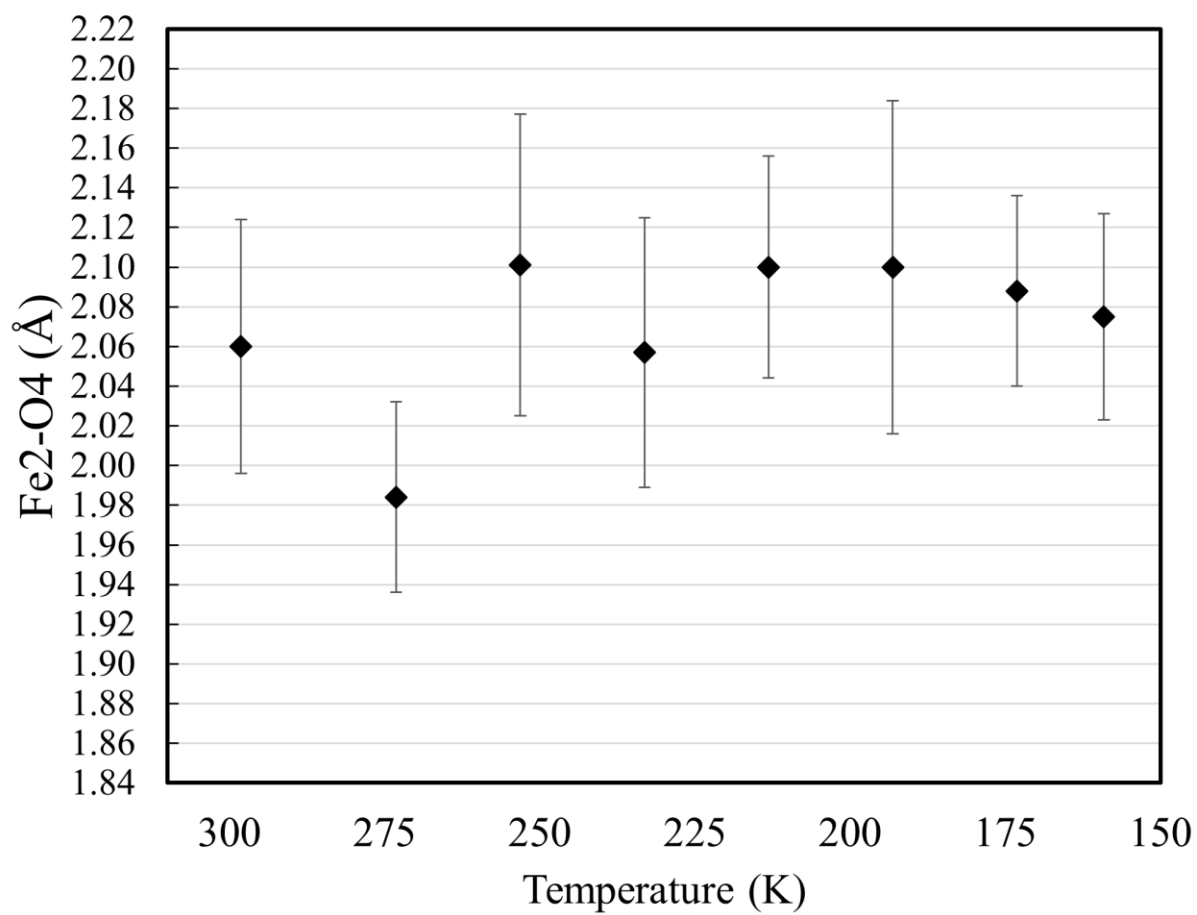


Figure 4.11. Fe2-O4 bond lengths within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

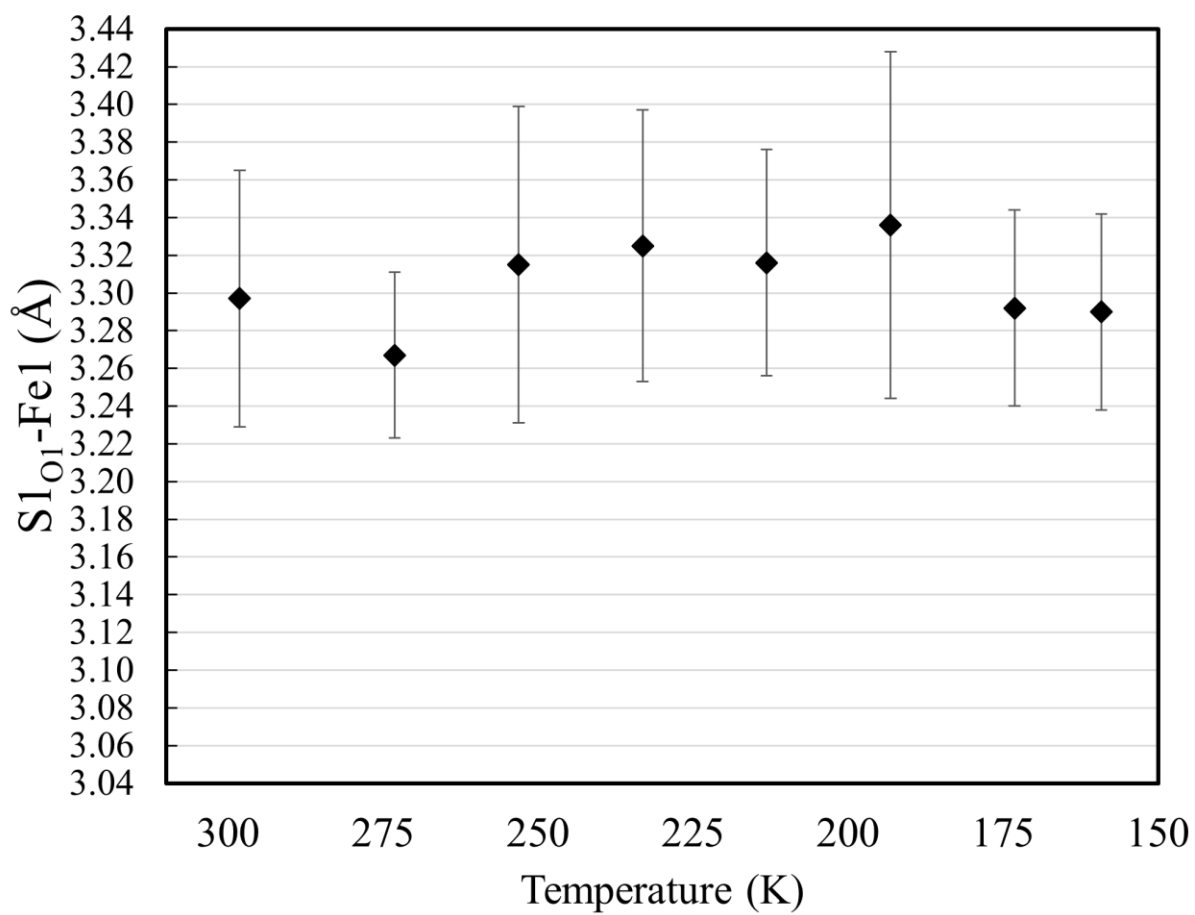


Figure 4.12. Distance between O1-sharing S1 and Fe1 within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

