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UNIVERSITY OF CALIFORNIA
SANTA CRUZ

**EXPERT-GUIDED INTEGRATION OF RAMAN SPECTROSCOPY, X-RAY
DIFFRACTION, AND MACHINE LEARNING FOR MINERALOGICAL
INTERPRETATION OF MARS-RELEVANT MATERIALS**

A dissertation submitted in partial satisfaction
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

EARTH & PLANETARY SCIENCES

by

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August 2026

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Abstract

Expert-Guided Integration of Raman Spectroscopy, X-ray Diffraction, and Machine Learning for Mineralogical Interpretation of Mars-Relevant Materials

Genesis Berlanga

Planetary exploration requires extracting physically meaningful information from incomplete measurements acquired under environmental, instrumental, and operational constraints. This dissertation integrates Raman spectroscopy, X-ray diffraction (XRD), mineral physics, and computational analysis to expand the information recoverable from measurements of Mars-relevant materials. Raman spectroscopy provides the central connection among these studies because its vibrational frequencies, intensities, and spectral shapes encode not only mineral identity, but also bonding, hydration, crystallinity, temperature, structural disorder, and crystallographic orientation.

Three studies progressively examine mineral phase identification, mineral physical state, and how it is crystallographically organized. A convolutional neural network trained using high-volume, wide within-class Raman datasets and demonstrated robust mineral classification under dusty, low-signal, and otherwise nonideal conditions relevant to Mars. These results establish that physically representative training populations and expert-guided dataset construction are critical to reliable machine-learning interpretation.

Chapter 2 included variable-temperature Raman spectroscopy and XRD characterization of progressive dehydration of magnesium perchlorate and

magnesium sulfate from -70 to 400°C. $\text{Mg}(\text{ClO}_4)_2$ undergoes discrete crystalline hydration transitions, whereas MgSO_4 progressively develops poorly crystalline and X-ray-amorphous products while retaining Raman sensitivity to local sulfate environments. Wilson GF force constants quantitatively connect vibrational frequencies to hydration-dependent changes in tetrahedral bond stiffness and coupling. A previously unreported Fermi resonance in crystalline $\text{Mg}(\text{ClO}_4)_2$ provides an additional hydration diagnostic and potential Raman thermometer. These results demonstrate that full-spectrum interpretation and quantitative vibrational analysis can constrain hydration, bonding, crystallinity, metastability, and environmental history beyond mineral identification alone.

Chapter 3 investigates co-registered Raman and synchrotron XRD rasters of Martian shergottite NWA 13276 using combined semi-supervised, human-in-the-loop mineral identification with E-WIMV texture reconstruction. Olivine exhibits strong non-random lattice preferred orientation, while its $\sim 810\text{--}870\text{ cm}^{-1}$ Raman doublet varies systematically with crystallographic orientation, establishing Raman intensity as an orientation-sensitive observable with potential applications to *Perseverance* rover SuperCam measurements on Mars.

This dissertation advances planetary spectroscopy from mineral classification toward physically constrained inference, demonstrating how independent crystallographic measurements, systematic experiments, mineral physics, and expert-guided computation can transform spectral variability from an analytical complication into information about mineral state, structure, and geological history.

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Thank you to my mom Ana, I dedicate this to you.

1.0 Introduction

Planetary exploration is fundamentally an exercise in inference from remote observations. Unlike terrestrial field geology, robotic exploration is constrained by the instruments delivered to a planetary surface, their measurement geometries and resolutions, finite mission resources, communication limitations, and local environmental conditions. Natural planetary materials also contain mixtures, solid solutions, variable crystallinity, preferred orientation, alteration products, dust, and other sources of complexity. At the same time, modern missions produce increasingly large volumes of spectroscopic, imaging, chemical, and mineralogical data. The challenge is therefore not only to acquire measurements from another planetary surface, but to extract as much physically meaningful information as possible from the measurements available. This dissertation approaches that problem through Raman spectroscopy, X-ray diffraction (XRD), mineral physics, and computational analysis, with a focus on Mars-relevant materials and rover observations. Raman spectroscopy provides the central connection among the three studies because it is nondestructive, mineralogically sensitive, capable of stand-off measurements, and currently operating on Mars aboard the Perseverance rover. Raman spectra also contain substantially more information than mineral identity alone.

Raman scattering originates from changes in molecular polarizability associated with lattice and molecular vibrations. Raman frequencies, intensities, widths, and spectral shapes therefore respond to composition, bonding, local coordination, structural order, temperature, hydration, symmetry, and crystallographic

orientation. Many of the same effects that make natural Raman spectra variable also provide information about the physical state and history of the material. XRD provides a complementary view. Diffraction probes periodic crystal structure through the geometry and intensity of scattering from the atomic lattice, providing constraints on phase, unit-cell structure, crystallinity, phase transitions, and crystallographic orientation. Raman spectroscopy instead probes the vibrational response of that structure. In simplified terms, diffraction probes how a crystal is shaped and organized, while spectroscopy probes how the atoms within that structure move and interact. This distinction is especially important for crystallographic texture. XRD, electron backscatter diffraction, and Laue diffraction derive orientation directly from crystallographic geometry. Raman spectroscopy approaches orientation indirectly through the dependence of vibrational intensities on Raman tensors and measurement geometry. If these relationships can be independently calibrated, however, Raman spectroscopy may provide access to crystallographic information where diffraction measurements are unavailable.

Mars rover payloads illustrate the value of such complementary measurements. Perseverance carries the SuperCam and SHERLOC Raman instruments but no X-ray diffractometer, while Curiosity carries the CheMin XRD instrument but no Raman spectrometer. Planetary spectroscopy therefore becomes more powerful when calibrated against independent measurements of the physical properties responsible for the spectrum. Laboratory experiments provide a way to establish these relationships under controlled conditions and apply them to

measurements that cannot presently be collected concurrently on Mars. XRD takes on the role of ground truthing and crystallographically anchoring Raman measurements throughout this Raman-centered dissertation. In Chapter 1, Raman, XRD, and X-ray fluorescence characterize mineral standards before construction of a machine-learning training set. In Chapter 2, XRD independently constrains hydration phases and crystallinity while Raman tracks local vibrational evolution. In Chapter 3, XRD supplies independent mineralogical and crystallographic texture measurements against which orientation-dependent Raman behavior is evaluated. In this way, diffraction provides the structural reference needed to physically interpret Raman spectroscopy.

1.1 Three Levels of Inference

The three studies progressively expand the level of inference attempted from Raman and diffraction data: Can we identify the mineral phase? What state is the mineral in, and what has happened to it? How is the material organized, and what geological process might that organization record? These questions move from classification, through physical interpretation, toward geological inference. Conceptually, the progression is to learn the spectrum, understand the spectrum, and use the spectrum to understand the rock.

Chapter 1 — Identifying the mineral

The first level of inference is mineral classification under conditions relevant to natural and planetary measurements. Raman spectra collected from rocks may vary because of dust, fluorescence, weak signal, focus, crystal orientation, surface

microtopography, chemical substitution, disorder, and mineral mixtures. Rather than treating this variability only as an obstacle, Chapter 1 asks whether a neural network can learn mineral identity across a broad range of realistic spectral conditions. The Machine Learning Raman Open Dataset was constructed from large populations of mineral spectra containing substantial within-class variability. Mineral standards were independently characterized by Raman spectroscopy, XRD, and XRF before being incorporated into the training set. A convolutional neural network trained on these data successfully classified minerals from dusty, low-signal, and otherwise nonideal Raman measurements. The principal lesson was that model performance depends strongly on the physical representativeness of the training set. A useful training population must span the mineralogical, compositional, crystallographic, instrumental, and spectral variability expected in the application. Constructing that dataset requires both computational knowledge and domain expertise in spectroscopy and mineralogy. Chapter 1 therefore establishes an important principle for the rest of the dissertation: machine learning is most useful when the training domain is physically meaningful and representative of the problem being solved. Computation extends expert interpretation across datasets whose scale and variability make exhaustive manual analysis impractical.

Chapter 2 — What state is the mineral in, and what is its evolution/history?

The second level of inference moves beyond phase identification toward physical state and history. Raman spectra contain information about bonding, symmetry, hydration, temperature, crystallinity, and structural evolution, but

extracting that information requires systematic experiments in which the variables controlling spectral behavior are independently constrained. Chapter 2 uses variable-temperature Raman spectroscopy and XRD to investigate the dehydration of magnesium perchlorate and magnesium sulfate under Mars-relevant conditions. The two systems contain tetrahedral oxyanions but follow different structural pathways during dehydration. Magnesium perchlorate progresses through discrete crystalline hydration phases, whereas magnesium sulfate develops increasingly poorly crystalline and X-ray-amorphous products while retaining Raman sensitivity to the local sulfate environment. The paired measurements demonstrate the complementary information provided by Raman spectroscopy and diffraction. XRD constrains long-range crystallographic order and phase transitions, while Raman spectroscopy remains sensitive to local bonding environments even when long-range periodicity decreases. Together, the methods relate Raman spectral behavior to crystal structure, hydration, crystallinity, temperature, and metastability.

Force constant calculations extend this interpretation from spectral peak position to quantitative bonding information. Wilson GF analysis converts Raman frequencies into estimates of stretching, bending, and vibrational coupling within the perchlorate and sulfate tetrahedra. These calculations constrain changes in bond stiffness, tetrahedral rigidity, symmetry, and hydration-dependent coordination. The result is a progression from identifying a sulfate or perchlorate to interpreting its hydration state, local bonding environment, crystallinity, and structural evolution. The systematic laboratory measurements also provide context for nonequilibrium

states that may occur on Mars as temperature and atmospheric conditions vary over diurnal, seasonal, and geological timescales.

Chapter 3 — How are the minerals organized, and what geological process/es might that organization record?

The third level of inference moves from mineral state to crystallographic organization and geological fabric. Preferred orientation within igneous rocks can record anisotropic crystal growth, accumulation, magmatic flow, deformation, and later modification. These textures are normally investigated with diffraction-based techniques, but Perseverance carries Raman spectroscopy rather than a diffraction instrument. Chapter 3 tests whether unpolarized Raman spectroscopy contains information about crystallographic orientation. High-density, co-registered Raman and synchrotron XRD rasters of Martian shergottite NWA 13276 provide mineralogical, spectroscopic, and crystallographic measurements from corresponding regions of an intact meteorite section. XRD provides the independent mineral identification and texture information used to evaluate the Raman response. Confirmed olivines exhibit strong, non-random lattice preferred orientations, while their co-registered Raman spectra show systematic variation in the relative intensities of the characteristic $\sim 810\text{--}870\text{ cm}^{-1}$ olivine doublet. The relationship is best treated as orientation-sensitive rather than as a unique single-spectrum orientation measurement because Raman intensity responds to the complete crystallographic and optical geometry. This still provides a potentially useful planetary observable. Spatially coherent variations in olivine Raman intensity across an exposed rock surface may

contain information about crystallographic fabric where direct diffraction measurements are unavailable. Applied to cliffs, crater walls, and layered outcrops, such measurements could help evaluate fabrics related to crystal accumulation, magmatic flow, anisotropic growth, cooling, or deformation.

1.2 Field Measurements and Natural Complexity

The three chapters address different aspects of natural measurement complexity. Chapter 1 considers dust, fluorescence, low signal-to-noise ratios, variable focus, surface geometry, and mixtures. Chapter 2 considers temperature, pressure, humidity, metastability, amorphization, spectral overlap, and nonequilibrium hydration. Chapter 3 considers mosaicity, mixed phases, incomplete diffraction coverage, crystallographic orientation, sampling scale, and measurement geometry. Real planetary materials are complex and rover measurements provide only part of their geological context. The goal is therefore to characterize that complexity, constrain it physically, and extract useful information from it. Spectral variability can itself be informative: peak shifts may reflect composition, temperature, hydration, or bonding; peak broadening may record disorder or shock; intensity changes may reflect orientation; and Raman spectra may preserve local structural information in materials that have lost long-range crystallinity. Independent physical measurements are therefore central to this dissertation. XRD, XRF, controlled experimental conditions, crystallographic refinements, and texture reconstructions provide external constraints on the physical properties inferred from the spectra. This

allows statistical or spectral relationships to be tested against measurable properties of the material.

1.3 Evolution in Computational Planetary Science

The computational approaches in this dissertation reflect an evolution in how machine learning can be applied to planetary datasets. Chapter 1 presents a problem well suited to deep learning: a large labeled dataset with broad within-class spectral variability. Under these conditions, a CNN can identify complex spectral patterns efficiently and accurately. Chapter 3 presents a different situation. The NWA 13276 XRD raster contains thousands of patterns, but there is no comparably large labeled training set spanning mineral mixtures, preferred orientations, mosaicity, partial grain sampling, phase abundance, and measurement geometry. Instead of relying on a fully supervised classifier, the analysis combines PCA, UMAP, cosine similarity, diffraction constraints, spatial information, and iterative expert review. These methods organize and prioritize the dataset while mineral identification remains physically and crystallographically constrained. The contrast between the chapters leads to a broader conclusion: the appropriate computational method depends on the amount, quality, and physical interpretability of the available data. Representative training data are fundamental. A model can only infer states contained within, or adequately represented by, its training domain.

This dissertation therefore argues for expert-guided or scientist-guided computational planetary science: machine learning informed by mineralogy, crystallography, spectroscopy, and geology rather than machine learning as a

scientific endpoint. Deep learning, dimensionality reduction, statistical similarity, diffraction refinement, physical modeling, and manual expert interpretation each have appropriate roles. The objective is to combine them in ways that preserve physical meaning while making large datasets tractable. A logical next step is to move beyond models trained only on categorical mineral labels. Composition, hydration, crystallinity, temperature, orientation, and measurement geometry can instead become physical parameters to predict or constrain. This shifts computational spectroscopy from classification toward physical inference.

1.4 Interrogating Mineral Structure Across Scales

The dissertation chapters interrogate mineral structure at several scales. At the atomic and local scale, Raman spectroscopy responds to bond vibrations, force constants, hydrogen bonding, coordination, and tetrahedral distortion. At the crystal scale, the measurements constrain or respond to unit-cell structure, hydration phase, crystallinity, symmetry, composition, and orientation. At the grain and rock scale, these properties contribute to mineral assemblages, lattice preferred orientations, textures, and fabrics. At the outcrop and planetary scale, those assemblages and fabrics may record magmatic flow, deformation, alteration, and aqueous history. Raman spectroscopy occupies an unusual position across these scales because its observables originate from atomic-scale interactions but can potentially provide information about progressively larger-scale geological processes. Changes in vibrational frequency can record hydration and structural evolution, while orientation-sensitive intensity variations can contribute information about crystallographic

texture. The challenge is to connect these scales while keeping each inference physically constrained. Planetary interpretation works backward from an instrumental measurement toward mineral identity, physical state, and ultimately geological process. Complementary measurements, systematic experiments, and computational analysis provide the constraints needed to make those steps increasingly quantitative.

1.5 Collective Contributions to Planetary Spectroscopy

This dissertation makes four related contributions. First, it expands what Raman spectroscopy can be used to infer in planetary science. Beyond mineral identity, the studies investigate composition, hydration, local bonding, symmetry, crystallinity, metastability, and crystallographic orientation. Second, it establishes experimentally grounded relationships between spectral behavior and independently measured physical properties. Raman observations are repeatedly interpreted alongside XRD, XRF, controlled experimental variables, and crystallographic texture measurements. Third, it develops approaches for extracting information from large and variable datasets. Chapter 1 uses a CNN trained on broad spectral populations, while Chapter 3 applies expert-guided statistical learning to thousands of heterogeneous diffraction patterns. Fourth, it translates laboratory mineral physics into planetary observables. The laboratory provides the controlled environment needed to determine the physical origin of spectral behavior, while Mars rover measurements provide the planetary context in which those relationships can be applied. Ultimately, these studies integrate mineral physics, spectroscopy,

crystallography, computation, and planetary geology to move from mineral identification toward physical and geological inference.

1.6 Limitations and Future Avenues of Exploration

Several limitations also define clear directions for future work. Raman observables are often non-unique: peak positions may respond to composition, temperature, pressure, hydration, or bonding, while intensities may respond to crystallographic orientation, surface geometry, mixtures, and instrumental response. Chapter 2 demonstrates substantial overlap among the ν_1 modes of different salts and phosphates, while Chapter 3 shows that the olivine doublet is orientation-sensitive rather than a unique orientation indicator. These results favor full-spectrum and multi-feature interpretation over reliance on a single diagnostic band. Laboratory-to-Mars transfer is another important consideration. Laboratory micro-Raman measurements provide higher spectral resolution, controlled geometry, known materials, and smaller sampling volumes than rover measurements. SuperCam operates with a larger footprint and lower spectral resolution, while SHERLOC uses different excitation and sampling conditions. Laboratory calibration is therefore most useful when the physical relationship being measured remains recognizable across these changing instrumental conditions. Training-domain completeness also remains central. Chapter 1 shows that an endmember-based CNN is most reliable for states represented within its training population. Chapter 3 encounters the same issue in a diffraction dataset for which a comprehensive labeled orientation and mixture library does not yet exist. Future training datasets can address this by systematically spanning composition,

temperature, hydration, crystallinity, orientation, mixtures, surface conditions, and instrumental response. Finally, this work bridges measurements made at microscopic scales with geological questions operating from individual grains to outcrops. Moving from a Raman spectrum to mineral identity is relatively direct; moving from a spectrum to hydration history, crystallographic texture, or magmatic flow requires progressively more physical constraints. This dissertation establishes steps toward making those larger-scale inferences experimentally testable.

1.7 From Classification Toward Physical Inference

The progression from classification toward inference changes the central question from “What is the mineral phase?” to a broader set of questions: What is the mineral composition? What hydration state is it in? What is its crystallinity? What orientation information does it contain? What physical and environmental conditions are consistent with those observations? Answering these questions requires systematic laboratory datasets in which spectra are paired with independently measured physical parameters. Composition, hydration, temperature, pressure, humidity, force constants, unit-cell parameters, crystallinity, orientation, and environmental conditions can become explicit components of the learning problem. The temperature-dependent datasets in Chapter 2 and co-registered Raman-XRD texture measurements in Chapter 3 are steps toward this type of physically parameterized training domain. Future computational models can incorporate these constraints through physical descriptors, multi-task outputs, experimentally derived labels, or relationships imposed during model training. The longer-term goal is not

simply autonomous mineral classification, but computational mineral physics capable of assisting interpretation of remote planetary measurements. Such systems could evaluate mineral identity together with composition, hydration, crystallinity, bonding, orientation, and geological context while retaining the uncertainty inherent to remote observations.

1.8 Expert-Guided Integration of Raman Spectroscopy, XRD, and Machine Learning

This dissertation develops methods for extracting physically meaningful information from measurements acquired under conditions relevant to planetary surface exploration. The three chapters progress from mineral classification, to physical-state interpretation, to crystallographic and geological inference. Across them, Raman spectroscopy is paired with independent structural, compositional, experimental, and computational constraints to extract information beyond mineral identity alone. The central contribution is therefore not a single algorithm, mineral system, or spectral calibration, but an integrated strategy for planetary spectroscopy: combine systematic laboratory experiments, independent physical measurements, mineral physics, high-volume datasets, and scientist-guided computation to expand the information recoverable from remote observations. This strategy is increasingly relevant as planetary exploration moves toward larger datasets, more autonomous instruments, more distant targets, and sample-return missions. Laboratory mineral physics establishes relationships among composition, structure, bonding, and environmental conditions; spectroscopy and diffraction provide complementary

measurements of those relationships; computational methods make large datasets tractable; and expert knowledge keeps the resulting interpretations physically grounded.