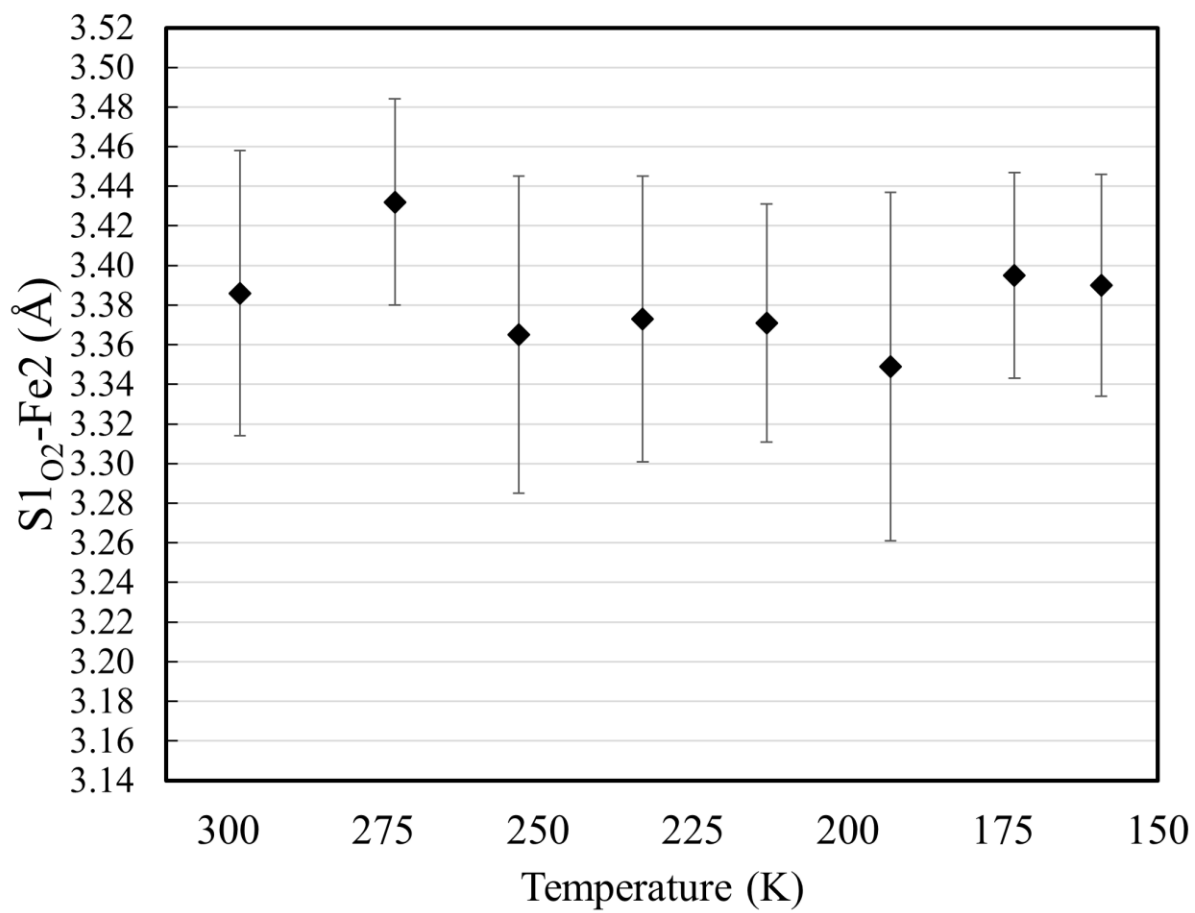


Figure 4.13. Distance between O2-sharing S1 and Fe2 within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

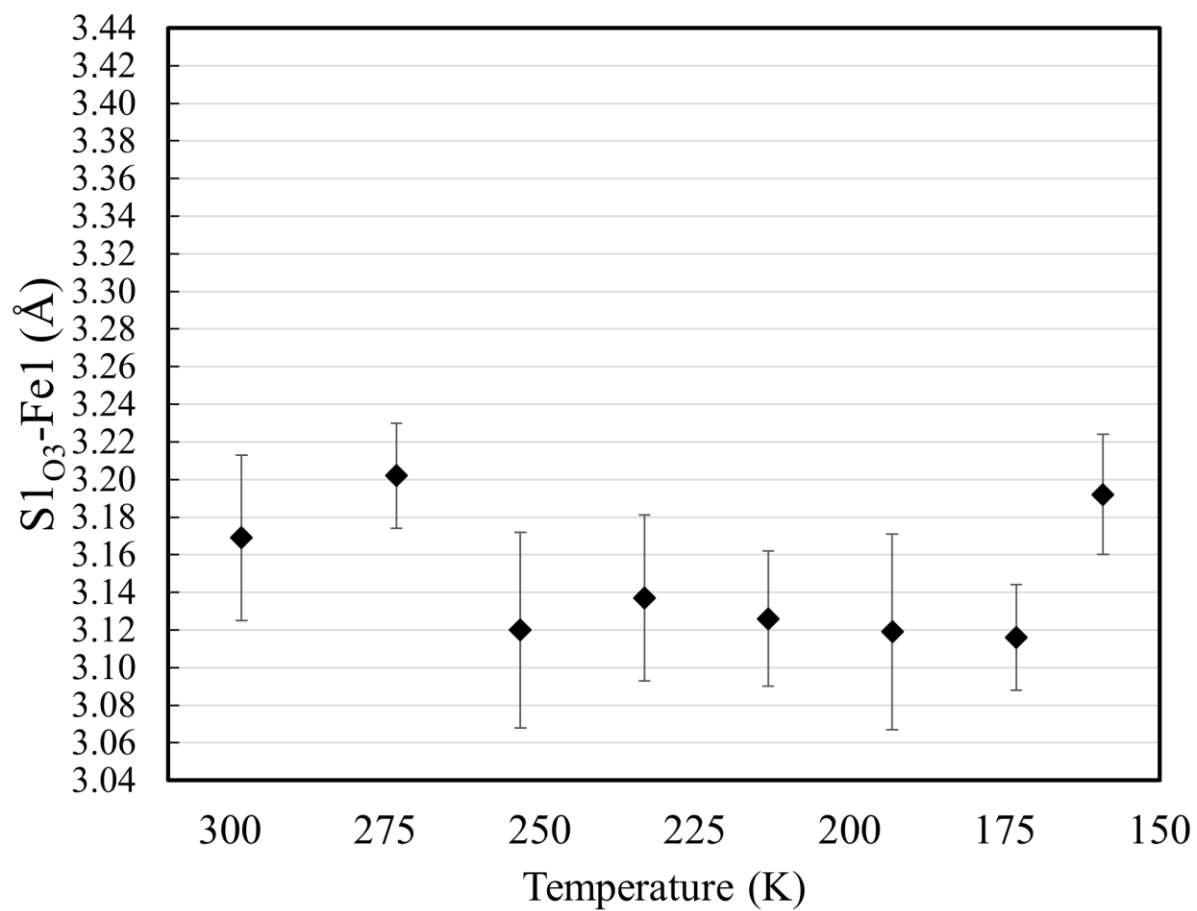


Figure 4.14. Distance between O3-sharing S1 and Fe1 within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

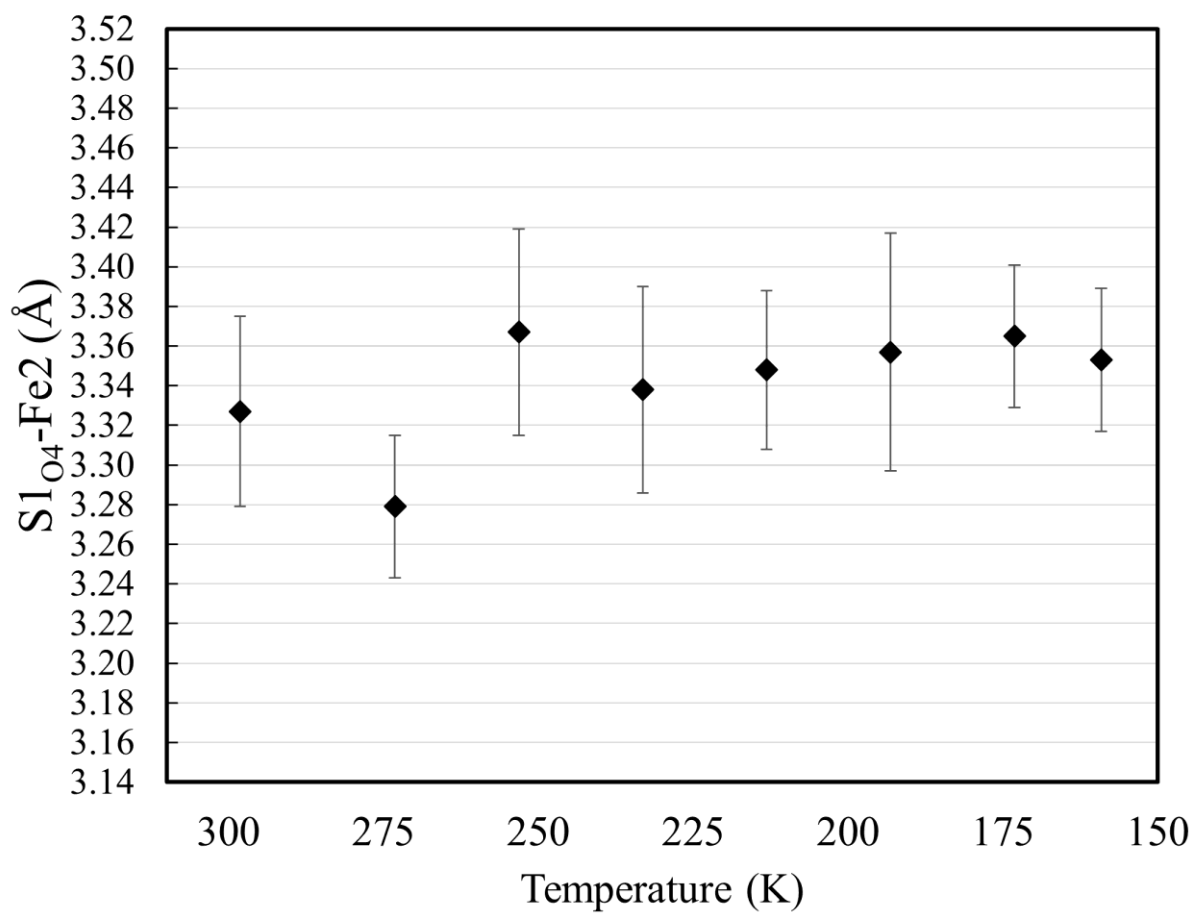


Figure 4.15. Distance between O4-sharing S1 and Fe2 within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