The broader vision is to continue this progression and apply it to current and future planetary surface missions. By expanding the interpretability of spectroscopic and diffraction measurements, planetary science can better reconstruct the mineralogical and geochemical evolution of environments such as Mars and constrain conditions relevant to past, present, and potentially future habitability. Rocks, minerals, and water form the physical and chemical matrix within which life as we know it emerges and is preserved. Expanding what can be inferred from remote measurements therefore expands our ability to understand planetary environments where habitable conditions may have existed.

Chapter 1: Convolutional Neural Networks as a Tool for Raman Spectral Mineral Classification Under Low Signal, Dusty Mars Conditions

Abstract

NASA's Mars2020 and ESA's ExoMars will collect Raman measurements in dusty field conditions obscuring underlying rocks. This presents a challenge for remote Raman measurements at distances where mechanical or ablative sample cleaning is not straightforward. Historically, probing broad lithostratigraphic suites has been thwarted by the need for pristine targets and high-quality spectra. We provide a means of identifying Raman spectra of common rock-forming silicate, carbonate, and sulfate minerals under low signal-to-noise-ratios (SNRs), Mars-like conditions using a convolutional neural network (CNN). The CNN was trained on the MLROD dataset with 500,000+ Raman spectra of hand samples/powder mixtures (5000+ spectra/mineral class). Diversity in sample microtopography, orientation, and crystallinity simulated varying laser focuses and spectral quality, and no traditional spectral preprocessing such as cosmic ray or baseline removal was employed. The CNN identified low-intensity Raman scatterers (micas and amphiboles), mixed minerals, and distinguished between mineral endmembers with +99% success. We present among the first known implementations of "big data" machine learning using varied, high-volume Raman spectral datasets. The pattern recognition abilities of CNNs can facilitate scientist Raman spectral interpretation on Earth and autonomous rover decision-making on planets like Mars; increasing scientific yield, correcting human classification errors, reducing the need for thorough target dust removal

during evaluative measurements, and streamlining the data communications pipeline—saving time and resources. This study examines an end-to-end development process for creating a deep learning algorithm sensitive to varieties of Raman spectra and provides guidelines for CNN model development at the interface of Raman spectroscopy, deep learning, and planetary science.

1.0 Introduction

Understanding the geology of a rocky planetary or lunar surface provides key insights into the terrestrial body's petrogenesis, surface evolution, and habitability. This process requires detailed understanding of morphological, physical, chemical, and mineralogical analysis of rocks and minerals within stratigraphic layers, units, outcrops, and landforms. Due to the risk involved in exploring the remote terrestrial reaches of Earth or extraterrestrial surfaces of the Moon or Mars, robotic rovers serve as valuable alternatives to the field geologist. Several relevant planetary rovers are currently exploring Mars or set to begin exploration in the coming years: NASA's Mars 2020 *Perseverance* rover and the Mars Science Laboratory *Curiosity* rover are currently acquiring thousands of images and spectra on the surfaces of Jezero and Gale Crater, respectively. (Farley et al., 2020; Mars Exploration Program & Jet Propulsion Laboratory for NASA's Science Mission Directorate, 2020b, 2020a; Maurice et al., 2012; Mustard et al., 2013) ESA's 2022 ExoMars rover is expected to begin data collection at Oxia Planum in late 2022 or early 2023 (Lopez-Reyes et al. 2014). With the exponential increase in the acquisition of information facilitated by remote planetary rovers, we will encounter an information abundance that requires

extensive labeling and sorting. This information is only useful if it is distilled and synthesized into conceptual models that can be used as diagnostic tools to unravel the region’s geologic history. In this paper, we present a machine learning-based mineral classifier that assesses the presence of common minerals in rocks (Berlangua, Temiquel, et al., 2022). We deploy illustrative examples from a gabbro and a granite, chosen to span a wide range of silica content, using Raman spectroscopy, one of the primary analytic techniques implemented aboard *Perseverance*.

The intended applications are three-fold: 1) to expedite and facilitate scientists’ Raman spectral interpretations, thereby increasing scientific yield; 2) to propose a method that can be used for future autonomous rover decision making; and 3) to develop a technique that can facilitate interpretation of low signal-to-noise, suboptimal spectra. In particular, we demonstrate the classifier’s robustness by simulating Mars’ dusty environment and testing it on gabbro and granite rocks covered in varying levels of basaltic dust. Several independent laboratory groups have conducted excellent applied machine learning and Raman spectroscopy studies using smaller spectral datasets (~1000-5200 total spectra) and employing network architectures fine-tuned to their respective dataset sizes (Carey et al., 2015; Ishikawa & Gulick, 2013; Kwiatkowski et al., 2010; Liu et al., 2017). We report an initial application of statistically significant, high-volume, “big data,” machine learning using over 100,000 individual Raman spectra (Emmanuel & Stanier, 2016). The effects of hyperparameter tuning and neural network architectures are discussed in light of varying dataset sizes and quality. We also present among the first machine

learning-specific Raman datasets (Machine Learning Raman Open Dataset (MLROD)) for open use to the scientific community (Berlanga, Williams, et al., 2022). Moving Raman spectral characterization into the “big data” regime enables the use of a sufficiently large teaching set for the deep learning algorithms to maximize detection and identification of weak scatterers or low-abundance constituents, and to create the prospect that mineralogic issues, such as solid solutions or multiple juxtaposed phases, can be treated as accurately as possible within potentially low signal-to-noise spectra. This study examines an end to end development process for creating an appropriate deep learning algorithm sensitive to the varieties of Raman spectra and provides general guidelines for targeted CNN model development at the interface of Raman spectroscopy, deep learning, and planetary science.

1.1 Raman Spectroscopy for Planetary Science Applications

Raman spectroscopy is an active-laser spectroscopic technique that provides bonding and symmetry information about the target material; practically, it is often deployed as a diagnostic identification technique for different minerals or mineral assemblages. A monochromatic laser light, such as a 532 nm green laser, is directed at a sample and the resulting scattered light is collected. A small fraction of the scattered light (typically of order $<0.0000001\%$) is shifted in energy from the laser frequency due to interactions between the incident electromagnetic waves and the bonds and atoms within the spectroscopic unit cell of the crystalline sample. This inelastic shift is called the Raman effect and occurs instantaneously at picosecond timescales (Berlanga et al., 2019a; Blacksberg et al., 2020; Johnson et al., 1985). A

Raman spectrum is then produced with peaks showing the intensity and wavelength position of the Raman scattered light. Each peak corresponds to the energy levels of different vibrational modes dictated by the analyte's symmetry and bonding vibrations, thus enabling unique sample identification akin to a barcode or fingerprint (Lewis & Edwards, 2001). Typically, stronger and more distinctive Raman scattering occurs from minerals or materials containing molecular-type units (e.g., carbonate-, sulfate-, and silicate-groups), but low-frequency lattice-associated modes may also prove to be diagnostic (Sharma & Egan, 2019; Sobron et al., 2019).

1.1.1 Complexity of Rock and Mineral Raman Spectra

Raman spectra provide basic molecular information about the targeted sample, and additionally, various aspects of rock or mineral petrogenesis, crystalline order, textural imprints, chemical variations, possible bounds on grain size, opacity, and fluorescence centers can be ascertained from the data. While informative, these nuanced spectroscopic signatures often have the effect of complicating actual mineral or rock identification by introducing Raman peak shifts, peak broadening, or baseline enhancement. Doppler, collisional, thermal, chemical, and physical effects homogeneously or inhomogeneously broaden Raman peaks (Artur et al., 2011). These broadening effects can be generated by poor crystalline order (Tuschel, 2017), shock effects (Heymann & Cellucci, 1988a), and smaller-sized grains (Foucher et al., 2013). Opaque, mafic minerals limit Raman visible laser penetration and reduce internal scattering, decreasing the resultant available Raman signal for peak detection. Fluorescence centers commonly contribute broad peaks and spectral baselines that

sometimes saturate whole spectrum intensities and can obscure or entirely mask Raman peaks (Jones et al., 2019); a few narrow-line fluorescent centers (such as the rare earths) can generate peaks that are comparable in width to Raman peaks (Lenz et al. 2013). Sample morphology or surface scattering, preferred orientation, and impurities contribute additional skewing of characteristic spectral signatures. With these complexities in mind, accurate mineral and rock identification through Raman spectroscopy alone can potentially become a very time-consuming task, requiring an experienced spectroscopist familiar with both the technique and the materials being analyzed.

1.1.2 Challenges with Raman Spectroscopy on a Dusty Mars

The surface of Mars is covered with vast expanses of dust and sand ranging from nanophase to millimeter-sized grains. The coarser material is ~55-71% crystalline and of basaltic origin, and the finer amorphous material is ~29-45% nanophase iron oxide (D. Bish et al., 2014; J. L. Bishop et al., 2002; D. F. Blake et al., 2013; Grotzinger, 2013). Much of this dust is mechanically derived from weathered Martian mafic or basaltic rocks, whose amorphous component is compositionally similar to Earth volcanic soils such as those from Mauna Kea volcano, Hawai'i (D. L. Bish et al., 2014; Certini et al., 2020; Morris et al., 2001; Ojha et al., 2018). This dust circulates globally and remains suspended in the atmosphere for months after dust storms (Kahre et al., 2017). Eventually, the aeolian dust settles on rocks and boulders strewn across the surface, leaving a fine veneer that may impart a compounding optical scattering and eclipsing of Raman peaks.

NASA's Mars 2020 *Perseverance* rover and the Mars Science Laboratory *Curiosity* rover are traversing through these challenging and dusty conditions common to Mars. Both rovers carry dust removal tools that employ either pressurized gas (Farias et al., 2020) or wire-bristle brushes (Schmidt et al., 2018) to clean off fine dust veneers, but in situations where target samples are beyond the reach of the turret arm, laser ablation is required for sample cleaning. *Curiosity* comes equipped with the ChemCam instrument suite which includes a laser-induced breakdown spectroscopy (LIBS) system that has the ability to ablate target samples prior to actual analysis (Maurice et al., 2012). This ability has the potential to remove veneers or dust coverage obscuring the target (Lanza et al., 2015). *Perseverance* comes equipped with the next generation SuperCam instrument that includes a dual remote Raman and LIBS spectrometer capable of ablation and the Scanning Habitable Environments for Raman and Luminescence for Organics and Chemicals (SHERLOC) instrument, a deep ultraviolet (DUV) Raman spectrometer. Due to the varying spot diameters used for LIBS, remote Raman, and DUV Raman techniques, analyzing dusty rocks on Mars will involve repeated LIBS ablation using a 500 μm maximum diameter beam across the surface area of the larger Raman laser's 8 mm maximum diameter collimated beam (SuperCam laser at distances over 12 m). It takes approximately 5 LIBS shots, or the equivalent of 17% of an average 30-shot LIBS observation, before being able to adequately sample the clean target area (Bhartia et al., 2021; Wiens et al., 2017a, 2021a). The time and laser power required to clean a target before actual analysis can take place provides a major impediment to the number of possible

analyses. As the progressive investment of time and power accumulates and the available consumable laser shots declines, serial laser ablation over multiple Mars years may ultimately become unsustainable. Here, we present a computational means of enhancing Raman spectral analysis and sample identification under dusty, low signal-to-noise (SNR) conditions, that saves resources by minimizing the use of extensive laser ablation during cursory exploratory spectral acquisitions.

1.1.3 Efficiency of Earth-Mars Communications

A communications lag and data bottleneck exist between Earth and Mars that hinders scientific data acquisition and human decision-making in directing rover operations. Round-trip interplanetary communications between Earth and Mars can take up to 48 minutes, and data rates range from 32,000 bits/sec (about half as fast as a current standard home modem) to 2 million bits per second. Maximum bandwidth is not always available due to rover-orbiter-Earth lines of sight, rover power limitations, or conflicts with other planned activities (Mars Exploration Program & Jet Propulsion Laboratory for NASA's Science Mission Directorate, 2020b, 2020a). This communications time lag limits the number of commands sent to Mars and the bandwidth bottleneck slows the transmission of large data volumes. Our proposed computational enhancement of Raman spectral analysis and sample classification can partially offload decision-making from scientists on Earth to the rover, reducing the number of commands sent to Mars, and streamlining data acquisition, increasing the quality and decreasing the volume of data relayed to Earth.

1.2 Machine Learning as a Tool for Spectral Interpretation and Robotic Autonomous Decision Making

Machine learning solves problems by discovering the rules, patterns, and statistical structure underlying a large dataset (C. M. Bishop, 2006; Chollet, 2018; Goodfellow et al., 2016; Witten et al., 2011). This opens the door for the creation of a new kind of toolset or assistant to the scientist – one that optimizes and expands problem solving and scientific output. We address the two-pronged case of 1) increasing volumes of spectral data arriving from remote robotic rovers on Mars and the Moon and 2) the data uplink and downlink bottleneck constrained by limited communications bandwidth between distant planetary rovers and scientists on Earth (**Figure 1**). The former case tasks scientists with a repetitive and ever-growing analysis and interpretation workload, while the latter interplanetary communications bottleneck increases the number of simplistic command cycles required to acquire and produce viable scientific knowledge. Machine learning can facilitate automation of spectral sorting, analysis, and interpretation in terrestrial laboratory settings as well as enhance autonomous decision-making in remote rovers equipped with intelligent onboard systems. This has the effect of streamlining scientific data analysis and reducing the number of command cycles between human and rover. We provide a method that tackles these problems and ultimately increases the volume, speed, and quality of scientific output.

The *Perseverance* and *Curiosity* rovers are equipped with existing machine learning software (Autonomous Exploration for Gathering Increased Science

(AEGIS)) for autonomous hazard navigation and blind laser targetting (Francis et al., 2017). On *Perseverance* this software uses a RAD 750 processor that runs at 200 MHz and has access to 16 MB of RAM. This hardware is sufficient to run complex image recognition and segmentation of rock and boulder 2-dimensional images. Running a 1-dimensional spectral classification pre-trained CNN algorithm using such hardware is not inconceivable, and would provide a significant enhancement to an AEGIS-type software that chooses targets pre-spectral analysis, and superimpose a decision-making layer post-analysis that can reduce repetitive blind targetting.

1.2.1 Neural Networks

In this work we introduce the use of high-volume datasets and convolutional neural networks (CNNs) in the context of Raman spectroscopy. Similar to synaptic communication in biological neural pathways, a neural network receives inputs and feeds them forward to subsequent layers of neurons. This process is mathematically modelled through CNNs using a standard sequence. First, input variables are multiplied by random weights at each node in the input layer. Nodes in each following inner layer sum the weighted inputs from the previous layer and generate an output by applying an activation function. The final output layer sums the weighted inputs from the last inner layer and generates a numerical output, or prediction, via an activation function. Back-propagation recursively adjusts the weights of the network connections so as to minimize loss (Rumelhart et al., 1986). Convolutional neural networks have the capacity to capture complex data relationships and produce accurate predictions for high-volume datasets. This makes

them ideal for synthesizing the multiple input variables found in spectra into a concise output.

Historically, Raman analyses pipelines have employed traditional statistics and machine learning requiring extensive spectral preprocessing such as cosmic ray removal, baseline smoothing and removal (Baek et al., 2014; Kneen & Annegarn, 1996; Lieber & Mahadevan-Jansen, 2003; Ruckstuhl et al., 2001; Schulze et al., 2005), and data dimensionality reduction (Boucher et al. 2015; Breitenfeld et al. 2018; Carey et al. 2015; Gautam et al. 2015; Lopez-reyes et al. 2014). These preprocessing steps are required regardless of whether the full spectrum or discrete peaks are used as the classification input. Few approaches accept raw or minimally processed Raman spectra as inputs (Liu et al., 2017), and to our knowledge, no approach to date has fully tapped the high data volume capabilities of a CNN without incorporating extensive synthetic data augmentation. Convolutional neural networks are designed to cope with large data volumes of thousands to millions+ inputs and have the ability to input raw data. Built within the architecture of the network are standardization, feature extraction, and classification steps. In one pass, the CNN learns all of the spectral features (identifying Raman peaks and positions) without having to engineer them during preprocessing (clustering, principal component analysis (PCA) etc.), before outputting classification probabilities (mineral assignment).

2.0 Methodology

Roughly polished gabbro and granite slabs, ground and sieved basaltic dust (a heterogeneous size distribution, limited to 50-150 μm grain diameters), and twelve hand sample mineral specimens, four of which were mixed into three binary powders, were used as the test data set for our Raman spectroscopic and machine learning investigation. The irregularly shaped and distributed dust allowed for a range of different dust, sample, and beam configurations, including partial eclipsing by dust of the Raman beam, near total eclipsing, and minimal (or zero) eclipsing. Sample chemistries were confirmed using X-ray fluorescence, and sample mineralogy was confirmed through both Raman spectroscopy and powder X-ray diffraction. Over 20,000 spectra were collected at progressively shifted locations on the gabbro and granite slabs, with half of these collected under idealized laboratory conditions, and the other half under a $\sim 50\%$ basaltic dust coverage that mimicked dusty, *in situ* field acquisitions on the Martian surface. Over 80,000 mineral spectra were collected to represent major silicate, carbonate, and sulfate mineral structures found on Earth and Mars: silicates containing isolated tetrahedra (nesosilicates), single and double chain tetrahedra (inosilicates), sheets (phyllosilicates), framework silicates (tectosilicates), carbonates, and sulfates. Again, these were collected from varying locations within polycrystalline samples, and hence sampled various crystallographic orientations, and varying surface topologies. Some, but not all, of these minerals were primary mineral components in the gabbro and granite slabs. Training reference sets also included twelve pure mineral samples and four binary powder mixtures: quartz, albite,

anorthite, microcline, hornblende, biotite, muscovite, forsterite, augite, enstatite, calcite, gypsum, a 1:1 quartz albite mixture, a 1:1 forsterite augite mixture, and a 1:1 forsterite albite mixture. Mineral localities and number of spectra obtained are tabulated in **Table 1**. This initial sample suite was chosen to encompass broad primary Raman peak coverage across the measured Raman wavenumber range as well as to include closely overlapping primary Raman peak instances in order to prevent training set biases while finetuning the CNN. Moreover, the distribution of samples incorporated the common silicate structural groups, as well as those bearing molecular-type units likely to be present on Mars. Future work will include additional Mars-relevant minerals, including intermediate plagioclase compositions, low-Ca and high-Ca pyroxenes like diopside and pigeonite, sulfates such as kieserite and anhydrite, and further exploration of Martian sedimentary minerals and phyllosilicate phases (Rogers & Hamilton, 2015).

Hawaiian basalt was finely ground and sieved to serve as a spectroscopic obscurant similar to what we expect from the fine Martian dust veneer found on the planet's surface. Care was taken that the dust was: 1) sufficiently fine-grained that it generated no resolvable crystalline spectral features, 2) coarse enough to not contribute Mie or Rayleigh scattering effects, 3) not detectably Raman-active, and 4) exhibited low fluorescence. The basaltic dust thus functions as an optical scatterer eclipsing Raman scattering from the underlying rock. In this sense, the dust functions as a spectroscopically passive reducer of the signal:noise ratio of the Raman spectra. Hence, the precise nature or chemistry of the dust (as long as it remains

spectroscopically inactive) is not critical for our results: our expectation is that similarly fine-grained basaltic dust or modestly compositionally tuned basaltic dust (such as Mojave Mars Simulant (MMS)-1 or MMS-2 (Peters et al., 2008)) will have similar signal:noise reduction effects as dust on the surface of Mars. Future studies will include the effects of Mie and Rayleigh scattering and incorporate more realistic Mars dust simulants.

Dust coverage percentages were measured out by mass and evenly spread and flattened across a 9 cm² surface whose perimeter contained all of the Raman measurements. Dust coverage percentages were computationally verified by acquiring a high definition black and white image of the 3x3 cm area and passing the image through a pixel color indexing filter. The shift in the integrated pixel value histogram (proportional to the dust percentage) and the increase or decrease in the RGB value bins corresponding to grey (Bins 0-20) basaltic dust were compared between the clean and dusty gabbro and granite slabs.

3.0 Experimental Design

3.1 Raman Measurements

Raman measurements were performed using a Horiba LabRAM HR Evolution single stage spectrometer equipped with an air-cooled solid-state laser emitting at 532 nm/100 mW and filtered through a long range 532 nm notch filter. The spectrometer includes high throughput achromatic coupling optics, a spectrometer focal length of 800 mm, and a grating of 1800 lines/mm with a spectral resolution of ~ 1 cm⁻¹. An

Open-Electrode CCD detector thermoelectrically cooled to -60° C collected the measurements. Raman scattering from the samples was collected using a long-distance aperture of 50x (NA=0.5). Samples were placed on an automated Märzhäuser XY mapping stage (resolution 0.1 μm , reproducibility 1 μm) and spectra were collected using scan and point counting techniques (Haskin et al., 1997; Wang et al., 1999) at ambient temperature and pressure. A synthetic silicon standard was used for spectral wavenumber calibration. High quality raw Raman spectra were collected in conjunction with relatively short collection times of 1-120 s, and introduced into the CNN with only minimal preprocessing to standardize wavelength scales, as described below in Section 4.1. Raman measurements were collected between 100 cm^{-1} and 1800 cm^{-1} to incorporate the fundamental range of vibrational modes for silicate, carbonate and sulfate minerals (Wang, Freeman, and Jolliff 2015; Williams 1995). Representative spectra for each training set are plotted in **Figure 2**. These spectroscopic measurement and laser excitation specifications fall within those of the SuperCam Raman measurements, enabling the use of the MLROD-trained CNN algorithm with SuperCam data. MLROD spectral resolutions can be downsampled within the software build to better match SuperCam or other spectrometer resolutions. The future addition of Raman training sets at a 248.6 nm laser excitation will allow the algorithm to be used on SHERLOC data. Relevant laser and spectrometer specifications between current Mars payloads implementing Raman spectroscopy and the Horiba spectrometer used to create MLROD are tabulated in Table **S3** in the Supplement section.

3.2 X-ray Diffraction and X-ray Fluorescence Measurements

To confirm the structures of our mineral standards, X-ray diffraction (XRD) patterns were measured between 5.0 to 65.0 2θ in 0.02° steps with a count time of 2 sec per step on an inXitu Terra diffractometer at NASA Ames Research Center. X-ray fluorescence (XRF) measurements were collected on an inXitu Terra diffractometer to measure chemical compositions. Elemental compositions confirmed the chemistry and solid solution series position of each mineral specimen. This mineralogical information, comprising both symmetries and unit cell parameters and elemental compositions, established the phase and compositional ground truthing for the Raman analysis. XRD/XRF data and mineralogical information are available in the Supplement section.

4.0 SOFTWARE DESIGN

Open-sourced and freeware software and environment options were used for our investigation. Programming was completed using Python 3.8 with Jupyter Notebooks on Google Collaboratory as our development environment. Data processing and manipulation was done using the Pandas and Numpy packages (Harris et al., 2020; Reback et al., 2021). Traditional statistics and spectral signal processing were done using the SciKit Learn package (Pedregosa et al., 2011). Machine learning algorithms were developed using the Keras library on top of Tensorflow (Abadi et al., 2016).

Two datasets provided inputs to our machine learning classifiers: 1) the experimentally acquired raw Raman spectra of rocks and pure minerals and 2) a subset of excellent to poor quality publicly available spectra of pure minerals from the RRUFF Project Raman database (Lafuente et al., 2015a) for independent CNN testing. No synthetic data augmentation was necessary due to our acquired data volumes being sufficiently extensive that they satisfied the training set size and variability needs for a CNN. The experimentally acquired pure and mixed mineral Raman spectra were used for CNN training, while the gabbro and granite spectra and the independent RRUFF Project Raman database spectra were used for testing. Two versions of the training and tests sets were inputted: a raw version and a minimally processed continuous wavelet transformed version.

4.1 Raw Raman Spectra Preprocessing

Prior to running the Raman spectra through the convolutional neural network, we standardized the wavelength range and interpolation intervals. This was the only pre-processing conducted on the spectra, with only truncations of data and sampling intervals being standardized. No cosmic ray removal or baseline corrections were applied. All spectra were trimmed to a wavelength range of 150 cm^{-1} to 1100 cm^{-1} in order to reduce file sizes and accelerate automatic processing and statistical analysis using standard commercial laptop processing speeds of 2.8 GHz and an Intel Core i7, while still including relevant primary Raman peaks for silicate or functional group identification.

Continuous wavelet transform-based (CWT) pattern matching was applied to the spectra due to the approach's sensitivity to peak shape *and* amplitude. Most peak detection algorithms identify peaks based solely on amplitude, sacrificing low-amplitude peak detection, and increasing the rate of false positives in low signal to noise situations (Du et al., 2006; C. Yang et al., 2009). By transforming the spectral data into wavelet space, we were able to simplify peak matching, increase the apparent signal to noise ratio, and bypass baseline removal and peak smoothing steps. Raman shift resolution and ranges were standardized by interpolating to discrete steps of 1 cm^{-1} in order to account for variations between dataset wavelength ranges and spectrometer resolution. For each 1 cm^{-1} bin, the minimum Raman intensity was chosen as the new intensity value for the interpolated pair. This step standardizes all input spectra and also has the added natural consequence of removing single pixel cosmic rays from the spectra. Care was taken to preserve adequate spectral peak information for identification. **Figure 3** illustrates the Ricker continuous wavelet transform (CWT) implementation.

Two datasets are outputted from the Ricker continuous wavelet transform:

1) a 10-feature matrix with the highest peak intensities in CWT space in descending order from highest to lowest for each spectrum:

<i>Peak Position 1</i>	<i>Peak Position 2</i>	<i>Peak Position 3</i>	<i>Peak Position 4</i>	<i>Peak Position 5</i>
<i>Intensity 1</i>	<i>Intensity 2</i>	<i>Intensity 3</i>	<i>Intensity 4</i>	<i>Intensity 5</i>

This set was used to test traditional statistics and machine learning classifiers.

2) The Ricker CWT of each spectrum with 190 features (one for every 1 cm^{-1} between 150 and 1100 cm^{-1}). These data are only used in the CNN. Traditional models

like support vector classifiers (SVC) or logistic regression cannot input this type of data due to the large number of features and noise. The general format is, where x_j and $y_{j,k}$ denote wavenumber and intensity, respectively:

150	155	x_j	...	1100
<i>Intensity 1</i>	<i>Intensity 2</i>	y_j	...	y_k

Table S1 (Supplement section) shows the tabulated top five peaks from the 10-feature dataset, for each mineral trained on the CNN, and the respective band assignments and vibrational modes. The top five peak positions were selected by taking a frequency distribution of the top five peak intensities in all spectra for each mineral and selecting the corresponding positions of the five peak intensities with the highest frequencies across the mineral class. While the CNN uses the entire Ricker CWT with 190 features, tabulating the top five peaks allows insights into the mechanics of how the CNN “thinks” about full spectrum matching. Not all primary peaks land in the top five for every mineral, but the Ricker CWT captures enough primary peaks to adequately influence the CNN node weights during classification. The weak peaks emphasized by the Ricker CWT provide identifying features throughout the entire spectrum, and within potentially diagnostic regions of the spectrum, instead of just being confined to grouped regions, in which the well-known vibrations of functional groups fall. These weak, often isolated features are not readily obvious to the untrained spectroscopist and may become crucial for spectral mineral identification when confronted with very noisy or highly fluorescent Raman spectra, or mixtures containing many mineral components. If the spectrum contains

no identifiable peaks, the CNN algorithm has a classification option of “Dusty/Low SNR/Unknown.”

4.2 Labeling Test Models

Prior to testing our neural network with the clean gabbro, clean granite, dusty gabbro, dusty granite, and RRUFF test spectra, it was necessary to label the true mineral classifications for the spectra. Over 30,000 spectra were manually labeled by the authors over the span of 500 hours and three full passes. These true labels were used to verify the success rate of our classifying models. With each pass, the test set was run through the CNN and the misclassified spectra often identified *human* mineral classification errors, effectively correcting any manual labeling mistakes.

4.3 Convolutional Neural Network for Raman Spectral Classification

We evaluated the performance of several supervised and unsupervised traditional classifiers and neural network classifiers using Raman spectra as inputs and compared them to convoluted neural networks. The inputs to the CNN consisted of a one-dimensional Raman spectrum fully sampled at regularly spaced wavenumber intervals. One version of the data included raw unprocessed spectra and the second version included spectra transformed through a Ricker CWT. Each kernel in the CNN was one-dimensional. A number of convolutional layers extracted features and two fully connected layers performed classification.

A CNN parameter optimization routine was implemented on the model to run through different values of all tunable hyperparameters and architecture parameters:

learning rate, batch size, drop rate, number of layers, filter number and size, activation functions, optimizer functions, and number of epochs or number of training iterations. The investigated CNN parameters and resulting optimized tuned values are listed in **Table 2**. The parameter ranges were intentionally not limited until there was obvious performance degradation at either range extreme. Three types of CNN architectures were tested: bilayer, trilayer, and quadlayer, across a range of varying filter map numbers and shapes. Four different activation functions were examined during parameter tuning to optimize the weight values generated by each neuron. The number of epochs, or learning cycles, was varied from 1-500 to adjust how much time the model had to converge. Learning rates were varied to control how much the model changed in response to the estimated error each time the weights updated. Varied batch sizes were explored to control the number of training spectra that passed through the CNN before its internal parameters updated. CNN regularization was examined across a range of drop out rates to avoid strong dependencies between portions of adjacent layers, reduce overfitting, and improve generalization error.

At each node in a neural network, the inputs are multiplied by randomly assigned node weights and summed together. This value is referred to as the summed activation of the node and is transformed via an activation function into an output or node activation. A LeakyReLU nonlinearity algorithm was implemented as the default activation function because it allows the network to backpropagate even for negative values. This algorithm is also able to learn more complex relationships and structures in the data without saturating and locking very small values to 0 or -1 or

very large values to 1. This feature avoids producing vanishing gradients and allows for the CNN to effectively learn. Near the end of the CNN the layers are fully connected in a dense layer and weights are passed through a TanH non-linearity function. At this juncture, most of the deep trainable spectral features have passed through the LeakyReLU activation in the feature extraction layers and the CNN generally benefits from any of the standard non-linear activation techniques. The final output layer implements a Softmax activation function with the same number of outputs as our number of mineral classes on which the training was conducted. Each individual training mineral or mineral mixture was manually encoded to its own integer (0 – 15). Softmax operates by standardizing the outputs to a probability range between 0 and 1, with the predicted class having the highest probability (Goodfellow et al., 2016). After each of the feature extraction layers, a 1-dimensional MaxPooling operation was implemented to downsample the input representation and extract broader and more general patterns that are more robust with respect to small changes in the input. MaxPooling downsamples by taking the maximum value over a spatial window (Keras Project, 2020). Batch normalization, dropout, and early stopping were implemented to avoid overfitting the model. Given that overfitting occurs when the CNN is learning the training samples, early stopping stops training when a performance drop is detected during validation (Goodfellow et al., 2016). **Figure 4** outlines the CNN architecture used for Raman spectral mineral classification. This architecture adheres to similar conventions as deployed by Liu et al. (2017) in their single mineral spectra-oriented CNN.

Outputs from the Softmax regression were fed into a sparse categorical cross entropy loss function to address the multi-class classification problem of assigning one mineral or mineral mixture identification to each spectrum from the multi-mineralic gabbro and granite rocks. The loss, or difference between “true” target mineral identifications and CNN predicted identifications, was measured by this function. The loss function does this by calculating the average difference between the actual and predicted probability distributions for all classes in the problem and then minimizing the score (perfect cross entropy = 0) (Goodfellow et al., 2016). Three optimizers were explored to minimize the loss: stochastic gradient descent (SGD), adaptive moment estimation (ADAM), and RMSProp. SGD incorporates frequent model parameter updates and converges quickly, but it suffers from high variance in model parameters, can overshoot global minima, and requires slow learning rate reduction (Robbins & Monro, 1951). ADAM converges quickly (although not as quickly as SGD and RMSProp) and rectifies the vanishing learning rate and high variance of SGD, but it is computationally costly (Kingma & Ba, 2015). RMSProp incorporates adaptive model parameter updates like SGD, but it does so after every batch. It converges the fastest from this group of optimizers and reduces variance, but suffers from sensitivity to initial manual learning rate selection (Hinton et al., 2012). This mini-batch approach capitalizes on large training set sizes, and drastically improves CNN parameter finetuning.

Appropriate neural network parameter tuning is highly sensitive to the input training and testing datasets. We explored varying CNN parameter and

hyperparameter effects on successful Raman spectra mineral identification. Our investigation led to slightly different finetuned network parameters and hyperparameters for optimal performance with preprocessed CWT Raman spectra relative to raw Raman spectra. These results are tabulated in columns 3 and 4 of **Table 2**, and are discussed in Section 5.0 along with the performance metrics.

4.4 Training the CNN on MLROD

Convolutional neural networks are data-intensive models that optimally work in the 10,000+ data input range and up into the millions and billions of inputs. We collected sufficient training spectra to adequately tap into the CNN capabilities. Alongside data volume, data variability is important for optimal neural network performance. The CNN needs to be able to generalize the spectral features it has learned during training to apply that knowledge to new, never before seen spectra such as the multi-phase granitic and gabbroic rocks used in this work or the RRUFF Project single-phase Raman spectra. We emphasized variability in spectral quality while acquiring the training sets for every mineral so that the CNN had a range of excellent to poor Raman spectra to train on for every mineral class. Training with large spectral variability is crucial for *in situ* Raman field measurements on Mars by autonomous rovers since dusty conditions, awkward analysis angles, topographically rough surfaces, and any other adverse environmental conditions are likely to compromise the quality of spectral measurements. The mineral sample micro- and macro- topography was used to ensure the laser was not always in focus while taking automated grid point grid measurements of the mineral surface. Additionally, grain

boundaries and mineral defects added noise, internal reflections, baselines and overarching variability to the spectra. **Figure 5** shows a randomly selected sample of 100 microcline training spectra from MLROD. The training set's variability ranges from spectra with high noise, high fluorescence, and weak peak intensities, to those with excellent quality, low fluorescence, and very strong peaks. In some very low SNR cases, or cases with unconventional reflection geometries, the primary and lower-intensity peaks are broader, have similar heights, or missing peaks. Such spectra are part of what make MLROD unique, since machine learning algorithms like the proposed CNN can generalize full pattern matching with consideration towards missing information or varied spectral shapes for the same mineral. If low intensity peaks occur in areas that don't overlap with peaks from different minerals, then those features can be diagnostic for mineral classification. Naturally, a large portion of the training spectra for each mineral do have conventional Raman spectra with the appropriate first and second order peak heights, positions, and cross sections. This allows the CNN to prioritize primary peaks (along with the full spectrum shape) for mineral identification so that lower intensity peaks are not confused for primary peaks of other minerals. Future training sets will consider additional mineral mixtures, and particularly those relevant to Mars materials. This training set enhancement will address situations where more complex mineral mixtures have peaks that overlap with primary and secondary peaks of minerals not included in the training set mixtures. Additionally, the broad suite of random cosmic rays across thousands of spectra effectively teaches a CNN to disregard whatever looks like a

cosmic ray (very sharp peak and high local signal:noise) regardless of its occurrence frequency, and to focus on and identify the Raman spectrum. This makes the MLROD training set neutral to raw test sets with varying cosmic ray occurrences. Additionally, the training sets have sufficient datapoint density to interpolate up to ~ 5 cm^{-1} bins without signal loss in order to match lower resolution data from instruments such as the SuperCam spectrometer.

The Raman instrument's laser interrogation area is 50 μm in diameter and the average gabbro and granite crystal sizes were >1 mm in diameter, allowing us to engage in Raman point counting techniques with few encounters of binary or ternary mineral mixtures in the Raman spectra. Three binary mixtures, one containing 50% quartz and 50% albite, one containing 50% forsterite and 50% augite, and one containing 50% forsterite and 50% augite were included in the training set to encompass the uncommon (for these sample geometries), but geologically critical, case that mineral mixtures were encountered within the spectral data base. Practically, extrusive or finer grained rocks are more likely to encompass mixtures, and our mixture data allowed us to demonstrate that the CNN algorithm can readily recognize mixtures of multiple mineralogic components. This represents a key capability, and this demonstration clearly expands the application of CNN approaches from single-mineral identification (e.g., Liu et al. 2017) to polymineralic rock characterization.

Rapid gradient descent within the loss function is necessary for rapid spectral training. We implemented the RMSprop optimizer to step through the gradients of our sparse categorical cross entropy loss function. This is a flexible learning rate

method that adapts the learning rate to the parameter modifications: smaller updates (low learning rate) for parameters associated with frequently occurring features, and larger updates (high learning rates) for parameters associated with infrequent features. RMSprop is not privy to aggressive monotonically decreasing learning rates, works well with sparse datasets, and complements our CNN mini-batch approach by employing mini-batch stochastic gradient descent. The optimizer deals with vanishing or exploding gradients by using a moving average of squared gradients to normalize the gradient. This normalization balances the step size (momentum), decreasing the step for larger gradients to avoid exploding, and increasing the step for small gradients to avoid vanishing. Essentially, the adaptive learning rate becomes a hyperparameter that optimizes over time (Hinton et al., 2012).

5.0 RESULTS AND DISCUSSION

We evaluated the CNN against the evaluation set to finetune the hyperparameters. Initial trials yielded an extremely fast training learning rate that took 1-2 epochs to reach 98-99% accuracy with a lagging validation set. Here, an epoch is defined in the neural network framework (by convention) as having the entire dataset moving forward and backward through the network a single time. Several runs with increasing epoch sizes were tested until the training and validation set loss and accuracy curves converge near epoch 145 as seen on Figure 6a. This is a classic case of overfitting and a common issue with convoluted neural networks. In this case, overfitting was the result of having an extremely high batch parameter of

40,000. The training spectra would thus iterate 40,000 times through the CNN for every mineral, in every epoch.

Reducing the batch parameter to 8-32 and taking the mini-batch approach produced adequate convergence of our loss and accuracy curves, implying that the network is correctly classifying the validation set as quickly and accurately as it has learned the training data. Since the validation set is a subset of the training data, its features should be familiar, even though the CNN has not specifically trained on it.