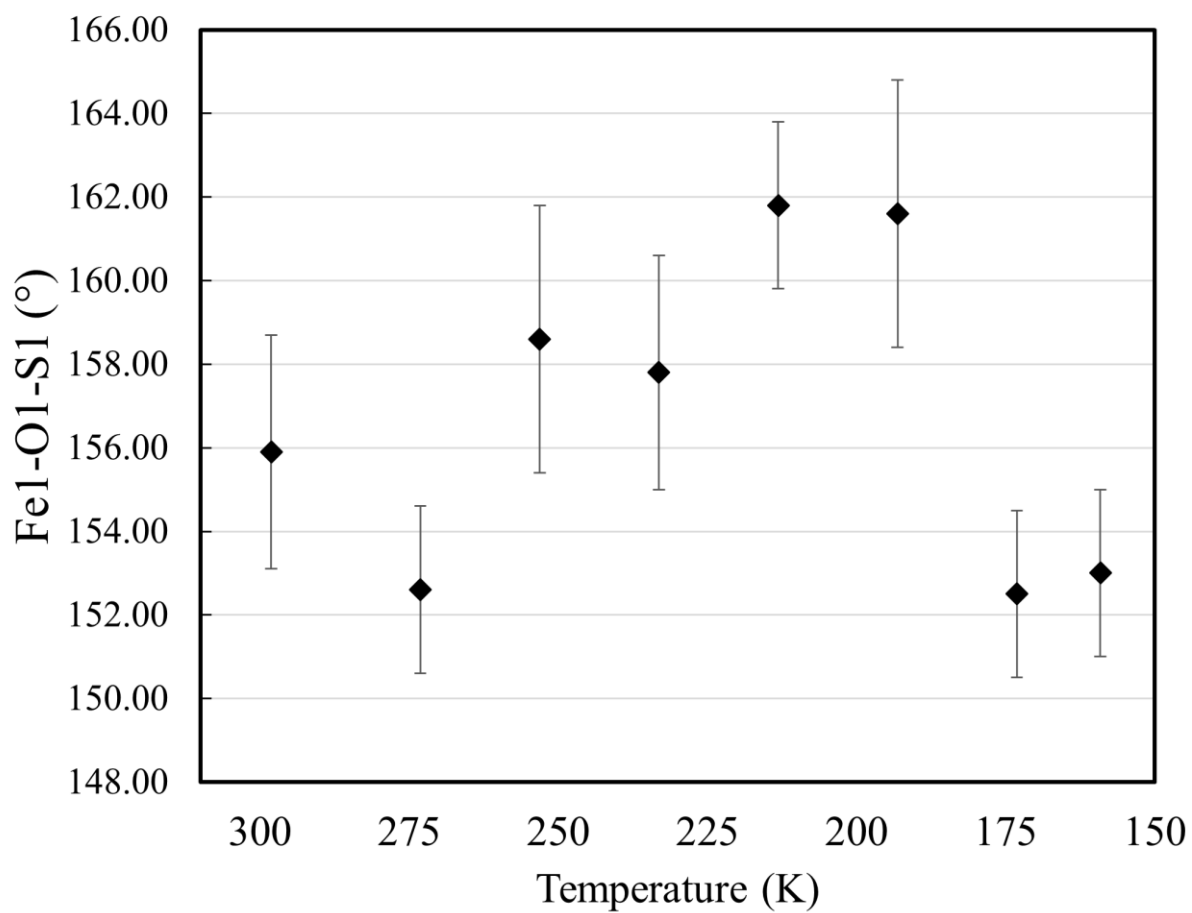


Figure 4.16. Angle between Fe1-O1-S1 within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

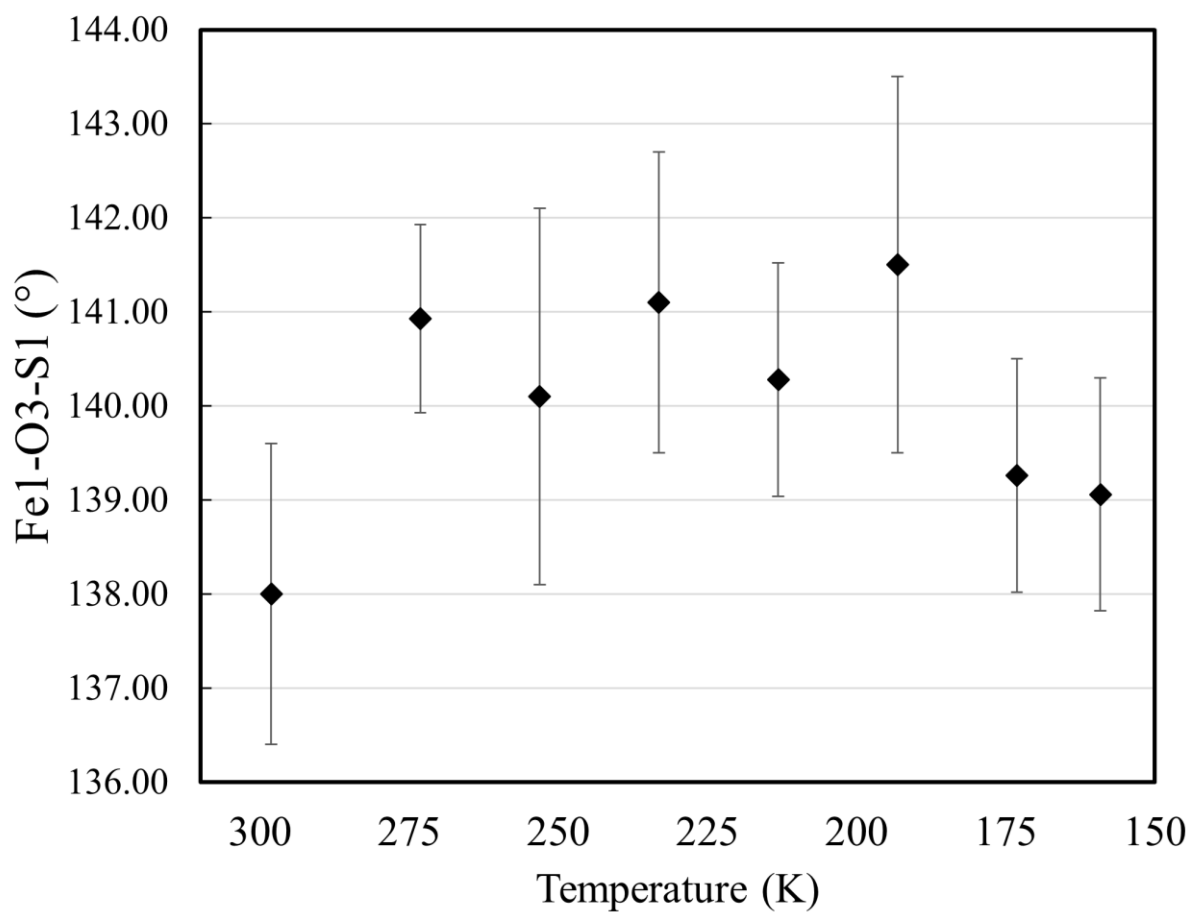


Figure 4.17. Angle between Fe1-O3-S1 within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