Figure 6b illustrates the updated learning curves. Notably, accuracy scores still converge at 98-99% within 2 epochs. Given the low dimensionality of 1-D spectra and the complexity of convoluted neural networks, this rapid convergence is expected. The best classification results were achieved by stopping training at 5-6 epochs—longer training caused generalization on the test set to begin to suffer.

5.1 CNN Classification Performance on Raman Spectra

The CNN was tested using Raman spectra of a roughly polished gabbro and granite slabs and of the same slabs covered in ~50% (by coverage area) Hawaiian basaltic dust, which is likely to be similar to dust found on Mars. We also tested the CNN with an independently acquired set of Raman spectra from the RRUFF Project Raman database. The RRUFF set included spectra from quartz, albite, muscovite, forsterite, augite, enstatite, and microcline. The granite test set included spectra from quartz, albite, hornblende, biotite, muscovite, and microcline. The gabbro test set included spectra from forsterite, augite, enstatite, anorthite, gypsum, and calcite. Together, all three test sets included every mineral in the training set of silicate

minerals. Dusty Raman spectra where the underlying material was only partially obscured exhibited visually detectable peaks and broad bands at diminished intensities. The overall effect of this fine veneer of 50-150 μ m-sized grains of dust does not invoke Raleigh or Mie scattering and only contributes optical scattering and eclipsing of laser light from interacting with the mineral surface. Hence, the predominant effects of dust coverage are to reduce the signal-to-noise ratio, and this thus provides a limit of detection test for the fidelities of different spectral identification techniques.

We tested our proposed CNN mineral classifier on multi-mineral gabbro and granite rock slabs and on the RRUFF mineral database and compared the success scores for various supervised and unsupervised classification methods across an average of 100 runs each. Regression, instance-based, decision tree, artificial neural network, and deep learning algorithms were employed to varying levels of success. The CNN outperformed the other methods and consistently scored >80%. **Table 3** reports the weighted F1 scores across all mineral classes for 0% and 50% dust covered granite. Individual per class metrics are available in the Supplement section and highlight successful classification across all minerals. Reported F1 scores are weighted due to the natural test set imbalance resulting from randomized rock measurements.

A limitation to the current CNN performance lies in the difficulty associated with classifying intermediate mineral compositions situated within mineral group endmembers series such as in the plagioclase albite-anorthite or microcline-albite

solid-solution series, unless a corresponding mineral training set that incorporates intermediate compositions is explicitly included. This is not a significant limitation with regards to CNN algorithm usage as an aid to scientist spectral interpretation, but is an aspect to recognize and address in future software iterations to better achieve onboard robotic autonomy. With the current training set comprising endmembers, the CNN typically forces intermediate compositions onto one endmember classification or the other. This forcing is expected to typically converge on the more abundant endmember within the solid solution. By including training sets for intermediate compositions, successful CNN metrics should be attainable: as such, future improvements to CNN rock and mineral identification algorithms will likely require a comprehensive data set for common solid solution series, including olivines, pyroxenes, amphiboles, and micas in addition to feldspars. The success with feldspar endmember identification indicates that this is simply a matter of enhanced data inclusion within the training set, rather than a limitation on the algorithm itself. Our expectation is that accurate characterization of subtly different members of solid solution series may require reduction of the width of our bin size during the wavelet transform step, or exclusive use of raw data inputs. This expectation is generated by the comparatively small shifts in peak locations or splittings that occur across many solid solutions series (e.g., Huang et al., 2000; Wang et al. 2001; Bersani et al. 2018).

Importantly, if a spectrum contains no identifiable peaks, MLROD has spectrally passive data as part of its training set and the algorithm classifies the unknown test spectrum as a “Dusty/Low SNR/Unknown” option for feature-less

spectra. The CNN algorithm will generally respond to minerals or mineral groups not included in the training sets by matching to the closest primary peaks, or the shape of the closest matching group of peaks within a particular region of the spectrum. For example, clays such as montmorillonite would default to mica or muscovite (matching the O-Al-O stretching region at $\sim 650\text{-}700\text{ cm}^{-1}$). Serpentine such as antigorite would default to either enstatite or augite (matching Si-O-Si vibrations at $\sim 660\text{-}690\text{ cm}^{-1}$). Serpentine could also default to muscovite if mixed with clays, and in rarer instances where the $\sim 1045\text{ cm}^{-1}$ peak is of very high intensity, the CNN might default to calcite (attempting to match the CO_3 symmetric stretching vibration at 1088 cm^{-1}) or gypsum (matching the SO_4 symmetric stretch at 1008 cm^{-1}). Because of the generally modest variations in vibrational frequencies of the sulfate unit in different crystallographic environments, sulfates should, with the current training set, default to gypsum (matching the strong SO_4 vibration at 1008 cm^{-1}) regardless of their hydration state since the MLROD training set does not currently span the $3000\text{-}3800\text{ cm}^{-1}$ OH stretching region, nor does it encompass variably hydrated sulfates.

We further tested the influence of training set size per mineral class on success scores to determine a lower limit training set size for our particular neural network. Training sets increased by powers of two: 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, 1024, 2048, 4096, 5000, to the full training set minimums per class. At approximately 700 spectra per mineral class we gain adequate success rates of $>80\%$, and by 5000 spectra we gain success rates of 98-99%. **Figure 7** shows weighted F1 scores using training sets of varying sizes.

The CNN was tested under various conditions in order to assess how its success might be reduced or slowed down. When tested on the independent RRUFF database spectra, it had an F1 success score of 96%, and even correctly identified potentially mislabeled or misidentified spectra in the database. More than half of the spectra labeled as enstatite on the database were identified as solid solutions; a few appeared to lie closer to the augite compositional field. This is not wholly unanticipated, as solid solutions are ubiquitous within pyroxenes (e.g., Morimoto 1988). Moreover, the effect on Raman spectra of the calcium substitution relative to the shift in symmetry associated with the *Pbca* symmetry of enstatites/pigeonites relative to the *C2/c* symmetry of augites is complex (Huang et al. 2000; Wang et al. 2001). The CNN correctly labeled 92% of the pyroxene endmembers. We further replaced all training spectra with 5000 synthetic spectra with random peaks and noise. The CNN replicated excellent learning curves between the training and validation sets but as expected from the randomized synthetic spectra, failed to predict any true spectra in the granite or RRUFF test sets. Consistent CNN behavior despite switching of data sets, and the high success scores using RRUFF Project test spectra verify robust CNN model performance in classifying gabbro and granite mineral components and exclude the presence of any potential biases introduced by our in-house Raman datasets.

In **Figure 8**, we show the CNN's classification performance. Plots for quartz, feldspar, hornblende, and biotite show examples of successfully labeled spectra with wide within-class variability of poor or dusty to excellent spectra. The top three

classification probabilities are presented below the top plot, with the green spectra indicating the correct mineral classification label. The CNN reports the prediction certainty by outputting prediction scores. This also enables the user of the model to assess classification quality. All of these examples show correct classifications, but in cases where misclassification occurred, dark, Fe-rich minerals with similar spectra were confused for each other, or confusion emerged for minerals sharing similar primary or secondary peaks like calcite or gypsum. Mafic minerals are typically iron-rich with low scattering cross-sections that generate weak peaks or poorer SNR spectra at fast integrations. However, hornblende was rarely misclassified as augite, and biotite was rarely misclassified as muscovite due to their distinctive Raman spectra. Feldspars were minimally misclassified within the mineral group. Occasionally, pure minerals were misclassified as mixed mineral spectra where one of the binary components was a correct match, such as between forsterite and augite and forsterite/augite mix or between quartz and albite and quartz/albite mix. Such misclassifications, classifications with intermediate confidence scores, and subsequent classifications that fall within intermediate confidence scores, also may indicate that the CNN has converged on a different member of the correct, or closely related, mineral family. This is a likely outcome for a mineral that is not present in the teaching set.

These results reflect typical challenges that a human observer would face when interpreting Raman spectra. Darker minerals exhibit greater internal absorption of common Raman scattering laser wavelengths (e.g., 530 nm), and yield smaller

Raman cross sections due to reduced Raman scattering exiting the mineral volume. Additionally, lower symmetries of minerals such as amphiboles tend to contribute to smaller polarizability tensors, and hence lower Raman scattering intensities. This complicates spectral identification, as few to no notable spectral features may appear in a mixed phase spectrum containing these minerals. Fluorescence and dust coverage impose similar effects to one another on Raman spectra, and these are areas that computational analysis and particularly, a properly trained and finetuned convolutional neural network, might excel at—potentially beyond all but the most experienced human abilities.

Receiver operating characteristic (ROC) curves for the CNN, multi-layer perceptron, and random forest binary classifiers (**Figure 9**) show the diagnostic ability of each classifier as their discrimination thresholds are varied. The true positive rate (TPR), also known as the sensitivity or recall, shows the probability of an actual positive classification while the false positive rate, also known as fallout, shows the probability of a false alarm during classification. These curves are for ungrouped mineral classes to illustrate the individual class label performance. While most algorithms classified intense or distinctive Raman scatters that are easy to identify such as quartz, muscovite, and forsterite, the CNN was able to successfully classify mafic minerals like biotite and hornblende, and better discriminate between minerals in silicate mineral groups such as the feldspars (albite, anorthite, microcline). CNN ROC curves for the RRUFF data are shown in the Supplement section, and illustrate almost perfect classifications, with the exception of the pyroxenes. The

discrepant enstatite ROC curve in the Supplement is generated by a subset of spectra that have Raman spectra that appear more similar to augite, and hence may either be misclassified in the RRUFF database or may be compositionally more complex than their assigned mineral name implies.

Preliminary CNN runs of SuperCam Raman measurements from Mars on Sol 152 (released on the NASA Planetary Data System Geosciences Node (<https://pds-geosciences.wustl.edu/missions/mars2020/supercam.htm>)) indicate our CNN algorithm can garner useful insight on the presence of silicate minerals. SuperCam peaks in the Si-O-Si vibrational region contributed to quartz and plagioclase predictions. Expansion of the MLROD training sets to include clay, serpentine, and sulfate minerals and mixed minerals will further enhance the variety of mineral identifications from SuperCam data.

5.2 Implications of Raman Spectral Data on CNN Parameters and Scientific Applications

A properly tuned, general-purpose CNN with static architecture and hyperparameters, trained on Raman spectra with sufficient within-class variability to encompass the complexity of rock and mineral Raman spectra, can identify Raman spectra that have matches in the training set. Importantly, the CNN can also generalize the results that it has learned to identify minerals within (for example) mixed-phase aggregates or rocks that it has not seen before. The CNN model and high-volume machine learning training sets presented in this work succeed in identifying minerals even in dusty, low SNR Raman spectra. Proper machine learning

training sets are critical for effective deployment of CNN models in spectroscopic mineral analysis, and should be the first and foremost consideration before developing deep learning algorithms for spectral classification. With this in mind, base CNN performance can be *further* optimized depending on the test set characteristics. Several models are proposed at the interface of Raman spectroscopy, deep learning, and planetary science, but few describe the results of model exploration and development. This is useful information that can be gleaned from model *error and misclassifications*. Based on insights derived from our current modeling, general guidance for custom-dataset CNN model development for Raman spectra mineral classification can be derived:

- Spectra from low SNR samples or low Raman scatterers such as dark mafic minerals (biotite, hornblende, augite) benefit from increased neural network depth, preprocessing, or both. This involves increasing the number of learning filter kernels in each feature extraction layer (detector) or applying a transform like the Ricker CWT to the training and test sets, respectively. Neural network simplicity is generally preferred, thus the more extreme measure of adding feature extraction layers should be considered as a last resort for spectra from particularly challenging lithologies.
- Spectra with pronounced baseline slopes or strong fluorescence that do not mask primary peaks also benefit from increased neural network depth, preprocessing, or both. As such, it is important to include a wide range of baselines for each mineral training set.

- Spectra from samples exhibiting very closely clustered primary Raman peaks such as feldspar doublets and triplets in the $500\text{-}520\text{ cm}^{-1}$ Si-O-Si bending-stretching region, or with similar mineralogies and continuously varying chemical compositions, such as in feldspar or olivine solid solution series, benefit from raw spectral inputs so as to not lose spectral fidelity.
- Mineral mixture spectra also benefit from raw spectral inputs and no preprocessing, but it is important to include a wide range of abundance ratios since the amplitudes of Raman peaks for mineral mixtures may be nonlinear.
- Spectra from high SNR and very Raman-active minerals such as gypsum, calcite, quartz, and feldspars do not require increased neural network depth for successful CNN models. Datasets that involve such high-quality spectra can benefit from CNN models with detector simplifications via smaller learning filter convolutions and wider filter maps.
- Higher drop out rates lead to improved generalization for smaller training sets or training sets with minimal within-class diversity. As training set size and within-class diversity increases, the parameter importance decreases, and a balanced dropout rate of 50-55% is sufficient.
- Larger batch sizes lead to lower asymptotic test accuracy. The largest possible batch size is equal to the total size of the smallest training set class or mineral. This lost test accuracy can be recovered from a larger batch size by increasing the learning rate. This comes at the expense of both time and computational

cost. A mini-batch approach with adaptive learning rate optimizers like RMSProp is preferred for 1-dimensional Raman spectra.

- Larger batch sizes are also very sensitive to the particular spectra drawn from the dataset. Such models can fluctuate between very large or very small gradient updates, leading to learning inconsistency. Using small batch sizes allows the model to reduce sensitivity to the data subset and thus make updates that are roughly the same size. Smaller batch sizes can capture and learn from within-class training set variability.

6.0 CONCLUSION

We present an open-sourced, accessible, convolutional neural network algorithm capable of classifying Raman spectra of silicate, carbonate, and sulfate minerals with outstanding performance even under challenging, low-signal conditions, such as dust-laden or poorly crystallized rocks and minerals on the surface of Mars. An accompanying machine learning-specific Raman spectra training (MLROD) set is presented and made available to the scientific community through the Open Data Repository. We expect that this CNN algorithm can be readily generalized to other mineral groups and complex solid-solution series given proper training set expansion. General CNN development guidelines are provided to adjust the model for custom-dataset-specific needs with an awareness of Raman spectral complexities and acquisition challenges.

This is among the first known Raman spectral implementation of upwards of 5000 training spectra per mineral label and upwards of 70,000 total training spectra. CNN classification potential was adequately tapped and the classifier's success greenlights the way for increasing the complexity of Raman spectral inputs to this type of algorithm. The pattern recognition abilities of convoluted neural networks have the potential of discriminating between spectra of adjacent mineral compositions within solid solution series and mineral groups, identifying mineral mixtures, as well as differentiating between physical processes that mimic out-of-class spectral behavior, and actually identifying spectral peaks. These qualities can facilitate Raman spectral interpretation both on Earth and Mars, and hold the prospect of increasing scientific yield and potentially correcting human classification error—particularly for relatively poor Raman scatterers or low signal-to-noise spectra. Given the current NASA Mars2020 and upcoming ESA 2022 ExoMars missions, deploying planetary surface rovers with Raman spectroscopic capabilities that have onboard CNN classifiers could facilitate autonomous rover decision-making, enabling scientists to delegate and automate increasingly complex tasks to the rover, saving time and resources.

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Data Availability Statement

The Machine Learning Raman Open Dataset (MLROD) supporting the conclusions in this paper can be obtained at the Open Data Repository: <https://odr.io/MLROD> (DOI: <https://doi.org/10.48484/pwrb-r137>) and the latest version of the source code and supporting scripts can be obtained on GitHub through Zenodo: <https://doi.org/10.5281/zenodo.7036374> (GitHub: <https://github.com/GenTeML/Spec-CNN>). The code can be compiled under any local or browser-based Python environment on Mac, Windows, or Linux. Source code and datasets are copyrighted under Creative Commons BY-NC. Corresponding author: Genesis Berlanga (genesis.berlanga@gmail.com).

Programming was completed using Python 3.8 with Jupyter Notebooks on the Google Collaboratory development environment. Data was processed using the Pandas and Numpy packages (Harris et al., 2020; Reback et al., 2021). Traditional statistics and spectral signal processing were done using the SciKit Learn package (Pedregosa et al., 2011). Machine learning algorithms were developed using the Keras library on top of Tensorflow (Abadi et al., 2016).

Chapter 2: Temperature-Dependent Raman Spectroscopy and X-ray Diffraction Investigation of Magnesium Perchlorate and Magnesium Sulfate Hydrates: Force Constants, Fermi Resonance, and Implication for Mars

Abstract

Magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) and magnesium sulfate (MgSO_4) are hydrated evaporites that occur in terrestrial hyperarid environments and on Mars, where their hydration states record aqueous history. This study combines variable-temperature Raman spectroscopy, X-ray diffraction (XRD), and force constant analysis to characterize the dehydration sequences of $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 hydrates under Mars-relevant conditions. Raman spectra collected from -70 – 400°C (100 – 3700 cm^{-1}) were correlated with XRD to relate crystal structure to changes in the fundamental tetrahedral vibrations, OH stretching modes, and low-wavenumber lattice modes. Although both materials contain analogous tetrahedral oxyanions, they undergo different dehydration pathways. $\text{Mg}(\text{ClO}_4)_2$ dehydrates through discrete crystalline phase transitions accompanied by lowered symmetry, systematic Raman evolution, and progressive Cl—O bond stiffening, whereas MgSO_4 transforms through poorly crystalline and X-ray-amorphous intermediates while retaining Raman signatures of local sulfate bonding environments. A previously unreported Fermi resonance in $\text{Mg}(\text{ClO}_4)_2$ provides a diagnostic marker for the hexahydrate phase and establishes a potential Raman thermometer for planetary applications. Although the ν_1 symmetric stretching mode is a sensitive indicator of hydration and temperature, substantial spectral overlap among hydrated perchlorates, sulfates, and phosphates demonstrates that reliable mineral identification requires interpretation of the full Raman spectrum

rather than the ν_1 region alone. Wilson GF and Herzberg-style force constant analyses quantitatively relate Raman frequencies to local bond strengths, with both yielding consistent trends throughout dehydration. The force constant relationships developed extend Raman spectral interpretation beyond mineral identification by quantitatively constraining local bonding environments and the evolution of hydrated salts detected by the SuperCam and SHERLOC instruments on Mars.

1.0 Introduction

Perchlorates are chlorine-oxygen salts that are hypothesized to play an important role in Mars' modern geochemical and hydrological cycles (Bishop et al., 2014b; Carrier & Kounaves, 2015; Catling et al., 2010; Clark & Kounaves, 2016; De Angelis et al., 2017; Kounaves et al., 2010; Li et al., 2022; Martin et al., 2020; Schuttlefield et al., 2011; Vaniman & Chipera, 2006; Wang et al., 2006; 2009). Magnesium perchlorate and its hydrates ($\text{Mg}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$) are of particular interest because of their strong hygroscopicity, low eutectic temperature, and relevance to deliquescence processes in hyperarid environments (Chevrier et al., 2009). Magnesium sulfate and its hydrates ($(\text{MgSO}_4) \cdot x\text{H}_2\text{O}$), while chemically distinct from magnesium perchlorate hydrates, represent an important structural and geochemical analog: they are a common evaporite mineral on Earth and Mars, and like perchlorate, possess a tetrahedral oxyanion basis that undergoes hydration-dependent structural evolution. In both magnesium perchlorate and magnesium sulfate, molecular water and tetrahedral oxyanions are coordinated to Mg^{2+} , and hydration state exerts a strong control on crystal structure, vibrational behavior, and phase stability. On Mars, low

temperatures and atmospheric pressure and large diurnal humidity fluctuations promote repeated hydration and dehydration cycles. Hence, these materials are expected to evolve through metastable hydration states rather than remaining in thermodynamic equilibrium (Bishop et al., 2014a; Chevrier et al., 2009, 2022; Primm, 2018; Robertson & Bish, 2011; Royle et al., 2017). Magnesium perchlorate can undergo deliquescence during nocturnal humidity cycles (relative humidity (RH) >40%, $T \approx -70^\circ\text{C}$), whereas magnesium sulfate does not deliquesce but instead commonly dehydrates through metastable poorly crystalline or X-ray-amorphous intermediates, particularly under the low-temperature and low-pressure conditions relevant to Mars (Hopkins et al., 2023; Meusburger et al., n.d., 2026; Toner et al., 2015; Vaniman & Chipera, 2006; Chipera et al., 2023). These contrasting dehydration pathways provide an opportunity to compare how two structurally analogous, but chemically distinct, tetrahedral oxyanion systems respond to hydration loss and how those differences are expressed in their crystal structures and Raman spectra.