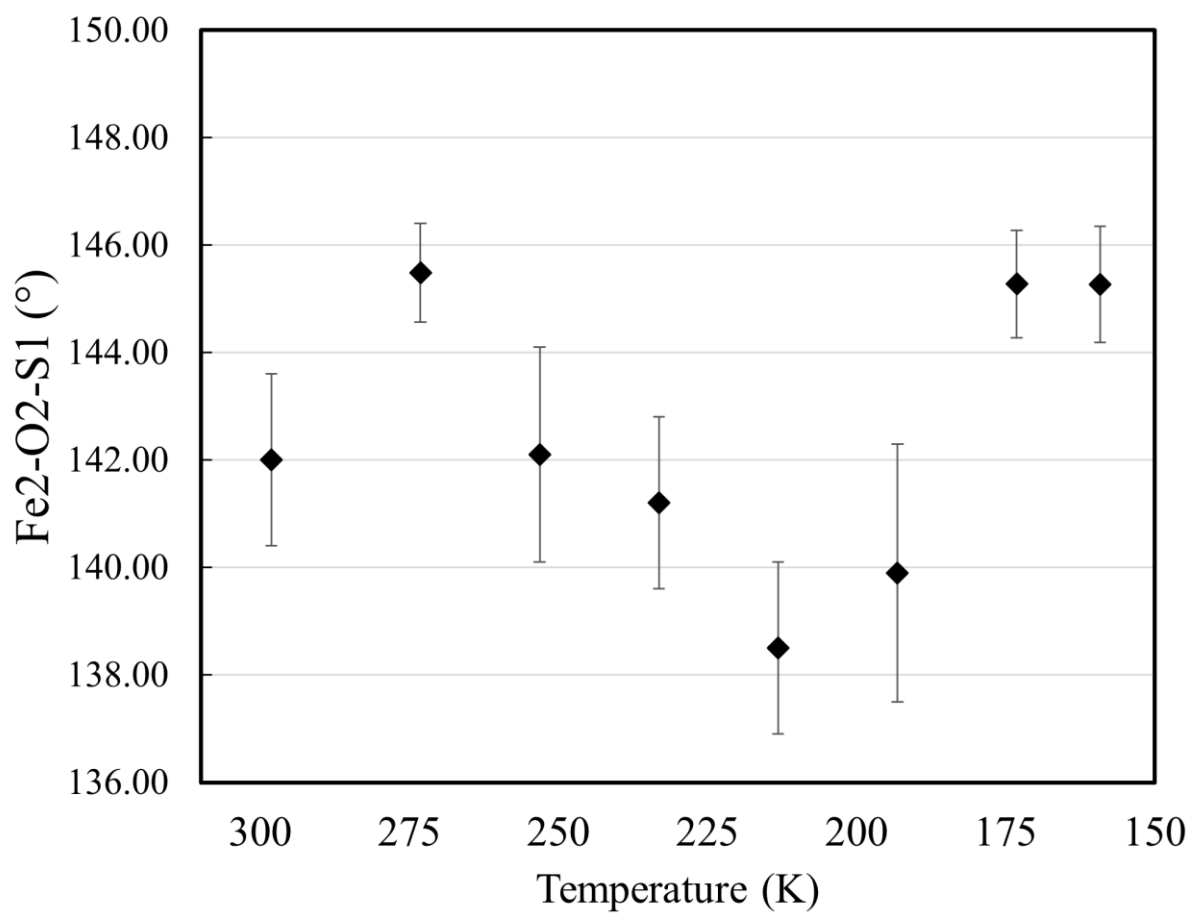


Figure 4.18. Angle between Fe2-O2-S1 within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

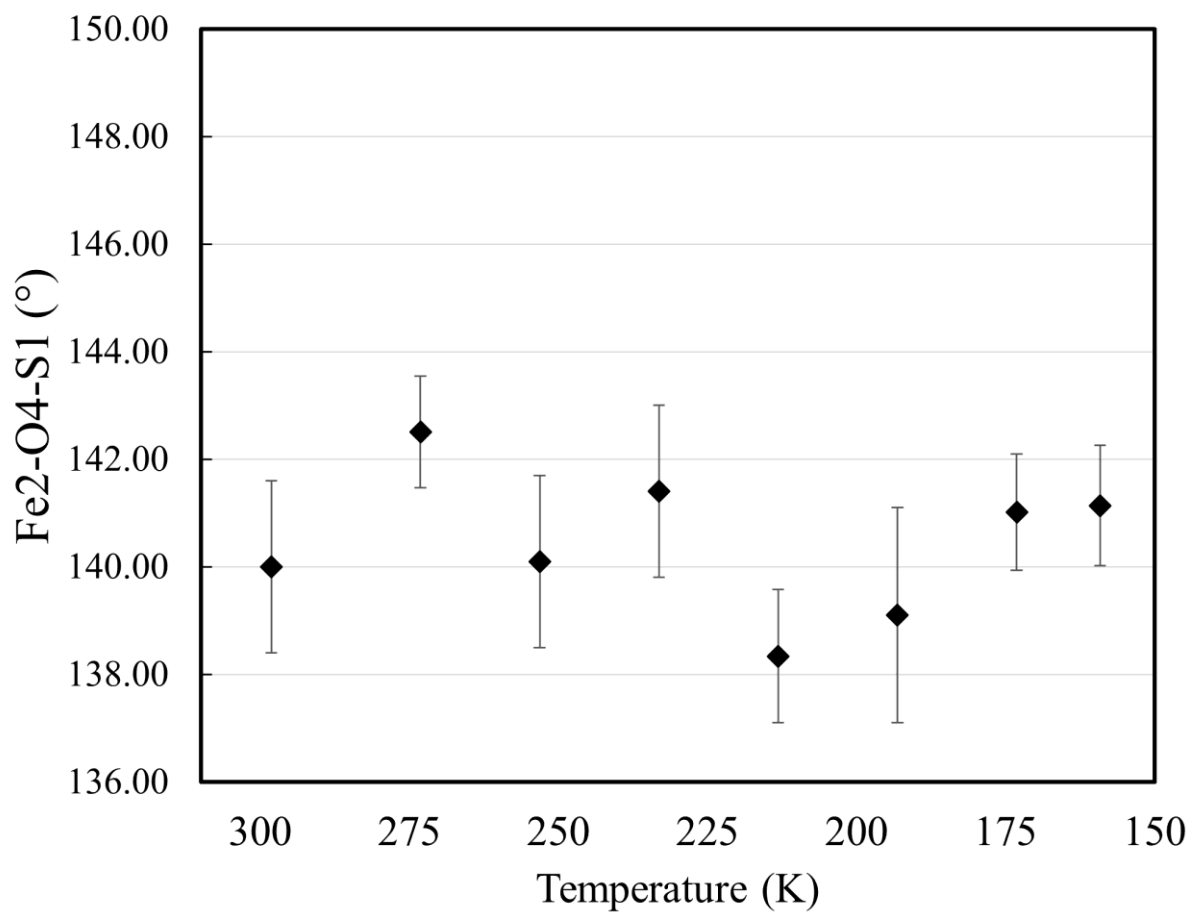


Figure 4.19. Angle between Fe2-O4-S1 within the refined mikasaite unit-cell at eight temperatures. Error bars are $\pm 4\sigma$.

4.3.4 Fe-Coordination Site Ellipsoid Parameters

Differing changes in adjacent Fe-O bond lengths, as well as associated O-Fe-O angles, can be characterized by analyzing temperature-dependent changes in the distortion of the Fe coordination polyhedron, which we characterize by analysis of an ellipsoid fit to the FeO₆ octahedra. These ellipsoids were modeled using the python-based program PIEFACE, which fits an ellipsoid to a coordination polyhedral with known coordinates (Cumby & Attfield, 2017). Using this program, we can characterize the distortion of the two FeO₆ octahedra using several parameters, all of which are summarized in Table 4.3. These parameters include the net center displacement of the center Fe atom with respect to the fitted ellipsoid's geometric center, the mean radius of the fit ellipsoid, the volume of the fitted ellipsoid, and whether the fitted ellipsoid is prolate or oblate. A graphical example of this ellipsoidal fit can be seen in Figure 4.20 and 4.21, for the Fe1 and Fe2 sites of -80 °C, respectively.

Table 4.3 Ellipsoid fit parameters of the Fe1 (top) and Fe2 (bottom) coordination sites in our refined mikasaite. Center Disp. (Å) is the net displacement of the Fe-atom from the geometric center of the fit ellipsoid. R_E is the mean radius of the fit ellipsoid in Å. Volume is the volume of the fitted ellipsoid in Å³. S is the shape parameter. S>0 indicates a prolate ellipsoid, S<0 indicates an oblate ellipsoid, and S=0 would indicate a sphere. R1, R2, and R3 are the semi-axes of the fitted ellipsoid in Å. The python program PIEFACE was used for all calculations (Cumby & Attfield, 2017).

<i>Fe1</i>								
T (°C)	T (K)	Center Disp.	R_E	Volume	S	R1	R2	R3
25	298.15	0.0237	1.905(50)	28.93	-0.055	1.940	1.940	1.834
0	273.15	0.0414	1.898(12)	28.47	-0.129	1.984	1.984	1.728
-20	253.15	0.0458	1.872(11)	27.48	-0.013	1.880	1.880	1.856
-40	233.15	0.0497	1.881(72)	27.81	-0.079	1.931	1.931	1.779
-60	213.15	0.0330	1.865(09)	27.19	0.010	1.878	1.859	1.859
-80	193.15	0.0672	1.867(14)	27.25	-0.015	1.876	1.876	1.848
-100	173.15	0.0379	1.880(100)	27.71	-0.109	1.951	1.951	1.738
-114	159.15	0.0240	1.885(84)	27.96	-0.092	1.944	1.944	1.766

<i>Fe2</i>								
T (°C)	T (K)	Center Disp.	R_E	Volume	S	R1	R2	R3
25	298.15	0.0400	2.081(34)	37.73	0.034	2.129	2.057	2.057
0	273.15	0.1260	2.050(95)	35.97	0.093	2.185	1.983	1.983
-20	253.15	0.0148	2.088(29)	38.12	0.029	2.129	2.068	2.068
-40	233.15	0.0407	2.077(42)	37.52	0.042	2.136	2.048	2.048
-60	213.15	0.0144	2.113(18)	39.49	-0.018	2.125	2.125	2.088
-80	193.15	0.0108	2.091(12)	38.32	0.122	2.109	2.083	2.083
-100	173.15	0.0047	2.080(110)	37.52	0.105	2.236	2.002	2.002
-114	159.15	0.0098	2.072(98)	37.12	0.094	2.211	2.002	2.002

Ellipsoid Summary

R1	:	1.8763
R2	:	1.8763
R3	:	1.8476
Centre	x :	0.0000
	y :	-0.0000
	z :	0.0672
Total	:	0.0672
<R>	:	1.8667
sigma(R)	:	0.013531289
Volume	:	27.2462
S	:	-0.0153
Fit Error	:	0.000001000

Fe1: Mikasaite -80 °C

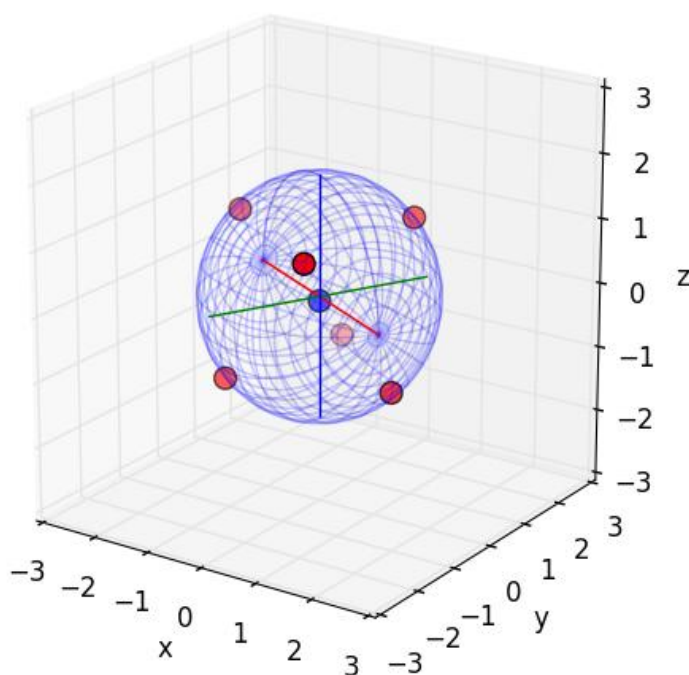


Figure 4.20. Summary of the ellipsoid fitting analysis of the Fe1 coordination site of the refined -80 °C mikasaite data. Ellipsoid was modeled and graphically displayed using PIEFACE (Cumby & Attfield, 2017).

Ellipsoid Summary

R1	:	2.1086
R2	:	2.0828
R3	:	2.0828
Centre	x :	0.0000
	y :	-0.0000
	z :	0.0108
Total	:	0.0108
<R>	:	2.0914
sigma(R)	:	0.012129826
Volume	:	38.3162
S	:	0.0122
Fit Error	:	0.000001000

Fe2: Mikasaite -80 °C

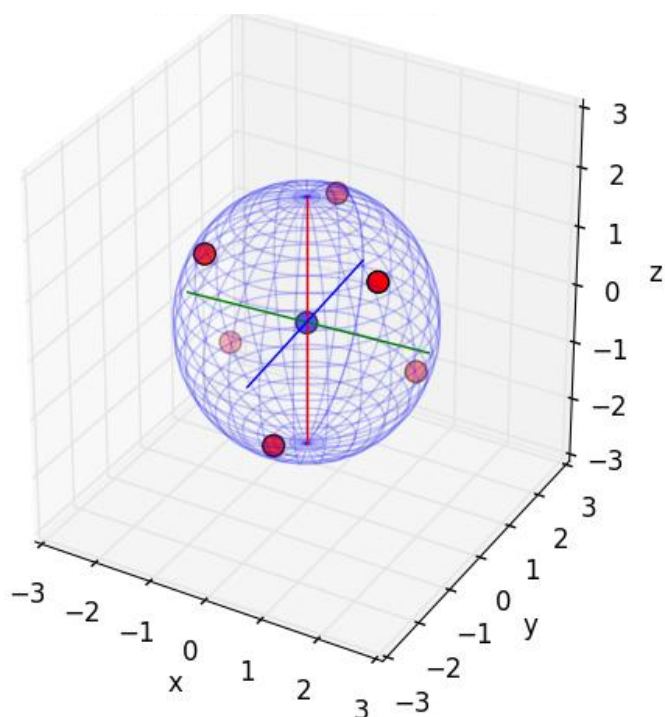


Figure 4.21. Summary of the ellipsoid fitting analysis of the Fe2 coordination site of the refined -80 °C mikasaite data. Ellipsoid was modeled and graphically displayed using PIEFACE (Cumby & Attfield, 2017).

4.4 Discussion

4.4.1 General Diffraction Observations

From the diffraction patterns of our mikasaite alone, there is no significant variation with decreasing temperature. Subtle changes with decreasing temperature cannot be taken at face-value, as factors such as sample displacement are not consistent between each diffraction pattern. This sample displacement discrepancy between diffraction patterns was addressed by refining each subsequent diffraction pattern iteratively, refining our sample displacement first, before refining any of the actual crystal structure parameters. This includes the phase fraction of monoclinic and trigonal mikasaite. Despite this, we see consistent phase fractions, with trigonal mikasaite consistently comprising 77-78.7 wt% of the sample, with the exception of the sample at 0 °C, which contained 83.4 wt% trigonal mikasaite. We did not see any evidence in the diffraction data of a phase change with decreasing temperature. While there is a lack of a more detailed thermodynamical study of trigonal mikasaite, we did not expect to see any phase change within our temperature range based on the thermodynamics of monoclinic mikasaite (Majzlan et al., 2005).

4.4.2 Unit-Cell Variations

As expected with decreasing temperature, our mikasaite unit cell contracted from 25 °C to -114 °C (Table 4.1). This contraction occurred primarily along the *a*-axis (Figure 4.4) with axis lengths consistently shortening from 8.267(6) Å to 8.245(5) Å, with no pattern breaking with the trend and no outliers. This shortening of the *a*-axis is primarily what is reflected in our overall contracting unit-cell volume. The thermal effects of the *c*-axis are far less consistent than the *a*-axis. There is an overall shortening of the *c*-axis, with a cell-length of 22.143(12) Å at 25 °C and 22.137 Å at -114 °C. However, we see the shortest *c*-axis cell length at -60 °C, with a length of

22.110(12) Å. Given this value, the *a*-axis and *c*-axis cell lengths across temperatures have a similar overall range, but only with the *a*-axis are these lengths arranged sequentially to contract with decreasing temperatures. If we were to disregard the anomalous *c*-axis cell length at -60 °C, we would still not see a consistent downward trend in cell length with decreasing temperature. We must also consider our 4σ uncertainty in the unit cell parameters (Bérar & Lelann, 1991), and these uncertainties for the refined *c*-axis cell lengths are about 2x greater than the cell length uncertainties for the *a*-axis. Given these uncertainties, variations in these cell length values are not unreasonable, but we can only point to the *a*-axis values to see a clear trend to relate to the unit-cell volumes.

4.4.3 Thermal Expansion Coefficient

We calculated a volumetric thermal expansion coefficient of $3.64 \times 10^{-5} \text{ K}^{-1}$ with an uncertainty of $0.64 \times 10^{-5} \text{ K}^{-1}$. Our relatively large uncertainty is due to the scatter of our eight unit-cell volumes, causing a linear regression $R^2 = 0.8457$ (Figure 4.6). Eight measurements is also a small sample size for this type of calculation, and it is possible that a non-linear fit for the *V* versus *T* data would be more appropriate, given a greater sample size. Nevertheless, $3.64 \times 10^{-5} \text{ K}^{-1}$ is a very reasonable thermal expansion coefficient, compared to other similar sulfate minerals. Table 4.4 compares the thermal expansion coefficient of mikasaite with several other sulfate minerals, including gypsum, anhydrite, jarosite, $\alpha\text{-MgSO}_4$, and $\beta\text{-MgSO}_4$. There are several more minerals more similar to mikasaite, that do not have any available published thermal expansion coefficient information, nor any published unit-cell volume versus temperature data. Of the available thermal expansion data for sulfates, our coefficient for mikasaite is most similar to other anhydrous sulfates, such as anhydrite and $\alpha\text{-MgSO}_4$, with volumetric thermal expansion coefficient of $3.66 \times 10^{-5} \text{ K}^{-1}$ for anhydrite (Evans 1979) and $3.74 \times 10^{-5} \text{ K}^{-1}$ for $\alpha\text{-MgSO}_4$ (Fortes

et al., 2007). Hydrated phases such as gypsum (Kyono et al., 2022) and jarosite (Xu et al., 2010) have higher coefficients, as water molecules in the crystal structure or hydroxyl-bearing layers allow for greater flexibility and compressibility of the crystal structure, leading to greater expansion/contraction with changing temperature. It is appropriate that our value for mikasaite, being anhydrous, is similar to that of two other anhydrous sulfates, which increases the confidence of this result despite the relatively small sample size and large R^2 value.