Both salt systems occur in terrestrial evaporitic environments that serve as analogs for Martian hydrated salts, including the Atacama Desert, Chile, Death Valley, CA, USA, saline lakes, sea ice, and polar ice deposits (Cannon et al., 2012; Elif Genceli et al., 2009; Fortes et al., 2017; Jackson et al., 2015). On Mars, perchlorates have been detected by the NASA Phoenix Lander (Chevrier et al., 2009; Cull et al., 2010; Hecht et al., 2009; Rennó et al., 2009; Zent et al., 2010), the *Curiosity* rover (Glavin et al., 2013; Leshin et al., 2013; Ming et al., 2014; Sutter et al., 2017), and the *Perseverance* rover (Scheller et al., 2022; Tice et al., 2022; Wiens

et al., 2022). Perchlorates have further been hypothesized to participate in transient brine formation and recurring slope lineae (Gough et al., 2019; Heinz et al., 2016; Ojha et al., 2015), whereas sulfates record longer-lived aqueous and evaporitic environments. Sulfate phases have likewise been identified or inferred across numerous Martian terrains through orbital and *in situ* rover observations (Bishop et al., 2009; Farley et al., 2022; Milliken et al., 2010; Rapin et al., 2019; Roach et al., 2010; Vaniman et al., 2018; Chipera et al., 2023; Phua et al., 2024; Silverstrom et al., 2024). Both magnesium perchlorate and magnesium sulfate exhibit multiple hydration states spanning highly hydrated to anhydrous forms, although magnesium sulfate commonly develops poorly crystalline or X-ray amorphous intermediates during dehydration. (Bravenec & Catling, 2025; Fisher et al., 2010) (Fortes et al., 2007; Hopkins et al., 2023; Vaniman & Chipera, 2006; L. Yang et al., 2020). Understanding these contrasting hydration pathways is therefore essential for interpreting hydrated evaporite materials and their spectroscopic signatures under Mars-relevant conditions.

The anhydrate and hydrated magnesium perchlorate structures have been described previously (e.g., Robertson and Bish, 2010; Lim et al., 2011; Solovyov, 2011), as have the anhydrate and hydrated structures of magnesium sulfate (Fortes et al., 2007; Vaniman & Chipera, 2006; Zalkin et al., 1963) (**Figure 1**). We provide a brief overview here with the aim of highlighting the similarities and differences in the crystal structure of these groups and how they change with hydration state.

The anhydrous form of magnesium perchlorate crystallizes in the monoclinic space group $P2_1/c$ and forms a 3-dimensional network structure with corner-sharing MgO_6 octahedra and ClO_4 tetrahedra. (Bishop et al., 2014a; Fortes et al., 2007; Lim et al., 2011; Solovyov, 2011). In the hydrous forms, the Mg^{2+} cation is octahedrally coordinated by oxygens bound to either water molecules or perchlorate tetrahedra (West, 1935). In the hexahydrate phase, Mg^{2+} is coordinated exclusively by water molecules, while decreasing hydration progressively replaces water with perchlorate coordination through monodentate, bidentate, and bridging configurations (Olmstead et al., 1982). This is a symmetry-lowering process where the free-perchlorate tetrahedral (T_d symmetry) geometry changes to lower site symmetries (C_{3v} or C_{2v}) (J. L. Bishop et al., 2014a). Molecular water can aid in stabilizing the monodentate coordination of other ligands to the magnesium ion, particularly in water-rich complexes (Bishop et al., 2014a; Robertson & Bish, 2010).

Magnesium sulfate hydrates exhibit analogous symmetry lowering of SO_4^{2-} tetrahedra with dehydration, although sulfate structures generally tolerate greater distortion and disorder (**Figure 1**). Anhydrous magnesium sulfate forms an orthorhombic structure (space group $Cmcm$ at ambient conditions), composed of corner-sharing MgO_6 octahedra and SO_4 tetrahedra forming a three-dimensional framework. The higher formal charge of the sulfate anion (SO_4^{2-}) leads to stronger Mg–O–S bonding and a more densely connected framework than in perchlorate-bearing structures, resulting in a comparatively rigid crystal lattice with fewer

structural channels and a greater tolerance for tetrahedral distortion (Vaniman & Chipera, 2006).

The phase stability of magnesium perchlorate hydrates has been explored in detail by Robertson and Bish (2010, 2011), who used XRD and charge-flipping methods to solve the crystal structures of the tetrahydrate and dihydrate phases and to track their dehydration pathways. Their work showed that the hexahydrate dehydrates through tetrahydrate (~348 K) and dihydrate (~423 K) intermediates before reaching the anhydrous phase under low relative humidities (RH), with each transition exhibiting kinetic persistence over temperature intervals of 5-25 K at a heating rate of 2 K/min. These transformations parallel those in analogous hydrated systems, including magnesium sulfate and perrhenate salts (ReO_4^-) (Matveeva et al., 1986), highlighting the broader structural similarities among hydrated perchlorate, sulfate, and related tetrahedral oxyanion frameworks.

Building on the crystallographic work of Robertson and Bish (2010, 2011), Bishop et al. (2014) investigated a broad suite of perchlorate salts, including magnesium perchlorate, using visible/near-infrared (VNIR) reflectance spectroscopy and differential scanning calorimetry (DSC). Their study demonstrated that both ClO_4^- and H_2O vibrational modes vary systematically with cation type and hydration state, highlighting the potential for confusion between perchlorate and sulfate spectral features and the need for detailed spectroscopic characterization under Mars-relevant conditions. However, the vibrational spectra were not monitored continuously during dehydration, leaving temperature-dependent evolution of individual vibrational

modes unconstrained. Subsequent Raman studies have provided only limited temperature-dependent measurements for magnesium perchlorate hydrates (Wu et al., 2016), while comparable magnesium sulfate investigations similarly lack continuous variable-temperature datasets acquired under identical experimental conditions (Talla et al., 2023; Wang et al., 2006, 2009).

Despite previous structural and spectroscopic investigations, continuous variable-temperature Raman and XRD datasets spanning the complete dehydration sequences of magnesium perchlorate and magnesium sulfate remain limited. Moreover, the relationships among hydration state, crystal structure, vibrational behavior, and local bond strengths have not been systematically examined across analogous perchlorate and sulfate systems. Here we combine variable-temperature Raman spectroscopy, X-ray diffraction, and force constant analysis to characterize the complete dehydration pathways of $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 under Mars-relevant conditions. By directly comparing two structurally analogous tetrahedral oxyanion systems that follow fundamentally different dehydration pathways, we establish experimentally validated relationships among hydration state, crystal structure, Raman spectral behavior, and local bonding that improve interpretation of hydrated perchlorates and sulfates in laboratory measurements and Mars rover observations.

2.0 Methods and Experimental Setup

Reagent grade (99+% purity) synthetic magnesium perchlorate from Sigma-Aldrich was used in this study in both single crystal and powdered form and measured using Raman and powder X-ray diffraction from $-70\text{ }^\circ\text{C}$ to $400\text{ }^\circ\text{C}$.

Anhydrous crystal grain sizes ranged from 0.1 mm – 0.5 mm in diameter. Powders were ground and sieved to $\leq 150 \mu\text{m}$. The magnesium perchlorate was allowed to hydrate into its hexahydrate phase at 1 atmosphere, 22°C, 40% relative humidity for 5 minutes, and Raman and XRD measurements were promptly collected before saturation from ambient humidity triggered deliquescence of the sample. Subsequent measurements were acquired under vacuum following the initial ambient condition measurements. Humidity and temperature conditions were closely monitored throughout the entire experiment using a high-performance Vaisala thermohygrometer with an HM141 indicator and HMP46 probe ($\pm 0.1 \text{ \%RH}$ and $\pm 0.1^\circ\text{C}$).

Raman spectra were collected using a Horiba LabRAM HR Evolution Raman spectrometer at the University of California Santa Cruz Mineral Physics Laboratory using a 532 nm excitation laser. The laser was focused to a spot size of $\sim 10 \mu\text{m}$ using a long-distance 50x objective ($\text{NA} = 0.5$), with an estimated laser power at the sample of $\sim 10 \text{ mW}$. Unpolarized Raman scattering was collected in 360° scattering geometry, passed through a 532 nm notch filter, and refracted through a grating with a density of 1200 lines/mm with a spectral resolution of $\sim 1 \text{ cm}^{-1}$, and received by an Open-Electrode CCD detector cooled to -60°C . Raman measurements were collected under vacuum from $100 - 3700 \text{ cm}^{-1}$ at 40 – 60 s integrations and 3 – 5 accumulations to rapidly capture phase changes. Six $< 0.5 \text{ mm}$ crystals were placed on a Linkam TS1500 temperature stage equipped with a T96 system controller. The chamber was pumped down to 0.1 Pa ($\pm 0.1 \text{ Pa}$) and the magnesium perchlorate crystals were heated from 20 – 400°C at user-selected temperature intervals of 1 – 10°C ($\pm 0.1^\circ\text{C}$),

at a rate of 5°C/min, and a hold time of ~10 min at each temperature to allow for sample equilibration. Additionally, an in-house portable Raman system was used at the NASA Ames Research Center's Planetary Mineralogy and Spectroscopy Laboratory to acquire low-temperature Raman measurements, employing a 532 nm/50 mW excitation laser with a spectral resolution of 1 cm⁻¹, and collected through a fiber optic aperture with a spot size of ~25 μm. With this system, Raman measurements were collected from 100 – 3100 cm⁻¹ with 30 s integrations across a temperature range from -70 to 20°C.

The low-temperature Raman spectra acquisitions were collected using the in-house portable Raman system with the fiber optic aperture aimed at the magnesium perchlorate sample within an Anton Paar TTK 450 environmental chamber. The sample was allowed to naturally warm back up at ambient pressure. This process occurred within minutes, and care was taken to collect the spectra before the sample could completely freeze over with water ice due to absorption of ambient humidity. Consequently, the low-temperature Raman spectra exhibit broader peaks and lower Raman signal intensities than the primary laboratory-resolution high-temperature Raman spectra, and were used only to monitor cryogenic phase change progression and vibrational mode behavior.

Powder XRD patterns for magnesium perchlorates and sulfates were collected using a Rigaku SmartLab X-ray Diffractometer at NASA Ames Research Center Planetary Mineralogy and Spectroscopy Laboratory. The Rigaku Smartlab employed a 3 kW CuKα X-ray generator ($\lambda = 1.54059 \text{ \AA}$) operating at 40 kV, 40 ma, in

conjunction with a D/teX Ultra 250 1D silicon strip detector in Bragg Brentano geometry, to acquire X-ray reflections over an angular range of $5 - 65^\circ 2\theta$ in 0.01° steps with collection times of 0.073 s/step. This setup is optimized for time-resolved analysis of rapid dehydration phase transitions. The sample was placed in the TTK 450 environmental chamber controlled by a TCU 110 temperature controller and cooled with a LNC Liquid Nitrogen Controller circulating chiller. Half a gram of powdered magnesium perchlorate was pumped down to 0.1 Pa (± 0.1 Pa) and XRD patterns were collected from -70 to 400°C at user-selected temperature intervals of 5 to 10°C ($\pm 0.1^\circ\text{C}$), heated at a rate of $5^\circ\text{C}/\text{min}$, with a hold time of ~ 10 min per interval to allow for sample equilibration. XRD acquisitions confirmed the dehydration phase changes at temperatures consistent with the results of Robertson and Bish (2010).

Powder X-ray diffraction patterns were refined using GSAS II software employing Rietveld refinement where sample measurements permitted and Le Bail refinement for datasets collected through Kapton tape. Initial structural models for the hexahydrate, tetrahydrate, dihydrate, and anhydrate magnesium perchlorate phases were taken from West (1935), Solovyov (2011), Robertson and Bish (2011), and Lim (2011). Magnesium sulfate heptahydrate and hexahydrate were taken from Baur (1964) and Falkin et al. (1963). CIF files can be found along with this study's supplementary data as part of the open access data availability policy. Background, scale factor, lattice parameters, zero shift, and profile parameters were refined, while atomic positions and occupancies were fixed unless otherwise noted. Thermal

expansion coefficients were calculated from the refined lattice parameters as a function of temperature.

3.0 Results

3.1 Temperature-Dependent Raman Spectroscopy of Mg-Perchlorate

(Mg(ClO₄)₂)

Mg(ClO₄)₂ Raman spectra were collected from -45°C to 400°C, revealing systematic shifts and intensity changes in the fundamental tetrahedral vibrational bands of the perchlorate unit, the ν_1 (symmetric stretch), ν_2 (symmetric bend), ν_3 (asymmetric stretch), ν_4 (asymmetric bend), as well as the OH stretch vibrational modes. (**Figure 2a**) The ν_1 band (at $\sim 935\text{ cm}^{-1}$ in the hexahydrate phase) is the most intense Raman mode of Mg(ClO₄)₂ and its shifts track changes in hydration (hydrogen bonding), structure (lattice contraction or expansion), and, with its behavior well-calibrated, temperature. A pure hexahydrate phase was observed between -45-125°C, characterized by a narrow, stable ν_1 peak consistent with the hexahydrate spectra reported by Wu et al. (2016). Within the hexahydrate phase, ν_1 broadened and shifted progressively toward higher wavenumbers with increasing temperature. A transition to the tetrahydrate phase ($\nu_1 = 946\text{ cm}^{-1}$) was observed between 135-155°C, with metastable coexistence of the two hydration states over part of this interval. Similar kinetic persistence of perchlorate hydrates beyond their thermodynamic stability fields has been reported from variable-temperature XRD experiments (Robertson & Bish, 2010). Following Robertson and Bish (2010), transition temperatures are reported using the first appearance of the higher-

temperature phase. Lorentzian peak fits of the deconvolved Raman spectra are provided in the **Supplement**. By 160°C, the first prominent dihydrate peak appeared at 962 cm⁻¹ alongside the tetrahydrate peak. then shifted gradually to 964 cm⁻¹ by 200°C. Between 250-280°C, a stable, phase-pure dihydrate was observed, with ν_1 exhibiting the expected decrease in wavenumber (962-961 cm⁻¹) with increasing temperature. The hexahydrate and dihydrate displayed the greatest metastable persistence relative to the tetrahydrate and anhydrate phases. Between 285-290°C, the dihydrate and anhydrate phases coexisted producing ν_1 peaks at 961 cm⁻¹ and 995 cm⁻¹, respectively. By 300°C, only the anhydrate remained, with a ν_1 peak at 994 cm⁻¹ that subsequently shifted toward lower wavenumbers with further heating. The temperature dependence of the Raman peak positions is shown in **Figure 3a**, representative spectra for each vibration mode region are presented in **Figure 2a**., and band assignments are summarized in **Table 1**. (Agarwal et al., 1985; J. L. Bishop et al., 2014a; Patel et al., 1983; White & Falk, 1986; Wu et al., 2016)

Spectral deconvolution of the ν_1 symmetric stretching band in Mg(ClO₄)₂ reveals a reproducible low-frequency shoulder that is well fit by a second component (**Figure 4a**). We interpret the higher-wavenumber peak centered at ~935 cm⁻¹ as the fundamental ν_1 mode and the lower-wavenumber shoulder centered at ~929.3 cm⁻¹ as an overtone-derived band ($2\nu_2$) whose Raman intensity is enhanced by Fermi resonance arising from its energetic proximity to the intense ν_1 Cl–O symmetric stretch. Neglecting anharmonic effects, the $2\nu_2$ overtone would be expected at 928.4 cm⁻¹, at an essentially identical frequency to that at which we observe the shoulder.

The shoulder generated by Fermi resonance is observed only within the low-temperature hexahydrate stability field, making it diagnostic of the magnesium perchlorate hexahydrate phase. Between -45 and 125°C , the separation between the fitted peak centers first decreases to a minimum near $15\text{-}20^{\circ}\text{C}$ before increasing systematically from $\sim 6\text{ cm}^{-1}$ to $\sim 9\text{ cm}^{-1}$ by 125°C ($\sim 50\%$ increase), while the relative intensity of the $2n_2$ component increases approaching 15°C and then decreases with increasing temperature. This behavior is consistent with the classical intensity borrowing associated with Fermi resonance: the $2n_2$ overtone is intrinsically weak in Raman scattering but acquires intensity through anharmonic coupling to n_1 when the two vibrational states are near-degenerate. As temperature increases, the mode shifts of the fundamentals drive the unperturbed n_1 and $2n_2$ levels further apart, reducing vibrational mixing and causing the overtone-like branch to markedly decrease in intensity (**Figure 4d**). The resonance persists until approximately 150°C , coincident with the onset of the tetrahydrate stability field, at which point the n_2 fundamental itself splits into a doublet. This symmetry-lowering and frequency detuning disrupts the resonance, effectively quenching the coupling between n_1 and $2n_2$. Although Fermi resonance enhancement of perchlorate overtones has been reported in aqueous magnesium perchlorate solutions (Ratcliffe & Irish, 1984), to our knowledge this is the first report of the phenomenon in crystalline magnesium perchlorate and the first demonstration of its utility as a diagnostic Raman feature for perchlorate hydrates relevant to Raman observations by SuperCam and SHERLOC on the Martian surface (Chio et al., 2003; Ratcliffe & Irish, 1984)

To quantify the interaction, we apply the avoided-crossing model commonly used to describe Fermi resonances, in which two same-symmetry states repel in frequency space and exchange character as they approach one another (i.e., they are “forbidden to cross”). Vennari and Williams (2021) and Knittle et al. (2001) express this interaction using the two-level coupling relation:

$$(n_+ - n_-)^2 = (n_a - n_b)^2 + 4\delta^2$$

where $n_{+,-}$ are the perturbed frequencies (the observed branches in **Figure 4b**), $n_{a,b}$ are the unperturbed mode frequencies, and δ is the coupling constant describing the coupling of the two modes. (Knittle et al., 2001; Lawns & Sherman, 1978; Shimizu, 1985; Vennari & Williams, 2021) In this model, the minimum observed separation equals 2δ . Although our measurements mostly capture one side of the avoided crossing over the -45 to 125°C interval, the minimum splitting near 15°C constrains the coupling constant to $\sim 2.3\text{ cm}^{-1}$, and the co-evolution of increasing splitting with decreasing shoulder intensity is the expected signature of diminishing mode mixing away from resonance.

The n_2 symmetric and n_4 asymmetric bending bands appear at 465 cm^{-1} and $\sim 630\text{ cm}^{-1}$, respectively, at 20°C in the hexahydrate phase (**Figure 2a**). Under ideal T_d symmetry, n_2 is Raman-inactive and doubly degenerate, whereas n_4 is Raman active and triply degenerate. In magnesium perchlorate hydrates, crystal-field effects, hydrogen bonding, and coordination within the lattice lower the local symmetry of the perchlorate tetrahedra. Site-symmetry and factor group analysis (Cotton, 1930; Fateley & Dollish, 1972; Nakamoto, 2009; Rousseau et al., 1981) indicate that the

hydrated phases place the perchlorate tetrahedra on approximate mirror-plane (C_s) sites, which lifts the degeneracy of the n_2 (E symmetry) and n_4 (F_2) modes. The n_2 mode begins to split at the onset of the tetrahydrate phase, coincident with the transition from the orthorhombic hexahydrate to the monoclinic tetrahydrate. This splitting persists through the monoclinic dihydrate before disappearing in the anhydrate phase, where n_2 shifts toward lower wavenumbers ($\sim 462\text{ cm}^{-1}$). The n_4 mode likewise splits upon formation of the tetrahydrate and remains split throughout the dihydrate as crystallographically distinct oxygen environments and hydrogen bonding interactions produce non-equivalent Cl-O bonds. In the anhydrate phase, n_4 remains split because the perchlorate tetrahedra still occupy a crystallographic environment of lower than T_d symmetry, although the separation between components decreases relative to the hydrated phases. In contrast, the n_2 splitting is no longer resolved. Thus, both n_2 and n_4 respond to symmetry lowering during dehydration, but only n_4 retains evidence of symmetry breaking even in the anhydrate phase. (Agarwal et al., 1985; J. L. Bishop et al., 2014a; Patel et al., 1983; White & Falk, 1986; Wu et al., 2016)

The n_3 asymmetric stretching band ($1015\text{-}1180\text{ cm}^{-1}$ region) is triply degenerate (F_2 symmetry) in an ideal T_d geometry and is highly sensitive to local symmetry reduction and structural distortion. Site symmetry and factor-group analysis (**Supplement**) predict that perchlorate tetrahedra occupying approximate C_s sites in the tetrahydrate and dihydrate phases may exhibit up to three Raman-active n_3 components through combined site symmetry and factor-group splitting. We observed

ν_3 to split into two peaks in both the hexahydrate and dihydrate phases and into approximately three to five partially resolved peaks in the tetrahydrate, whereas no clearly resolved ν_3 -associated bands are observed in the anhydrate phase. The splitting between the ν_3 peaks is substantially larger in the dihydrate than in the hexahydrate, consistent with greater tetrahedral distortion. Robertson and Bish (2010) reported only one crystallographically distinct perchlorate site in the unit cells of the dihydrate and tetrahydrate phases, indicating that the observed ν_3 splitting does not arise from multiple inequivalent tetrahedral sites. Instead, the increased complexity of the tetrahydrate ν_3 envelope likely reflects stronger local distortion, factor-group splitting, disorder broadening, and overlap among symmetry-allowed components. Some Raman-active components predicted by factor-group analysis may remain unresolved because of weak intensity, near degeneracy, or disorder-induced broadening. (Agarwal et al., 1985; J. L. Bishop et al., 2014a; Patel et al., 1983; White & Falk, 1986; Wu et al., 2016)

In the OH stretching region (3530–3565 cm^{-1}), the Raman spectra show a clear progression with dehydration that reflects changes in the hydrogen-bonding environment of coordinated water. At low temperature, the OH band appears as a broad peak centered at 3531 cm^{-1} in the hexahydrate phase. With increasing temperature and progressive dehydration, the band shifts toward higher wavenumbers and narrows slightly, indicating that there is weaker hydrogen bonding in the less hydrated phases. By the dihydrate phase, the OH stretch is centered at 3565 cm^{-1} , consistent with reduced water content and changes in the local hydration environment

accompanying increased coordination of ClO_4 by Mg^{2+} . Robertson and Bish (2010) reported that the shortest hydrogen-bond distance increases from $\sim 2.16 \text{ \AA}$ in the tetrahydrate to $\sim 2.33 \text{ \AA}$ in the dihydrate, consistent with the observed increase in OH stretching frequency. The OH band disappears entirely by $\sim 300^\circ\text{C}$, marking the complete loss of structural water and formation of the anhydrate. A weak HOH bending mode (δHOH) at 1630 cm^{-1} likewise decreases in intensity with dehydration, further confirming the progressive loss of coordinated water. (Agarwal et al., 1985; J. L. Bishop et al., 2014a; Patel et al., 1983; White & Falk, 1986; Wu et al., 2016)

The low-frequency Raman modes of $\text{Mg}(\text{ClO}_4)_2$ have rarely been reported, likely because of their low intensity relative to the internal tetrahedral vibrations. Several bands were observed between 100 and 390 cm^{-1} (**Figure 5a**). Modes below 135 cm^{-1} are tentatively assigned to Mg^{2+} translations/lattice modes. Bands between 130 - 150 cm^{-1} likely correspond to Mg–O translational vibrations and librational (“cage-rattling”) motions of the octahedrally coordinated hydration shell associated with Mg–O(H_2O) bending/stretching. The broad band between 169 - 180 cm^{-1} is consistent with librational motions of coordinated water coupled with lattice-bending vibrations. By analogy with calculations on $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite) (Caracas & Bobocioiu, 2011), the bands between 300 - 390 cm^{-1} are likely associated with framework vibrations involving weak ClO_4^- interactions or constrained rocking and twisting librations of water molecules within the lattice. In the hexahydrate, the well-ordered water molecules form discrete $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ complexes such that water libration is coupled to deformation of the MgO_6 octahedra through Mg–O bond

bending and stretching. The sensitivity of these low-frequency modes to hydration state suggests that, under suitable observational conditions, this spectral region may provide an additional diagnostic indicator of perchlorate hydration state.

As temperature increases and dehydration proceeds to the dihydrate phase (155°C), the 130-150 cm^{-1} peaks merge into a broad doublet centered at 145.2 cm^{-1} and 169.4 cm^{-1} , indicating changes in the local Mg^{2+} environment. Concurrently, the $\sim 350 \text{ cm}^{-1}$ peak shifts to 356 cm^{-1} . By 180°C, the persistence of the 145.2 cm^{-1} and 169.4 cm^{-1} doublet indicates stabilization of the low-hydration coordination environment. The 355.5 cm^{-1} peak subsequently shifts to 342.7 cm^{-1} with further dehydration, consistent with continued reorganization of the lattice vibrational modes accompanying formation of the anhydrate. These systematic changes demonstrate that the low-frequency Raman region is highly sensitive to the structural evolution accompanying dehydration.

Figure 3a summarizes the temperature dependence of the n_1 , n_2 , n_3 , and n_4 vibrational modes and the OH stretch. The n_1 symmetric stretch and OH stretching mode exhibit the largest increases in frequency across dehydration, whereas the barycenters of the split n_2 , n_3 , and n_4 bands undergo comparatively modest shifts despite pronounced symmetry-induced splitting. Thus dehydration is expressed primarily through symmetry-induced band splitting in the bending modes and through systematic frequency shifts of the n_1 and OH stretching vibrations.

Pronounced kinetic effects were observed during both the hexahydrate-to-tetrahydrate and dihydrate-to-anhydrate phase transitions. Spectral signatures

characteristic of the hexahydrate and dihydrate phases remained detectable over temperature ranges of approximately 135°C and 130°C, respectively, indicating substantial metastable persistence and suggesting that water loss and associated lattice reorganization occur slowly on laboratory timescales (minutes to hours). During the tetrahydrate-to-dihydrate transition ($\sim 135^\circ\text{C}$), the n_1 peak, two n_3 peaks, one component of each n_2 and n_4 doublet, and the OH stretch first shift to higher wavenumbers. Upon stabilization within the dihydrate field, these same peaks reverse direction and shift toward lower wavenumbers by $\sim 1\text{-}3\text{ cm}^{-1}$.

3.2 Temperature-dependent Raman Spectroscopy of Hydrated Mg-Sulfate (MgSO₄)

To compare the trends observed in the perchlorate spectra, temperature-dependent MgSO₄ Raman spectra were collected from -70°C to 300°C , and the fundamental internal vibrational modes of the sulfate tetrahedron were identified and analyzed similarly to those of the perchlorate anion (**Figure 2b**). As in the perchlorate system, under ideal T_d symmetry, SO_4^{2-} exhibits four fundamental internal vibrational modes, all of which are Raman-active, with n_2 , n_3 and n_4 being doubly, triply, and triply degenerate, respectively. Deviations from ideal tetrahedral symmetry caused by cation coordination and hydrogen bonding lift these degeneracies, producing band splitting, frequency shifts, and changes in relative intensity.

The n_1 symmetric stretching mode (~ 983.2 to $\sim 1033.8\text{ cm}^{-1}$ in the heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and lower hydrates) is the most intense Raman mode of all the MgSO₄ phases examined, and exhibits the strongest and most systematic

response to dehydration (**Figure 2b**). The heptahydrate phase was observed from -70 to 40°C. Dehydration to the hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) begins at 45°C with the ν_1 band shifting down to 982.5 cm^{-1} . Above 70°C, ν_1 broadens substantially and shifts up to ~1023.7 cm^{-1} , indicating complete transformation to a new phase by ~90°C. We interpret this 20°C interval as associated with a low-hydration, partially amorphous phase consistent with trihydrate-like composition as reported in prior Raman work, and tentatively assigned to $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ (Wang et al., 2006b, 2009). This interpretation is consistent with the diffuse scattering observed in our XRD patterns, and previous Raman experiments that identify $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ as an intermediate phase (L. Yang et al., 2020). From ~90°C to 300°C, the broad sulfate bands indicate that the sample remains largely amorphous. Although long-range crystallinity is lost, the sulfate fundamental vibrations persist, indicating preservation of the SO_4 tetrahedra while ν_1 continues to track the average local bonding environment (Vaniman & Chipera, 2006; Wang et al., 2006). The hydroxyl stretching vibrations progressively lose intensity and resolvability, consistent with continued dehydration. Within this high temperature phase, the broad ν_1 band continues to shift to higher wavenumbers with increasing temperature, approaching ~1033 cm^{-1} at 175°C, which overlaps with the corresponding band in sanderite ($\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$) (Wang et al., 2006). We therefore interpret the high-temperature ν_1 position as reflecting an average hydration state approaching that of the dihydrate, even while the structure remains amorphous. Our spectra agree with previous Raman and XRD studies of dehydrating magnesium sulfate hydrates, which similarly report progressive ν_1 broadening, shifts toward

higher wavenumbers, and increasing structural disorder during dehydration (De Angelis et al., 2017; Fortes et al., 2006, 2007; Meusburger et al., n.d.; Vaniman & Chipera, 2006; Wang et al., 2006, 2009; Yang et al., 2020). Band assignments for the sulfate phases and their peak positions are summarized in **Table 1**. Lorentzian peak fits of the deconvolved Raman spectra are provided in the **Supplement**.

In the heptahydrate phase, the ν_2 symmetric bending mode appears as a single band near 456 cm^{-1} , while the ν_4 asymmetric bending mode is observed near 609 cm^{-1} . As dehydration proceeds to the hexahydrate, ν_2 splits into two peaks near 443 and 462 cm^{-1} , whereas ν_4 splitting is not readily apparent; however, deconvolution of the ν_4 region reveals two broad overlapping peaks near 610 cm^{-1} . The persistence of ν_2 splitting despite the crystallographic equivalence of the sulfate sites reported by (Batsanov, 2000) indicates continued sulfate tetrahedral distortion and vibrational coupling within the crystal lattice. In the proposed trihydrate phase, ν_2 reconverges toward a single feature near 447 cm^{-1} , or its splitting becomes less well resolved due to progressive disordering, while ν_4 shifts upward to $\sim 615\text{ cm}^{-1}$. In each instance, the peaks are broader than in the lower temperature, more hydrated phases, consistent with the overarching amorphous environment. In the dihydrate, ν_2 again splits into two peaks near 452 and 491 cm^{-1} , whereas ν_4 continues to shift to higher wavenumbers, reaching $\sim 625\text{ cm}^{-1}$. Together, these changes indicate progressive evolution of the sulfate tetrahedral environment with dehydration and an increasing influence of amorphization on the Raman band shapes at lower hydration states.

The ν_3 asymmetric stretching region exhibits the strongest sensitivity to symmetry lowering and disorder, with pronounced splitting and broadening across the hydration states. In the heptahydrate, ν_3 is resolved into multiple peaks near 1060, 1094, and 1129 cm^{-1} , while the hexahydrate exhibits dominant peaks near 1079 and 1144 cm^{-1} . The proposed trihydrate retains a strong ν_3 feature near 1144 cm^{-1} . In the amorphous phase, the ν_3 region broadens substantially ($\sim 1090\text{--}1320\text{ cm}^{-1}$), consistent with increasing structural disorder and overlapping vibrational contributions from inequivalent sulfate environments.

The behavior of the OH stretching region further corroborates these structural changes. The heptahydrate exhibits multiple OH bands between ~ 3200 and 3410 cm^{-1} , indicative of well-defined hydrogen-bonding environments. As dehydration proceeds, the OH stretching bands shift to higher wavenumbers and broaden, with the hexahydrate showing peaks near 3272 and 3426 cm^{-1} , the proposed trihydrate near 3281 and 3457 cm^{-1} , and the dihydrate dominated by a broad feature near 3514 cm^{-1} . This progressive shift to higher wavenumbers and loss of the hydroxyl are consistent with weakening hydrogen bonding and progressive water loss during dehydration.

Low-frequency Raman modes of MgSO_4 are observed below 400 cm^{-1} (**Figure 5b**) and arise from a combination of $\text{Mg}^{2+}\text{—O}$ lattice vibrations, external SO_4^{2-} framework deformations, and hydration shell motions. At 22°C, weak bands near 125 and 150 cm^{-1} are attributed to Mg^{2+} translational lattice modes and $\text{Mg}^{2+}\text{—H}_2\text{O}$ motions within the hydration shell octahedra. More prominent peaks at 204.6 cm^{-1} , 238.8 cm^{-1} , 249.9 cm^{-1} , and 369.9 cm^{-1} are assigned to lattice-coupled external

SO_4^{2-} motions and coordinated water librations constrained by the local crystal environment. Comparable low-frequency features have been attributed to mixed Mg—O—SO_4 lattice vibrations and hydration shell dynamics in crystalline epsomite and hexahydrate (Buzgar et al., 2009). At 50°C, several low-frequency bands become unresolvable, the 249.9 cm^{-1} peak shifts to 242.2 cm^{-1} , and the 369.9 cm^{-1} peak shifts to 357.3 cm^{-1} . These changes are consistent with distorted sulfate rocking or wagging motions accompanying progressive dehydration of the hydration framework. This dehydration-dependent evolution persists to at least 75°C and is accompanied by progressive band broadening and loss of fine structure, consistent with loss of crystallinity and the formation of intermediate hydration states.

Figure 3b summarizes the temperature dependence of MgSO_4 n_1 , n_2 , n_3 , and n_4 vibrational modes together with the OH stretching bands. Similar to $\text{Mg}(\text{ClO}_4)_2$, systematic changes in peak positions accompany dehydration, although the numbers of bands, their separations, and the nature of the phase transitions differ between the two systems. The n_1 symmetric stretch exhibits the largest and most systematic increase in frequency, while the OH stretching bands shift to higher wavenumbers and progressively lose spectral resolution with dehydration.

The n_2 and n_4 bending modes and the n_3 asymmetric stretch exhibit comparatively modest net frequency shifts but substantial changes in band multiplicity and broadening, reflecting progressive symmetry lowering and increasing structural disorder. Between approximately 45 and 90°C, the spectra evolve from the hexahydrate into a lower-hydration, partially amorphous intermediate characterized

by increased scatter and band broadening rather than the abrupt spectral discontinuities observed in $\text{Mg}(\text{ClO}_4)_2$. Above $\sim 100^\circ\text{C}$, the n_1 and n_3 bands continue shifting toward higher wavenumbers, approaching values associated with $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ (Wang et al., 2006), while the bending-mode barycenters remain comparatively stable. Overall, the Raman peak position trends indicate a dehydration pathway dominated by progressive amorphization and continuous structural evolution rather than discrete crystalline phase transitions.

3.3 Phase Transitions and XRD Patterns for $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4

Powder XRD data were collected over a temperature range of -70 to 425°C to constrain phase stability, structural transitions, and crystallinity of anhydrous and hydrous $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 . Phase transition temperatures observed in XRD patterns and Raman spectra in both materials were within 50°C of each other, indicating variability arising from kinetic effects, resulting from differences in sample preparation, grain size, and sample environment. Despite the differences in sample preparation and state during measurement, heating rates were equivalent across both techniques. XRD measurements provided a crystallographic framework for interpreting the temperature-dependent Raman spectra. In this context, powder XRD serves as ground truth for phase identification and transitions observed in the Raman data.

X-ray diffraction of magnesium perchlorates confirms a sequence of four distinct hydration phases corresponding to hexahydrate ($6 \cdot \text{H}_2\text{O}$), tetrahydrate ($4 \cdot \text{H}_2\text{O}$), dihydrate ($2 \cdot \text{H}_2\text{O}$), and anhydrate $\text{Mg}(\text{ClO}_4)_2$. Each phase exhibits distinct

diffraction patterns consistent with previous structural studies (Baur, 1964; Lim et al., 2011; Robertson & Bish, 2010, 2011; Solovyov, 2011; West, 1935; Zalkin et al., 1963). The hexahydrate phase displays strong reflections consistent with an orthorhombic structure with Mg^{2+} octahedrally coordinated by H_2O molecules. Progressive dehydration leads to lower-symmetry monoclinic phases in the tetrahydrate and dihydrate, reflecting increasing bonding of the ClO_4^- tetrahedra into a mixed Mg^{2+} and water coordination environment. This transition hence represents a reorganization from isolated hydration complexes to extended polyhedral frameworks (Robertson & Bish, 2010). Continued dehydration produces the anhydrate phase, characterized by a fully connected $\text{MgO}_6\text{-ClO}_4$ network with no interstitial water (Lim et al., 2011). While Robertson and Bish (2011) previously conducted a comprehensive XRD study of perchlorate hydration states between -20°C to 250°C , our work extends to a broader temperature range, including conditions that overlap with Mars equatorial temperatures. Here, XRD is used to constrain hydration states and validate phase transitions observed in the Raman spectra. **Figure 6a** shows the XRD patterns and corresponding Raman spectra for the hexahydrate, tetrahydrate, dihydrate, and anhydrate phases. Magnesium perchlorate crystal structure parameters and thermal volume expansion are summarized in **Table 2**, showing excellent agreement with previous studies.