Table 4.4 Volumetric thermal expansion coefficients ($\alpha_V \times 10^{-5} \text{ K}^{-1}$) of various sulfate minerals.

Formula	Mineral	<i>T</i> (K)	α_V
$\text{Fe}_2(\text{SO}_4)_3$	Mikasaite	159-298	3.64 ¹
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Gypsum	303-413	13.1 ²
CaSO_4	Anhydrite	295-1273	3.66 ³
$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_2$	Jarosite	298-550	10.1 ⁴
$\alpha\text{-MgSO}_4$		5-300	3.74 ⁵
$\beta\text{-MgSO}_4$		5-300	4.11 ⁵

¹This study. ²Kyono et al. (2022) ³Evans (1979). ⁴Xu et al. (2010) ⁵Fortes et al. (2007)

4.4.4 Fe-Site Ellipsoid Fitting

The parameters of the ellipsoids fit to each Fe site give insight into the distortion of the FeO_6 octahedra, and differences between the two distinct Fe coordination sites in mikasaite, Fe1 and Fe2. The three semi-axes of the fitted ellipsoid R1, R2, and R3 (Table 4.3) describe the shape of the fitted ellipsoid along three orthogonal axes. For each site at each temperature, two of these lengths will always be equivalent due to the 3-fold symmetry of the site. The relative lengths of the two equivalent semi-axes compared to the third semi-axis describe the degree of compression along that axis. For our Fe1 site, $R1 = R2 > R3$ in all cases, except for the pattern taken at -60°C . This is not the first instance of the -60°C pattern acting anomalously, as the c -axis of the unit cell appeared as an outlier because of its short length (Figure 4.5). We see a similar picture with the Fe2 site, as patterns at all temperatures show $R3 = R2 < R1$, except for the pattern at -60°C . For this site, we can see how this change in the distortion at -60°C relates to the orientation between the SO_4 tetrahedra and FeO_6 octahedra, as the angles between Fe2-O2-S1 (Figure 4.18) and Fe2-O4-S1 (Figure 4.19) appear noticeably smaller than at temperatures slightly warmer or colder. These shape distortions are summarized in the shape parameter (S) of each Fe site at each temperature (Table 4.3). The S parameter shows how prolate ($S > 0$) or oblate ($S < 0$) the ellipsoid fitted to FeO_6 octahedra is, with respect to a sphere ($S = 0$). From the S parameter, we can see an anticorrelation between Fe1 and Fe2. Fe1 is oblate and Fe2 is prolate at every temperature, with the exception of -60°C , where Fe1 becomes prolate and Fe2 becomes oblate. It is unclear exactly why the unique axis switches at -60°C , but it is significant that it does so simultaneously for both the Fe1 and Fe2 sites at the same temperature. This reflects parameters within the refined diffraction data at -60°C . In PIEFACE, each site is modeled independently of one another (Cumby & Attfield 2017), thus, the switching of degenerate and unique axes at -60°C is not due to

PIEFACE itself. The magnitude of distortion to cause this flip at -60 °C is very slight, thus it is possible that a minor error in the Rietveld refinement of the pattern at -60 °C has caused this sign reversal in S, as well as the anomalously short *c*-axis length.

The center displacement of Fe1 and Fe2 also show different trends with decreasing temperature (Table 4.3). Fe1 maintains a fairly consistent center displacement across the entire temperature range, from ~0.024 – 0.067 Å, with no substantial trend with changing temperature. This suggests that this center displacement of the Fe1 site is a normal characteristic of mikasaite, and not a result of any thermally-induced structural changes. The Fe2 site is much more variable, with an overall trend towards the ellipsoid center with decreasing temperature. There is one outlier at 0 °C, where the center displacement spikes to 0.126 Å. This center displacement spike at 0 °C is correlated with the lower Fe2-O4 bond length (Figure 4.11), and noticeably higher bond angles for Fe2-O2-S1 and Fe2-O4-S1 (Figures 4.18, 4.19). The displacement of the Fe2 center is much more variable at temperatures above -60 °C, and after this temperature, there is a far more systematic trend towards zero displacement with decreasing temperature. This change in the displacement trend may be related to the axis-switching at -60 °C, suggesting that the change in the diffraction data which causes this axis switch also constrains the Fe2 octahedra site more rigidly to its ellipsoid center.

The volume and mean radius (R_E) of the fitted ellipsoids are also different for the Fe1 and Fe2 (Table 4.3). The Fe1 site consistently has a smaller mean radius (~1.87 – 1.91 Å) than the Fe2 site (~2.05 – 2.11 Å). The mean radius and volume of the Fe1 site follows the trend expected from thermal contraction from 25 °C to -60/-80 °C, with R_E shortening from ~1.91 Å to a minimum of ~1.87 Å at -60/-80 °C within uncertainty, and the volume decreasing from 28.93 Å³ to 27.19 Å³. This is a total contraction of the Fe1 site of $\Delta 0.04$ Å in R_E and $\Delta 1.74$ Å³ in volume, which

physically is consistent with other trends in bond length and unit cell contraction. This trend is reversed at temperatures colder than -60 °C, with the mean radius lengthening back up to ~1.89 Å and the volume increasing to 27.96 Å³ at -114 °C. This trend reversal at the -60 °C temperature where we see the distortion axis flip is another confirmation that the data at this temperature is an outlier. For the Fe2 site, the mean radius (~2.05 – 2.11 Å) and volume (~35.97 – 39.49 Å³) have a less consistent pattern than the Fe1 site, without any overall trends. The previously discussed anomalies at 0 °C and -60 °C are both mirrored with these values, with the largest and smallest volumes at -60 °C and 0 °C. Above -60 °C, the fitted ellipsoid volume appears to grow from 37.73 Å³ to 39.49 Å³, which should not be physically plausible with the expected thermal contraction. Below -60 °C, the trend returns to normal thermal behavior, with R_E decreasing from 2.11 Å to 2.07 Å and the volume decreasing from 39.49 Å³ to 37.12 Å³.

Across both Fe-sites, the data at 0 °C and -60 °C appear as inflection points, with trends across multiple fit ellipsoid parameters switching or reversing at these temperatures. This suggests that there may be multiple superimposed systems contributing to these trends. These reversing trends are often anti-correlated between the Fe1 and Fe2 sites, and these sites have opposite behavior. It should also be noted that the uncertainty associated with each mean radius calculation is significant (Table 4.3) and should be weighed heavily when considering the credence of our interpretations.

4.5 Conclusions

We acquired diffraction data of synthesized mikasaite at eight temperatures from 25 °C to -114 °C. Rietveld refinement of each diffraction pattern resulted in reliable structural data of the mikasaite, with refinement wR consistently between ~1.8 - 2.5%. With the exception of the pattern taken at 0 °C, the Rietveld refinement showed a consistent mixture of trigonal (~78.7 wt%) and

monoclinic (21.3 wt%) mikasaite. We did not see any phase transitions of the mikasaite. The unit cell of trigonal mikasaite contracts with decreasing temperature, driven primarily from the shortening of the *a*-axis, which shows a clear trend with decreasing temperature from 8.267(6) Å to 8.245(5) Å. This mirrors the shrinking of the unit cell volume, from 1310.5(1.6) Å³ to 1303.2(1.0) Å³. A linear regression of ln(*V*) versus *T* results in a volumetric thermal expansion coefficient of $3.64 \pm 64 \times 10^{-5}$, which is consistent with other anhydrous sulfate minerals. The Fe1 and Fe2 octahedral sites show consistently different fitted ellipsoid geometries, but the degeneracy in the principal axes at both sites reflects the trigonal symmetry of mikasaite as part of the $R\bar{3}$ space group. The -60 °C pattern is anomalous outlier across multiple parameters from both the basic Rietveld refinement and ellipsoid fitting, including *c*-axis length, ellipsoid shape, and Fe-O-S bond angles), suggesting the diffraction pattern and/or refinement at this temperature may carry additional uncertainty or unknown artifacts. Overall, this study has provided the first low-temperature structural data of mikasaite, filling a knowledge gap given its importance as a Mars-analog material and anhydrous endmember of the ferric sulfate system.

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Chapter 5

Conclusions

5.1 Review

In this dissertation, I use a combination of several analytical tools to thoroughly characterize amorphous ferric sulfate, amorphous magnesium sulfate, and mikasaite. I've described some of the fundamental properties of these sulfates, and determined their atomic structures under conditions relevant to Mars. My hope is that the spectra and structural data I produced throughout this work provide a solid foundation and reference for the interpretation of these sulfates in Gale crater.