Rietveld refinements including crystal structure parameters and thermal volume expansion were obtained for the hexahydrate and tetrahydrate phases (-70 to 110°C), yielding excellent agreement with prior work (**Table 2**). Above $\sim 110^\circ\text{C}$, rapid

dehydration to the dihydrate phase caused sample saltation off the sample holder, preventing stable sample surface alignment. Kapton tape was used to physically stabilize the sample during high-temperature measurements. XRD patterns collected through Kapton tape clearly resolve phase transitions across the full dehydration sequence, allowing robust phase identification. Rietveld refinement was used except in cases where multiple hydration phases were present and Le Bail refinement yielded a better fit. We recorded XRD measurements of magnesium perchlorate covered with Kapton tape from 60 to 425°C, encompassing the full range of hexahydrate, tetrahydrate, dihydrate, and anhydrate phases. All $\text{Mg}(\text{ClO}_4)_2$ phases remain crystalline throughout dehydration, with no evidence for X-ray amorphization. The transitions are abrupt and phase-pure, consistent with reconstructive structural changes rather than progressive disordering. This behavior contrasts strongly with that of MgSO_4 as described in the next section. All refined powder XRD data for magnesium perchlorate phases are available in the **Supplement**.

Refined unit-cell parameters for $\text{Mg}(\text{ClO}_4)_2$ phases are summarized in **Table 2** and are in close agreement with previously published structures by West (1935), Solovyov (2011), Robertson and Bish (2011), and Lim (2011). The Kapton-covered dihydrate and anhydrate measurements also yield cell volumes consistent with published values, despite the reduced refinement fidelity imposed by Kapton scattering. Across the dehydration sequence, the unit-cell volume decreases systematically from 555.8 Å³ in the hexahydrate to 504.5 Å³ in the tetrahydrate, 388.3 Å³ in the dihydrate, and 282.3 Å³ in the anhydrate. This monotonic volume collapse

reflects progressive water loss and increasing replacement of H₂O ligands by perchlorate oxygens in the Mg coordination environment. Volumetric thermal expansion coefficients (VE) for the crystalline phases are on the order of 10⁻⁴/K (VE = 1/V(dV/dT)), indicating relatively limited volumetric sensitivity to temperature within a given hydration state over our temperature range. This suggests that the dominant structural changes in Mg(ClO₄)₂ are driven by discrete dehydration transitions rather than continuous thermal expansion. Among the hydrated polymorphs, the tetrahydrate is alone in having a negative thermal expansion: this is an unexpected result (the thermal expansion of this phase was not reported by Robertson and Bish (2011)), and may be associated with internal rotations of the perchlorate tetrahedra relative to the magnesium octahedra within the structure. Notably, heavily hydrated magnesium sulfates (11 and 7 water molecules in their formula unit) are known to have low thermal expansions near ambient temperature, with the 11 water molecule magnesium sulfate having a negative thermal expansion at low temperatures (Fortes et al., 2007). Moreover, compounds with two coordinate M1—O—M2 linkages (as are partially present in the tetrahydrate with its Mg—O—Cl linkages) can exhibit negative thermal expansion (Winiarz et al., 2025).

In contrast, MgSO₄ exhibits a fundamentally different dehydration pathway characterized by progressive loss of long-range crystallinity (**Figure 6b**). The heptahydrate (epsomite) and hexahydrate phases display sharp diffraction peaks indicative of well-ordered crystalline structures. However, upon further dehydration ($\geq 90^\circ\text{C}$), diffraction peaks broaden substantially, decrease in intensity, and collapse

into diffuse scattering, marking the transformation to X-ray amorphous or poorly crystalline material. Minor peaks near $43^\circ\ 2\Theta$ arise from Fe in the sample stage. Because XRD cannot uniquely constrain the hydration states of amorphous materials, Intermediate compositions near $\sim 3\cdot\text{H}_2\text{O}$ and $\sim 2\cdot\text{H}_2\text{O}$ are identified from the accompanying Raman spectra. All refined powder XRD data for the magnesium sulfate phases are provided in the **Supplement**.

The formation of amorphous intermediate sulfate hydrates is consistent with previous dehydration studies under rapid or low-humidity conditions. (Meusburger et al., 2025, 2026; Vaniman & Chipera, 2006; Wang et al., 2006; L. Yang et al., 2020) Despite the loss of crystallinity, Raman spectra retained well-defined ν_1 sulfate stretching modes. The position and evolution of these bands (e.g., shifts to ~ 1020 - 1035 cm^{-1}) indicate changes in local bonding environments and hydration state, demonstrating that Raman spectroscopy remains sensitive to short-range order. Accordingly, the $\sim 3\cdot\text{H}_2\text{O}$ and $\sim 2\cdot\text{H}_2\text{O}$ compositions are interpreted as amorphous or partially amorphous phases, with hydration state inferred from the Raman ν_1 peak position rather than the crystallographic structure. These results highlight that under progressive dehydration conditions at short timescales, XRD alone is insufficient to characterize MgSO_4 dehydration pathways, but is highly effective when used in conjunction with Raman spectroscopy.

Refinement results (**Table 2**) further show that the crystalline MgSO_4 phases are well constrained prior to amorphization. In contrast to $\text{Mg}(\text{ClO}_4)_2$, MgSO_4 exhibits a significantly larger degree of thermal expansion of the crystal lattice (**Table**

2), with epsomite and hexahydrate showing volumetric expansion coefficients on the order of 10^{-3} – 10^{-2} /K. This increased volumetric sensitivity to temperature likely reflects a weaker hydrogen-bonded framework, which contributes to the structural instability and rapid transformation to a disordered material during dehydration.

3.4 Force Constants and Vibrational Mode Analysis for $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4

Systematic shifts in the tetrahedral vibrational frequencies, particularly ν_1 , accompany dehydration in both magnesium perchlorate and magnesium sulfate. To quantify the associated changes in local bonding, we calculated internal force constants for the ClO_4^- and SO_4^{2-} tetrahedra using Wilson GF matrix methods (Wilson et al., 1955). The tetrahedra were approximated as ideal XO_4 units ($\text{X} = \text{Cl}$ or S), and the experimentally observed ν_1 (A_1 symmetric stretch), ν_2 (E symmetric bend), ν_3 (F_2 asymmetric stretch), and ν_4 (F_2 asymmetric bend) frequencies were used to determine four internal force constants describing X-O stretching (f_r), O-X-O bending (f_θ), stretch–bend coupling ($f_{r\theta}$), and bend–bend coupling ($f_{\theta\theta}$) (Caracas & Bobocioiu, 2011; G. Herzberg, 1945; Hahn et al., 2017; Wilson et al., 1955). The Wilson GF formalism relates the observed vibrational frequencies to these four internal force constants through the normal-mode equations (Equations 1-4), which were solved simultaneously to obtain the force constants (Equations 5-8). A detailed derivation of the Wilson GF matrices and symmetry-coordinate transformations is provided in the **Supplement**. Herzberg-style force constants were also calculated independently for both mineral systems (**Supplement**). These closely reproduced the trends obtained from the Wilson GF analysis, providing independent validation of the

hydration-dependent evolution of the local bonding environment. The calculated force constants derived from the experimentally observed ν_1 — ν_4 frequencies are shown in **Figure 3c,d**.

$$\mu_r(2\pi c\nu_1)^2 = f_r + 4f_{r\theta} + 6f_{\theta\theta} \quad (1)$$

$$\mu_\theta(2\pi c\nu_2)^2 = f_\theta + 2f_{\theta\theta} \quad (2)$$

$$\mu_r(2\pi c\nu_3)^2 = f_r - 2f_{r\theta} \quad (3)$$

$$\mu_\theta(2\pi c\nu_4)^2 = f_\theta - f_{\theta\theta} \quad (4)$$

Where ν_i are the observed vibrational mode frequencies in cm^{-1} , c is the speed of light in cm s^{-1} , μ_r is the reduced mass for the X-O stretching coordinate, and μ_θ is the effective reduced mass for the O-X-O bending coordinate. For magnesium perchlorate, $X = \text{Cl}$, and for magnesium sulfate, $X = \text{S}$.

Solving the four normal-mode equations yields the four internal force constants:

$$f_{\theta\theta} = \frac{1}{3}(2\pi c)^2 \mu_\theta(\nu_2^2 - \nu_4^2) \quad (5)$$

$$f_\theta = (2\pi c)^2 \mu_\theta \nu_4^2 + f_{\theta\theta} \quad (6)$$

$$f_{r\theta} = \frac{1}{6} [(2\pi c)^2 \mu_r(\nu_1^2 - \nu_3^2) - 6f_{\theta\theta}] \quad (7)$$

$$f_r = (2\pi c)^2 \mu_r \nu_3^2 + 2f_{r\theta} \quad (8)$$

The force constants are reported in N m^{-1} .

3.4.1 $\text{Mg}(\text{ClO}_4)_2$ Tetrahedron 4-Parameter Force Field Behavior

The four internal force constants evolve systematically across the hexahydrate, tetrahydrate, dihydrate, and anhydrous phases (**Figure 3c**). Throughout the dehydration sequence, the Cl–O stretching constant (f_r) is the largest contributor to the force field, accounting for approximately 60–63% of the total internal stiffness, followed by the O–Cl–O bending constant (f_θ ; ~28–32%). The stretch–bend ($f_{r\theta}$) and bend–bend ($f_{\theta\theta}$) interaction terms each contribute approximately 3–6%. The Cl–O stretching constant (f_r) remains nearly constant throughout the hexahydrate field (~885 N m⁻¹), increases during formation of the tetrahydrate (~900 N m⁻¹), increases further during formation of the dihydrate (~955 N m⁻¹), remains relatively constant throughout the dihydrate stability field, and reaches its maximum near formation of the anhydrous phase before decreasing slightly at higher temperatures. The remaining force constants also vary systematically with dehydration, although their changes are smaller than those observed for f_r . The stretch–bend coupling constant ($f_{r\theta}$) decreases during formation of the tetrahydrate, remains relatively constant throughout the dihydrate field, and increases again following formation of the anhydrate. The angular bending constant (f_θ) increases through the tetrahydrate transition and bifurcates within the tetrahydrate and dihydrate fields, as dictated by the splitting of the ν_2 and ν_4 Raman bands, before partially reconverging in the anhydrous phase. In contrast, the bend–bend interaction constant ($f_{\theta\theta}$) varies only modestly throughout dehydration, remaining between approximately –80 and –88 N m⁻¹. Collectively, the force constants demonstrate systematic redistribution of the internal forces within the

tetrahedra across the dehydration sequence, with the largest changes occurring during the tetrahydrate and dihydrate phase transitions.

3.4.2 MgSO_4 Tetrahedron 4-Parameter Force Field Behavior

The sulfate force constants likewise evolve systematically with dehydration but display more gradual trends than those observed for magnesium perchlorate (**Figure 3d**). Throughout the dehydration sequence, the S–O stretching constant (f_r) remains the dominant contribution to the force field, while the bending (f_θ), stretch–bend ($f_{r\theta}$), and bend–bend ($f_{\theta\theta}$) terms contribute progressively smaller fractions of the total internal stiffness. Unlike $\text{Mg}(\text{ClO}_4)_2$, the S–O stretching constant (f_r) increases smoothly across the dehydration sequence without distinct stepwise transitions. Values increase from approximately $805\text{--}880\text{ N m}^{-1}$ in the highly hydrated phases to approximately $970\text{--}1020\text{ N m}^{-1}$ within the low-hydration regime, remaining elevated throughout the higher-temperature interval where the material becomes largely X-ray amorphous. The remaining force constants evolve gradually throughout dehydration. The stretch–bend coupling constant ($f_{r\theta}$) decreases continuously from approximately $45\text{--}55\text{ N m}^{-1}$ in the hydrated phases to approximately $10\text{--}25\text{ N m}^{-1}$ at higher temperatures. The angular bending constant (f_θ) increases modestly from approximately $395\text{--}405$ to $415\text{--}430\text{ N m}^{-1}$ without the bifurcation observed in magnesium perchlorate, whereas the bend–bend interaction constant ($f_{\theta\theta}$) remains nearly invariant between approximately -70 and -80 N m^{-1} . Overall, the sulfate force field evolves more continuously than that of magnesium perchlorate, without the abrupt changes associated with discrete hydration-state transitions.

4.0 Discussion

4.1 Magnesium Perchlorate and Magnesium Sulfate Dehydration Pathways and Kinetic Metastability

The combined Raman and XRD results demonstrate that hydration states in both $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 are governed not only by temperature and humidity, but critically by kinetic limitations on water loss and lattice reorganization. In conjunction, Raman spectroscopy and XRD reveal complementary aspects of these dehydration pathways: Raman spectroscopy probes local tetrahedral bonding environments, whereas XRD constrains long-range crystallographic order. Although both salts progressively dehydrate upon heating, they accommodate dehydration through fundamentally different structural pathways. This contrast is particularly notable because $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 contain analogous tetrahedral oxyanions (ClO_4^- and SO_4^{2-}) with comparable internal vibrational modes. By combining Raman spectroscopy, XRD, force constant analysis, and thermal expansion measurements, our results demonstrate how these two tetrahedral systems evolve through fundamentally different dehydration pathways and provide a framework for interpreting hydrated salt mineralogy, hydration state, and crystallinity in Mars rover Raman and XRD datasets.

In magnesium perchlorate, distinct hexahydrate, tetrahydrate, dihydrate, and anhydrous phases are spectroscopically distinct, yet each transition exhibits metastable persistence beyond their equilibrium stability fields. This behavior is

particularly pronounced for the hexahydrate–tetrahydrate and dihydrate–anhydrate transitions, where Raman signatures of the lower-temperature phase persist over temperature intervals of $\sim 10\text{--}50^\circ\text{C}$ under laboratory heating rates, even though the sample has clearly thermally equilibrated. Such kinetic persistence is consistent with previous studies demonstrating that dehydration temperatures depend strongly on experimental timescale and heating rate (Devlin & Herley, 1986; Robertson & Bish, 2010; Willard & Smith, 1922). Importantly, Willard and Smith (1922) reported mixed hydration states after months of vacuum dehydration at $\sim 20^\circ\text{C}$, whereas Devlin and Herley (1986) observed substantially higher apparent dehydration temperatures under rapid heating. Likewise, our Raman and XRD results show that $\text{Mg}(\text{ClO}_4)_2$ retains structurally bound water to temperatures approaching 300°C .

Dehydration is additionally accompanied by splitting and broadening of the ν_2 and ν_4 bending regions beginning near the tetrahydrate transition, consistent with the symmetry lowering observed crystallographically as the orthorhombic hexahydrate transforms into monoclinic tetrahydrate and dihydrate phases. This evolution reflects progressive replacement of hydrogen-bonded water by direct Mg—ClO_4 coordination and provides a Raman spectroscopic counterpart to the crystallographic reorganization resolved by XRD. The systematic increase in ν_1 frequency, together with the shift of the OH stretching band toward higher wavenumbers and its eventual disappearance in the anhydrate, is consistent with progressive strengthening of the Cl—O bonds and weakening of the hydrogen-bonding network during dehydration, a trend independently supported by our force constant analysis. Changes in the low-

frequency lattice modes likewise reflect reorganization of the Mg coordination environment as hydration-shell motions are progressively replaced by Mg—ClO₄ framework vibrations. The disappearance of resolved ν_2 splitting in the anhydrate, while ν_4 remains split with reduced separation, suggests that complete dehydration results in less tetrahedral distortion but that the perchlorate ions continue to occupy crystallographic environments of lower than T_d symmetry. The persistence of crystallinity throughout the dehydration sequence, together with the discrete evolution of the Raman spectra, indicates that Mg(ClO₄)₂ accommodates water loss through successive crystalline phase transitions rather than progressive disordering/amorphization.

Unlike Mg(ClO₄)₂, magnesium sulfate does not transform abruptly between successive crystalline hydrates, but instead dehydrates through poorly crystalline or X-ray-amorphous intermediate phases, consistent with previous laboratory studies (Vaniman & Chipera, 2006; Wang et al., 2006, 2009). Despite the amorphization observed by XRD, vibrations of the sulfate tetrahedra remain well defined throughout dehydration. The systematic increase in ν_1 frequency, together with the progressive shift of the OH stretching bands toward higher wavenumbers and their eventual disappearance, indicates strengthening of the S—O bonding environment and weakening of the hydrogen-bonding network during dehydration. Unlike Mg(ClO₄)₂, however, the ν_2 and ν_4 bending modes exhibit comparatively modest shifts in their spectral barycenters while progressive band broadening increasingly obscures their splitting as structural disorder develops. Similarly, the ν_3 asymmetric stretching

region progressively broadens, consistent with a growing distribution of local sulfate environments within the amorphous matrix rather than discrete symmetry-lowering transitions between crystalline phases. The accompanying evolution of the low-frequency lattice modes is likewise consistent with progressive reorganization of the hydration framework and increasing disorder.

These results confirm that Raman spectroscopy primarily probes short-range tetrahedral bonding environments, whereas XRD constrains long-range crystallographic order. The hydration behavior of these amorphous sulfate intermediates should therefore be interpreted in the context of local bonding environments and kinetic persistence rather than equilibrium phase diagrams alone. Together, these observations demonstrate that hydration-state evolution in both $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 is strongly kinetically controlled rather than governed solely by equilibrium phase boundaries, although the two systems accommodate dehydration through fundamentally different structural pathways. The kinetic behavior observed here has important implications for hydrated salts on Mars. Temperature and relative humidity cycles on Mars occur over diurnal and seasonal timescales that differ substantially from laboratory heating experiments. However, the low temperatures and highly variable relative humidity on Mars are likely to allow metastable hydration states to persist outside their equilibrium stability fields. Consequently, hydrated perchlorates and sulfates detected by rover instruments may not necessarily reflect equilibrium mineral assemblages but instead may preserve

hydration states shaped by kinetically controlled dehydration pathways and local environmental history.

4.2 Fermi Resonance as a Diagnostic of Perchlorate Hydration and Temperature

A key finding of this study is the identification of a reproducible low-frequency shoulder on the $\text{Mg}(\text{ClO}_4)_2$ ν_1 symmetric stretch, interpreted as a $2\nu_2$ overtone enhanced by Fermi resonance. This resonance persists from low temperatures through the hexahydrate stability field and disappears near the hexahydrate-to-tetrahydrate phase transition, indicating that the coupling is strongly hydration-dependent. While Fermi resonance in perchlorate solutions has been reported previously, its observation here in a crystalline perchlorate hydrate is, to our knowledge, unprecedented. The temperature-dependent evolution of the Fermi resonance demonstrates that vibrational coupling within the perchlorate tetrahedron is sensitive to hydrogen-bonding geometry and local lattice environment. As dehydration proceeds, the ν_1 and $2\nu_2$ modes evolve differently, altering the energetic proximity required for resonance coupling. The progressive weakening and eventual disappearance of the overtone shoulder therefore provides an additional spectroscopic indicator of hydration state beyond simple ν_1 peak position tracking alone.

From an observational standpoint, this feature has three important implications. First, it provides an independent spectroscopic marker for the hexahydrate phase, supplementing the ν_1 peak position alone. Second, its presence emphasizes that subtle shoulders near the ν_1 region in high-resolution Raman data should not automatically be interpreted as evidence for mineral mixtures or multiple

perchlorate species without careful consideration of anharmonic coupling effects. Recognition of this resonance effect expands the suite of Raman observables available for identifying perchlorate phases and hydration states and highlights the importance of considering anharmonic interactions when interpreting high-resolution laboratory Raman spectra. This is particularly relevant to current *in situ* rover measurements, which commonly use the ν_1 region as a diagnostic peak for sulfate and perchlorate identification (Corpolongo et al., 2023; Lopez-Reyes et al., 2025), and to future Mars Sample Return analyses, where laboratory-grade spectral resolution will far exceed that of rover instruments. Conversely, the resonance is unlikely to affect mineral identification by current rover-based Raman systems such as SuperCam or SHERLOC, whose spectral resolution, along with the challenges associated with *in situ* measurements, is unlikely to resolve the shoulder (Corpolongo et al., 2023; Lopez-Reyes et al., 2025). In those datasets, the ν_1 region can reasonably be treated as a single band, provided that interpretations remain cognizant of hydration-dependent shifts.