In Chapter 2, I found and discussed the effects of an iron-rich amorphous coating on the X-ray diffraction of crystalline samples, using Raman spectroscopy and an XRD instrument analogous to CheMin in Gale crater. In both the Raman and XRD data, I found significant effects of AFS coatings on the interpretation of crystalline Ca-sulfate in mixtures. In the Raman spectra, I found that the AFS coatings cause a significant sampling bias, as the laser is more likely to interact with an AFS coating rather than a clean gypsum surface. On Mars, if the sample morphology and bulk chemistry are unknown, then Raman spectroscopy may not accurately characterize the composition of a mixed amorphous-crystalline sample. In the XRD data, I found that AFS coatings have a significant effect when analyzed with a Debye-Scherrer XRD method with a Co radiation source because of two key factors: X-ray scattering/absorption, and X-ray path-length through the sample. For an X-ray to interact with a coated crystalline grain and diffract to the detector with the Debye-Scherrer method, it must pass through amorphous layers multiple times. The iron in the AFS coatings can scatter and/or absorb these X-rays before and after the X-

rays interact with each crystalline grain. This is particularly true with CoK α X-rays, which are more susceptible to absorption and scattering due than CuK α X-rays. With a greater volume of sample for the X-rays to pass through with the transmission geometry of the Debye-Scherrer method, the more opportunity for scattering and absorption to increase the X-ray path-length and decrease the peak-to-background ratio. CheMin uses a Debye-Scherrer XRD with CoK α radiation and is thus susceptible to these effects of Fe-rich amorphous coatings. The process for estimating the amorphous composition relies on the assumption that CheMin is not missing any of the crystalline material above the detection limit. With the morphology of coatings potentially having a significant effect on the samples measured with CheMin, I would suggest a reevaluation of the amorphous composition estimates, or at least the uncertainties of these estimates.

In Chapter 3, I determined the short-range order and structure of amorphous ferric sulfate and amorphous magnesium sulfate at Mars-relevant temperatures using pair distribution function analysis. The most interesting and perplexing results of this study were the lack of any significant differences in the PDF patterns throughout the measured temperature range from 300 K to 100 K. I attribute this as a result of a Δr PDF resolution of ~ 0.37 Å. Over a comparable temperature range, the study described in Chapter 4 shows that distance between the SO₄ tetrahedra and FeO₆ octahedra only contracts at most by ~ 0.25 Å, even considering the shortest and longest reasonable atomic distances with $\pm 4\sigma$ uncertainty. Within the first-order shell, the S-O and Fe/Mg-O bonds of the polyhedra in AFS and AMS are too rigid to contract with any measurable difference, and at higher order shells, the Δr PDF resolution and combination of broader PDF peaks makes it impossible to discern any significant thermal contractions with the data available. I was, however, able to determine the coherence length of both AFS and AMS. Using the last discernable PDF feature, I interpret the coherence length of AFS to be 8.33 Å and the coherence length of AMS to

be 8.42 Å. I also characterized the S-O, O-O, Fe-O and S-Fe distances within the first-order shell in the PDF data. Overall, this chapter provides valuable low-temperature diffraction data of AFS and AMS, which should prove useful as a baseline for future studies of these materials.

Finally, in Chapter 4, I conducted the first low-temperature structural characterization of the mineral mikasaite. I completed detailed Rietveld refinement of eight diffraction patterns acquired between 25 °C to -114 °C. I characterized the thermal behavior of mikasaite over this temperature range, and using a linear regression of $\ln(V)$ vs T , I calculated a volumetric thermal expansion coefficient of $3.64 \pm 64 \times 10^{-5} \text{ K}^{-1}$. I found that the contraction of the unit cell of mikasaite is driven primarily by contraction along the a -axis. Ellipsoidal analysis of the two Fe coordination sites in Mikasaite shows that these two sites are not identical and may behave differently with decreasing temperature. However, there were several anomalies in this dataset, such as the -60 °C data, so any further interpretation of these Fe-coordination sites would require a repeat Rietveld refinement, or additional data collection at -60 °C to remedy this anomaly. Nevertheless, this fundamental characterization of mikasaite at low temperature may prove useful for several Mars-related experiments in which mikasaite is used as a component.

5.2 Future Work

The spectra and structural data I produced throughout this work provide a solid foundation and reference for the interpretation of these sulfates in Gale crater. My dissertation also highlights the need for multiple observational and analytical perspectives when interpreting the composition of any one sample. In situ on the surface of Mars, the data from a single instrument is rarely enough to fully characterize a rock or mineral, and it is critical to always consider and reconsider the assumptions and uncertainties associated with each analytical technique. There are several avenues

for future research that would continue to better our understanding of these amorphous sulfates, and improve our ability to characterize and interpret them on the Martian surface.

Regarding the detectability of amorphous sulfates on the Martian surface, and their effects on the measurement of other phases using instruments onboard Curiosity, there are a few directions of future research one could follow. First, it would be important to reexamine some of the previous estimates of the amorphous composition of Gale crater, with updated uncertainties based on the “worst case” amorphous coatings. The potential for coatings could be approximated from phases within the current estimated amorphous component. For example, as discussed in Chapter 2, Ca-sulfate should not form an amorphous solid, so if any mass-balance calculation results in the inclusion of Ca-sulfate in the amorphous fraction, it may infer the presence of coatings that have hidden this crystalline Ca-sulfate from CheMin. In this case, the overall amorphous composition may have to be adjusted, to compensate for coated crystalline grains. It may be possible to use the difference of detected and undetected crystalline grains as a measure of the amount of coated material within a bulk sample, as a ‘degree of coating’, to make interpretations regarding the overall coatings and cementation of a sediment or sedimentary rock. This becomes much more difficult if the coated crystalline grain is a phase that can exist both as an amorphous and crystalline form, such as various Mg-sulfates. In this case, one would have to estimate the degree of coating from analysis of phases such as Ca-sulfate, which can only exist as a crystalline phase, and then extrapolate this degree of coating to the bulk sample. This of course comes with its own assumptions and uncertainties, such as the homogeneity of these coatings within a bulk sample, which would require a more visual analysis to determine. An additional avenue of research regarding these amorphous coatings would be the effects of mixed-phase or mixed-cation

amorphous coatings, such as a mixture of AFS and AMS, and how varying percentages of CoK α -absorbing Fe in the coatings affects the detection of coated crystalline grains with XRD.

In general, the fundamental characteristics and atomic structure of amorphous sulfates are not well studied. While Chapter 3 of this dissertation makes significant progress, there are a few improvements and additional analyses that should be completed in future studies. First, the interpretations from deciphering the PDF patterns of AFS and AMS were strongly limited by the Δr resolution of PDF data, which is controlled by the Q_{max} in our PDF calculations. To improve the PDF data resolution, the optimal Q_{max} would need to be increased. This would be best accomplished by improving the data quality at high-Q, through more optimized signal-to-noise, thinner Kapton capillaries, and longer beam exposure times per scan. It would also be an improvement to reduce ice condensation across the sample, which would in turn require a reduction in the data masking required before integration, further improving the signal-to-noise. It may also be useful to repeat this analysis with neutron scattering, as a complimentary analysis with the potential to collect higher quality data at high-Q. Another further study of these materials would be Reverse Monte Carlo modeling of AFS and AMS to determine atomic bond angles and the relative orientations of the SO₄ tetrahedra and Fe/MgO₆ octahedra sites within AFS and AMS. While the PDF data resolution of this dissertation did not allow me to see any changes to bond distances of AFS or AMS with decreasing temperature, future analysis with Reverse Monte Carlo modeling may give insight into the atomic-scale distortions of AFS and AMS at cold temperatures.

Part of the motivation behind the analysis of mikasaite in Chapter 4 was the lack of any published low-temperature structural data for mikasaite. While researching potential comparisons for the thermal expansion coefficient of mikasaite, I was surprised at the similar inadequacy of available thermal expansion data for most Fe-sulfates. Martian surface temperatures can vary

significantly, so it is important to have a solid understanding of how common surface materials such as Fe-sulfates on Mars behave with these thermal changes. For terrestrial materials, extensive libraries of structural and crystallographic data exist for common rock-forming minerals. As we collect more and more geochemical data from Mars at an accelerating rate, it is becoming increasingly important to prepare an equivalent crystallographic database and reference library for common Martian materials, and one that is not exclusively tied to specific missions or instruments.

5.3 Final Conclusions

Through my dissertation work, I have made significant contributions to understanding the nature of amorphous sulfates. I have characterized the atomic structure of amorphous ferric sulfate, amorphous magnesium sulfate, and mikasaite. I have outlined several directions of future research that would continue to improve our grasp on the structure and behavior of these sulfates, and other sulfates, in the Martian environment. I identified a potential flaw in the mass-balance calculations used to estimate the composition of the amorphous component in Gale crater due to Fe-rich amorphous coatings obscuring crystalline materials. My hope is that the research outlined in this dissertation lays the groundwork for further research to comprehensively understand the suite of sulfates on Mars, from crystalline to amorphous.

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Appendix A

Chapter 2 of this dissertation was published in the Journal of Geophysical Research: Planets. The citation of this publication is as follows:

Hopkins, R. J., Rogers, A. D., & Ehm, L. (2026). Obscuration of crystalline Ca-sulfate in XRD and Raman data when coated by amorphous ferric sulfate: Implications for the amorphous components at Gale crater. Journal of Geophysical Research: Planets, 131, e2025JE009299. <https://doi.org/10.1029/2025JE009299>

All of the data associated with this study was published in a Zenodo data repository alongside the publication in JGR: Planets. This Zenodo repository can be accessed with the following link:

<https://doi.org/10.5281/zenodo.17575248>

Citation: Hopkins, R., Rogers, A. D., & Ehm, L. (2025). Obscuration of crystalline Ca-Sulfate in XRD and Raman data when coated by amorphous ferric sulfate: Implications for the amorphous components at Gale Crater [Dataset]. Zenodo. <https://doi.org/10.5281/zenodo.17575248>

Explanation of data structure:

Raman Data: There are 5 data files in txt format that contain several Raman spectra of the samples studied in the associated journal article. These five file names are listed below.

- *AFS Raman.txt*: Raman spectra of the pure amorphous ferric sulfate (AFS).
- *Gypsum Raman.txt*: Raman spectra of 25-63 μm gypsum.
- *Mikasaite Raman.txt*: Raman spectra of Mikasaite
- *Coated Gyp-AFS Raman.txt*: 50-50 wt% mixture of AFS and gypsum, with the AFS coating the gypsum.
- *Uncoated Gyp-Raman.txt*: 50-50 wt% mixture of AFS and gypsum, with the AFS and gypsum in separate discrete grains.

File Structure: Each txt file for each sample contains 5 spectra. Below is a guide to each column in the files

- Column 1: Raman Shift (1/cm)
- Column 2: Raw uncorrected spectra
- Column 3: Baseline

- Column 4: Baseline-Corrected spectra
- Column 5: Normalized Baseline-Corrected spectra, with offset shown in Figure 1.

XRD Data: The raw diffraction data of both the coated and uncoated Gyp-AFS mixtures from both XRD instruments are available. The file names are listed below, with descriptions

- *50-50_gyp-AFS_Coated_DS_XRD.txt*
- *50-50_gyp-AFS_Uncoated_DS_XRD.txt*
- *Gyp-AFS-Coated_BB_XRD.ras*
- *Gyp-AFS-Uncoated_BB_XRD.ras*

The two files ending with ‘.txt’ with ‘DS’ in the file name contain diffraction data taken with the Olympus BTX XRD instrument. The two files ending with ‘.ras’ with ‘BB’ in the file name contain diffraction data taken with the Rigaku Miniflex XRD.

SEM/EDS Data: There are 13 SEM images available in high-resolution of both the uncoated and coated Gyp-AFS samples. The file name states that whether the sample is coated or uncoated. The scale bar and scan information is at the bottom of each SEM images. Additionally, a word document 'Gyp-AFS SEM-EDS Full.docx' holds all of the full EDS analyses of each image, with spot spectra and line scans.

Appendix B

This appendix provides supplementary information to Chapter 3 of this dissertation, including the calibration parameters used in Dioptas (Prescher & Prakapenka, 2015) in Table B1, and an example configuration file used in the ‘PDFgetX3’ program (Juhás et al., 2013).

Table B1. Calibrated Fit2d parameters in Dioptas, used in the integration of diffraction data collected at the XPD beamline of NSLS-II, discussed in Chapter 3

Detector Distance	223.2668 mm
Wavelength	0.181 Å
Polarization	0.99
Center X	1056.764 px
Center Y	1014.891 px
Rotation	35.00187°
Tilt	0.842047°
Pixel width	200 µm
Pixel height	200 µm

Below is an example configuration file used in the ‘PDFgetX3’ program for calculating the pair distribution functions in Chapter 3 of this dissertation. The template below shows the setup for AMS as an example, but an equivalent setup was used for AFS. This configuration file does not include any irrelevant commented-out sections from the original configuration file template provided by the PDFgetX3 developers (Juhás et al., 2013).

Begin configuration file:

```
## Format of input files. Available formats are: "twotheta", "QA", "Qnm"
## corresponding to a 2-column text data where the first column is either
## twotheta in degrees, Q in inverse Angstroms or Q in inverse nanometers.
dataformat = twotheta

## Optional background intensities from container and air scattering
backgroundfile =Kapton_empty_300k_masked.xy

## Output file name, write to the standard output when "-".
## This may contain @f, @h, @r, @e, @t, @b, @o tokens which expands as follows:
##
## @f dir1/dir2/filename.dat   input file path
## @h dir1/dir2               input file head directory or '.'
## @r dir1/dir2/filename      input path with extension removed
## @e dat                     input file extension without '.'
## @t filename.dat            tail component of the input file
## @b filename                 tail component with extension removed
## @o gr                       output extension iq, sq, fq or gr
##
## An empty value works the same as "@b.@o", i.e., saves the data
## in the current directory with a proper data type extension.
#output = series1/foo@b-01.@o
output =@b.@o

## Types of output files to be saved. Possible values are
## "iq", "sq", "fq", "gr", also used as filename extensions.
## No files are saved when empty, "none" or "NONE".
outputtype = fq, gr

## Flag for overwriting existing output files. By default False.
## It is probably safer to use it from command line.
```

force = yes

The PDF calculator configuration mode or a name of the calculator

setup. The available modes correspond to the radiation type.

The supported modes are:

'xray', 'neutron', 'sas'

mode = xray

X-ray, neutron, or electron wavelength in Angstroms.

Required for the "twotheta" dataformat.

wavelength = 0.181

Chemical composition of the measured sample. Supported formats are

"PbTi0.5Zr0.5O3", "Pb (TiZr)0.5 O3" or "Pb 1 (Ti Zr) 1/2 O 3".

composition = Mg S O6 H4

r-limit for the maximum frequency in the F(Q) correction polynomial.

The PDF is unreliable at shorter r, however a too small rpoly

disables polynomial correction and yields noisy PDF. Too large

values may smooth-out useful signal in the data.

rpoly = 1

The Q cutoff for the meaningful input intensities in inverse Angstroms.

This is the upper boundary for the qmax parameter. It is also used as

the upper boundary for the polynomial fits in S(Q) corrections.

qmaxinst = 30

Lower Q cutoff for Fourier transformation in inverse Angstroms.

Use 0.0 when not specified.

qmin = 0

Upper Q cutoff for Fourier transformation in inverse Angstroms.

Use maximum Q in the data when not specified.

qmax = 17

Limits and spacing for the calculated PDF r-grid.

All values in Angstroms.

rmin = 0

rmax = 30

rstep = 0.01

```
## Plot the specified results and activate interactive mode.  
## A comma separated list with items such as "iq", "sq", "fq", "gr".  
## No plot is produced when empty, "none" or "NONE".  
plot = iq, sq, fq, gr  
  
## Start an IPython interactive session after processing all files.  
## Useful for tuning the configuration parameters or interactive plotting.  
## This is always on when plot option has been set.  
interact = no
```

End configuration file.

Appendix C

This appendix provides a link to a Zenodo repository for the integrated diffraction data of AFS and AMS from beamtime at NSLS-II, discussed in Chapter 3. This data, as well as the collected diffraction data of the empty Kapton capillaries, is available here:

<https://doi.org/10.5281/zenodo.19746634>

or,

https://zenodo.org/records/19746634?token=eyJhbGciOiJIUzUxMiJ9.eyJpZCI6ImYxZTEuNWUxLTc5M2UtNDJmNC1hMzdkLTM2ZjY5MWM3NjdiMyIsImRhdGEiOnt9LCJyYW5kb20iOiJkZGU3OWU4NDgyYjI4YjA3NjcxdDg0YjgyOWRiZjc3NiJ9.m0SkSuZSOqBT6N3jkNSLR19h16GSxZos_zRj6dkeRdaG-oS2KPIcHnOakT2SKn56KhFDyApoKKMkP1xqjlwPag

Appendix D

The Crystallographic Information Files (.cifs) resulting from the Rietveld refinement of mikasaite at each temperature are available in the following Zenodo repository:

<https://doi.org/10.5281/zenodo.19748183>

or,

https://zenodo.org/records/19748183?token=eyJhbGciOiJIUzUxMiJ9.eyJpZCI6IjA1OTEzODRjLWQwMjMtNGVjZS1hMjM1LTcyZDY1NWE1ODg2ZCI6ImRhdGEiOnt9LCJyYW5kb20iOiIyMDY4Y2MwZjBmNWM4YjRlMzYwOTdhZWY2MDBiNjY2YyJ9.WtXdaZCmpxJEDxq-6zWLI_J-xyRXOUx3g-lj6Ox5ov_VA_Qr_mmCxV64TebXb3o7N2ZwFQ-XtDrmTcary8Wcnw

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