Third, the presence of this Fermi resonance-induced shoulder provides a means for quantitatively assessing the temperature of magnesium perchlorate hexahydrate-bearing materials, specifically how much a perchlorate-bearing surface is heated by solar radiation. The complex superposition of the effects of solar absorption, re-radiation, reflection, and vertical thermal diffusion renders the magnitude of surface heating (the “asphalt effect”) difficult to calculate directly. As shown in **Figure 4**, the relative amplitude of the shoulder varies systematically with

temperature and is well described by an empirical cubic calibration throughout the hexahydrate stability field. This relationship therefore provides a potential Raman vibrational thermometer for magnesium perchlorate hexahydrate-bearing deposits and may offer a quantitative proxy for assessing solar heating of exposed perchlorate surfaces.

4.3 Raman Spectroscopic Indicators of Hydration State, Mineralogy, and Temperature

Across both the $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 series, the ν_1 symmetric stretching mode exhibits the largest and most systematic response to dehydration and shifts in temperature, reflecting progressive strengthening of Cl–O and S–O bonds as hydrogen bonding is reduced. In magnesium perchlorate, ν_1 shifts from $\sim 935 \text{ cm}^{-1}$ in the hexahydrate to $\sim 994 \text{ cm}^{-1}$ in the anhydrous phase, while in magnesium sulfate it shifts from $\sim 983 \text{ cm}^{-1}$ (epsomite) to $>1033 \text{ cm}^{-1}$ in low-hydration, disordered states. This spectral behavior has two implications for planetary Raman spectroscopy. First, ν_1 can act as a combined hydration-state indicator and effective thermometer within the perchlorate and sulfate mineral systems, particularly when interpreted alongside OH stretching and low-frequency lattice modes. (Phua et al., 2024) Second, ν_1 positions for magnesium perchlorate and its hydrates ($\text{Mg}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$) overlap spectrally with those of sulfates like epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), starkeyite ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) ($\sim 1000 \text{ cm}^{-1}$), sanderite ($\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$), and kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), other perchlorates and their hydrates such as calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$) and sodium perchlorate ($\text{Na}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$), and phosphates like apatite (with a PO_4 ν_1

observed at $\sim 960\text{ cm}^{-1}$). (**Figure 7**) This overlap reinforces the necessity for caution when assigning mineralogy based on a single Raman peak, particularly in rover datasets with limited spectral coverage and/or low signal-to-noise ratios.

Our data explicitly demonstrate that reliable identification of hydrated perchlorates and sulfates requires interpretation of the full Raman spectrum rather than reliance on the n_1 region alone. In addition to n_1 , the n_2 , n_3 , and n_4 fundamental tetrahedral vibrations, OH stretching modes, low-frequency lattice modes, peak widths, and, where spectrally resolvable, the Fermi resonance together provide complementary constraints on mineralogy, hydration state, local bonding environment, and crystallinity. Collectively, these features provide the full spectral context necessary to distinguish perchlorates from sulfates while also resolving hydration-dependent structural evolution within each mineral system. This approach is particularly important under Mars-relevant conditions, where kinetic persistence, metastability, and amorphization can produce spectra that differ substantially from equilibrium crystalline reference materials.

Kieserite-type monohydrates and amorphous or poorly crystalline magnesium sulfate hydrates are expected to be common in near-surface Martian environments, where low water activity and strong kinetic limitations favor metastable hydration states over equilibrium crystalline phases (De Angelis et al., 2017; Vaniman & Chipera, 2006; Wang et al., 2009; Wildner et al., 2022). These predictions were recently confirmed by *in situ* XRD experiments at Gale Crater (Chipera et al., 2023; Tutolo et al., 2025; Meusburger et al., 2026). As a result, spectroscopic identifications

of MgSO_4 hydration states on Mars may commonly reflect amorphous sulfate environments giving rise to broad spectroscopic bands, rather than sharper peaks characteristic of crystalline phases. Band broadening of the ν_1 region in amorphous sulfate phases complicates resolving peak position and phase identification. Consequently, reliable identification of low-hydration sulfate environments, particularly when poorly crystalline or amorphous, requires interpreting the full Raman spectrum rather than the ν_1 region alone.

4.4 Force Constants as Quantitative Probes of Hydration-Dependent Local Bonding

Force constants represent a primary quantitative product of this study, providing a direct measure of bond stiffness and linking observed Raman frequencies to changes in the local bonding environment during dehydration. Whereas Raman peak positions record changes in vibrational frequencies, Wilson GF matrix analysis translates these shifts into physically meaningful changes in the strengths of individual Cl—O and S—O bonds. In addition to the Wilson GF analysis, Herzberg-style force constants closely reproduce the same hydration-dependent trends, providing independent validation that the observed vibrational changes reflect systematic evolution of the local bonding environment.

In $\text{Mg}(\text{ClO}_4)_2$, progressive dehydration produces systematic increases in the Cl—O stretching force constants derived primarily from the ν_1 and ν_3 stretching modes, indicating progressive Cl—O bond stiffening as structural water is removed from the coordination environment. The largest changes occur during the tetrahydrate

and dihydrate transitions, coincident with the onset of n_2 and n_4 mode splitting, crystallographic symmetry lowering, and structural reorganization observed in both the Raman spectra and XRD patterns. In contrast, the stretch–bend coupling constant ($f_{r\theta}$) exhibits non-monotonic behavior, indicating that dehydration reorganizes rather than simply weakens coupling between stretching and bending motions. The angular bending force constant (f_θ) evolves more gradually but bifurcates during the tetrahydrate and dihydrate phases, reflecting the lifting of vibrational degeneracies as symmetry lowering produces inequivalent tetrahedral environments during dehydration before partially reconverging in the anhydrous phase. By comparison, the bend–bend interaction constant ($f_{\theta\theta}$) varies only modestly throughout dehydration, indicating that higher-order angular interactions are comparatively insensitive to hydration state. These trends indicate that dehydration primarily stiffens individual Cl–O bonds while reorganizing collective angular interactions within the perchlorate tetrahedron as coordination shifts from hydrogen-bonded to Mg-coordinated environments.

MgSO₄ exhibits fundamentally different behavior. Although sulfate stretching force constants also increase during dehydration, their evolution is smoother, exhibiting smaller changes between successive hydration states, and they lack the abrupt discontinuities observed in Mg(ClO₄)₂. This behavior is consistent with progressive structural disordering rather than discrete symmetry-changing phase transitions. Even under largely amorphous conditions, the sulfate tetrahedra remain as discrete, locally symmetric units from a vibrational perspective, explaining why

strong Raman sulfate signatures persist despite the diminished crystallinity observed in XRD patterns. Unlike perchlorate, the sulfate bending force constants do not exhibit bifurcation, consistent with the absence of well-defined symmetry-lowering transitions and the development of increasingly disordered local environments. The monotonic decrease in stretch–bend coupling further indicates progressive decoupling of stretching and bending motions as dehydration proceeds. This difference likely arises from the higher charge density of SO_4^{2-} relative to ClO_4^- , which stabilizes sulfate tetrahedra as coherent units across a wider range of disordered and amorphous environments. From a geochemical perspective, this suggests that perchlorate tetrahedra are more sensitive probes of local coordination environment, whereas sulfate tetrahedra are more robust recorders of average hydration state. Ultimately, the force constant calculations reinforce the interpretation that perchlorate dehydration is dominated by discrete hydration phase transitions and symmetry changes, whereas sulfate dehydration is governed more strongly by progressive disordering and the kinetic persistence of local tetrahedral environments during hydration phase transitions over relatively short timescales of hours to days.

The force constant calculations provide the physical basis for interpreting our spectroscopic observations presented throughout this study. Raman spectroscopy reveals how vibrational frequencies evolve with dehydration, XRD constrains the accompanying crystallographic changes, and the force constants quantify the underlying evolution of local bond strengths responsible for those spectral shifts. The agreement among the Raman, XRD, and force constant analyses provides strong

evidence for the dehydration pathways identified in both mineral systems. Collectively, these observations establish experimentally validated relationships among vibrational frequencies, crystal structure, and local bonding environments that provide a physically grounded basis for interpreting hydration-dependent structural evolution. Applied to planetary Raman datasets, these relationships extend spectral interpretation beyond mineral identification to quantitative characterization of hydration state, local bonding environments, and the hydration and diagenetic history recorded by Martian evaporites.

4.5 Mars Relevance and Raman Mineral Identification

The laboratory relationships established in this study provide a physically grounded basis for interpreting hydrated salts detected by Raman and X-ray diffraction instruments on Mars. The Mars 2020 *Perseverance* rover carries the Raman instruments SuperCam and SHERLOC, and the Mars Science Laboratory *Curiosity* rover carries the CheMin X-ray diffraction instrument (D. Blake et al., 2012; Kyle Uckert et al., 2021; Wiens et al., 2017b). Because these instruments operate on different rover missions at different locations, laboratory datasets that directly relate Raman spectra to crystallographic structure are essential for integrating their complementary mineralogical observations. **Figure 7** demonstrates substantial overlap in the ν_1 Raman bands of hydrated Mg, Ca, and Na perchlorates, Mg sulfates, and phosphates in both laboratory and Mars rover datasets, with several phases differing by only a few wavenumbers, despite representing distinct minerals and hydration states. Indeed, perchlorates detected on Mars may exist in metastable

hydration states not predicted by equilibrium models, and sulfate-like Raman signatures could plausibly originate from dehydrated perchlorates under hydration-dependent conditions. This reinforces the importance of multi-mode analysis and cautions against assigning mineralogy from single-peak mineral assignments in rover datasets.

To date, Raman spectroscopy at Jezero crater has been used primarily to identify mineral phases and to reconstruct aqueous rock or mineral alteration histories. These interpretations generally rely on comparison with laboratory reference spectra and characteristic Raman band positions. Our results suggest that planetary Raman spectra contain substantially more information than mineral identity alone, encoding quantitative constraints on hydration state, local bonding environment, crystallinity, and the environmental history of hydrated salts.

Robust mineral identification therefore requires analysis of the full vibrational spectrum rather than the ν_1 region alone. In particular, we show that the ν_2 and ν_4 bending modes, low-wavenumber lattice vibrations, OH stretching features, and Raman peak shapes provide critical constraints on hydration state, crystallinity, and local bonding environments. The complementary use of Raman spectroscopy and XRD is especially important for hydrated salts on Mars because Raman remains sensitive to local tetrahedral environments even when solid materials are poorly crystalline or X-ray amorphous. Together, these complementary observations improve interpretation of hydrated evaporite assemblages at Gale crater, Jezero crater, and

other sulfate-rich regions on Mars by linking mineral identity to hydration state, crystallinity, and the evolution of local bonding environments.

To evaluate the applicability of the experimentally calibrated force constant relationships to planetary datasets, force constants were calculated from previously reported SHERLOC and SuperCam Raman spectra of perchlorate- and sulfate-bearing targets (processed RRS files and cr1 files, respectively), and compared with the laboratory-derived $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 force constant trends (**Figure 3**) (J. V. Clark et al., 2026; Corpolongo et al., 2023; Jakubek et al., 2024; Lopez-Reyes et al., 2025; Phua et al., 2024). The rover data points are plotted at arbitrary horizontal axis positions for clarity (since typical Mars equatorial temperatures are near $\sim 70^\circ\text{C}$), so only the calculated force constant values (N m^{-1}) are physically meaningful in these comparisons. Because the SHERLOC spectral response is less reliable below $\sim 800 \text{ cm}^{-1}$ and includes a secondary laser peak near $\sim 650 \text{ cm}^{-1}$ that partially overlaps the ν_4 sulfate band, force constants derived from SHERLOC spectra should be regarded as first-order estimates, although they remain sufficiently robust for comparison with the laboratory calibration trends. Select ν_1 regions are plotted for Guillaumes, Dourbes, Reids Gap, and Bellegarde in **Figure 7**. Guillaumes and Bellegarde represent sodium- or mixed sodium-magnesium-calcium perchlorate-bearing materials identified within altered igneous rocks of the Máaz formation. Dourbes contains hydrated Mg sulfate within the olivine-rich Séítah formation. Reids Gap contains crystalline anhydrite within a sulfate-bearing fracture of the Jezero western fan. Quartier represents a

mixed hydrated Mg sulfate-anhydrite assemblage, and Uganik Island is an anhydrite-bearing sedimentary target within the Yori Pass member of the Jezero delta front.

The rover-derived force constants are consistent with the published mineralogical and hydration-state interpretations while providing additional quantitative information about the local bonding environments of the detected salts. The Guillaumes and Bellegarde perchlorates exhibit similar Cl–O stretching force constants, indicating comparable local ClO_4 tetrahedral stiffness despite occurring in different geological settings. Likewise, the sulfate force constants distinguish the hydrated Mg-rich sulfate identified at Dourbes from the predominantly anhydrous sulfate assemblages at Reids Gap, Quartier, and Uganik Island, with systematic differences in S–O stretching and O—S—O bending force constants consistent with their differing hydration states and local bonding environments. Thus, the force constant analysis supports the published rover mineral identifications while extending them beyond phase assignment alone. Rather than identifying only the mineral present, the calculated force constants quantify local X–O bond stiffness, tetrahedral rigidity, and hydration-dependent bonding environments. These parameters provide a physically based complement to conventional Raman mineral identification and enable quantitative interpretation of hydrated evaporites on Mars, particularly where hydration state, crystallinity, or structural disorder remain uncertain. In cases where mineral assignments inferred from Raman peak positions are inconsistent with the local bond stiffness or tetrahedral rigidity predicted from experimentally calibrated force constants, such discrepancies could indicate the need to re-examine mineral or

hydration-state assignments or they may instead reflect more complex salt assemblages involving mixed cations, mixed hydration states, poorly crystalline or amorphous phases, or reflect other nonequilibrium geochemical processes. Expanding these laboratory calibrations to additional Mars-relevant salt systems, including variable-temperature studies of NaClO_4 , $\text{Ca}(\text{ClO}_4)_2$, mixed perchlorates, chlorides, and other sulfate hydrates, will enable broader application of force constant analysis to planetary Raman datasets and further improve quantitative interpretation of hydrated salts on Mars.

The experimentally calibrated force constant relationships developed here extend interpretation of planetary Raman spectra beyond mineral identification alone. By linking Raman frequencies to local bond strengths, crystal structure, and hydration-dependent coordination environments, these relationships distinguish discrete crystalline hydration transitions from progressive disordering in poorly crystalline or X-ray–amorphous salt assemblages, identify metastable hydration states, and constrain the hydration and diagenetic history of Martian evaporites. Rather than serving solely as mineral fingerprints, Raman spectra preserve quantitative information about the structural evolution of hydrated salts under Martian conditions. The complementary sensitivities of Raman spectroscopy and XRD provide a more complete understanding of hydrated salts than either technique alone, particularly where metastability and amorphization complicate hydration-state determination. Although Raman and XRD measurements on Mars are presently acquired by different rover missions at different locations, the laboratory force

constant calibrations developed here provide a quantitative basis for integrating these datasets and improving interpretation of hydrated salt evolution on Mars.

5.0 Conclusions

This study combines variable-temperature Raman spectroscopy, X-ray diffraction, force constant analysis, and thermal expansion measurements to investigate the dehydration behavior of magnesium perchlorate and magnesium sulfate under Earth- and Mars-relevant conditions. Although both mineral systems contain analogous tetrahedral oxyanions, they accommodate dehydration through fundamentally different structural pathways. Magnesium perchlorate undergoes discrete crystalline hydration transitions accompanied by symmetry lowering, systematic evolution of Raman vibrational modes, and progressive Cl–O bond stiffening while preserving long-range crystallinity. In contrast, magnesium sulfate progressively loses crystallinity through poorly crystalline and X-ray–amorphous intermediates while retaining distinct Raman signatures that record local sulfate bonding environments. The agreement among Raman spectroscopy, X-ray diffraction, thermal expansion measurements, and force constant analyses provides complementary evidence supporting these contrasting dehydration mechanisms.

A previously unreported hydration-dependent Fermi resonance in crystalline magnesium perchlorate provides an additional spectroscopic indicator of the hexahydrate phase and demonstrates that anharmonic vibrational coupling can influence interpretation of the ν_1 region. The temperature dependence of this resonance further establishes a potential Raman vibrational thermometer for

magnesium perchlorate hexahydrate. More broadly, although the ν_1 symmetric stretching mode serves as a sensitive indicator of hydration state and temperature, substantial spectral overlap among hydrated perchlorates, sulfates, and phosphates demonstrates that reliable mineral identification requires interpretation of the full Raman spectrum. In addition to ν_1 , the ν_2 , ν_3 , and ν_4 tetrahedral vibrations, OH stretching modes, low-frequency lattice vibrations, peak shapes, and, where spectrally resolvable, Fermi resonance together provide complementary constraints on mineralogy, hydration state, local bonding environment, and crystallinity.

The comprehensive, experimentally validated Raman and X-ray diffraction reference datasets developed here span the complete dehydration sequences of $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 under Mars-relevant conditions and provide quantitative linkages between hydration state, crystal structure, vibrational behavior, force constants, and thermal expansion. Thus, these measurements establish a physically grounded basis for interpreting hydrated salts detected by the SuperCam, SHERLOC, and CheMin instruments. Application of the experimentally calibrated force constant relationships to planetary Raman spectra provides quantitative constraints on local X–O bond stiffness, tetrahedral distortion, and hydration-dependent coordination environments. Together, these laboratory calibrations strengthen the connection between Raman spectroscopy and crystallography, enabling more quantitative interpretation of hydrated salts and their hydration histories on Mars.

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Open Research Data Availability

Experimental data supporting the conclusions in this paper are available at the NASA AHED Open Data Repository (<https://ahed.nasa.gov/>). Datasets and Python programming scripts are archived through Zenodo (<http://doi.org/10.5281/zenodo.21524255>). All SuperCam and SHERLOC data described in this manuscript are accessible through the NASA Planetary Data System (PDS) archive (<https://pds-geosciences.wustl.edu/missions/mep/index.htm>). Rover data was sourced from the processed spectroscopy data collections: SHERLOC RRS products and SuperCam cr1 products. VESTA was used to process CIF files and create crystal structure figures.

Chapter 3: Raman and XRD Exploration of Lattice Preferred Orientations in Martian Shergottite NWA 13276 via High-Volume Point Count Grids and Semi-Supervised Human-In-the-Loop Active Learning

Abstract

Martian meteorites preserve important records of magmatic crystallization, shock metamorphism, and secondary alteration, but reconstructing crystallographic textures at sub-millimeter scales remains challenging because conventional techniques such as electron backscatter diffraction (EBSD) require extensive sample preparation and are difficult to apply to highly mosaicized materials. Here, we present high-volume co-registered Raman and synchrotron powder X-ray diffraction rasters of the Martian shergottite NWA 13276 to investigate the mineralogy and lattice preferred orientations (LPOs) of olivine-bearing assemblages and assess whether Raman spectroscopy can recover crystallographic information relevant to Mars exploration. A novel semi-supervised, human-in-the-loop mineral identification workflow combining diffraction peak matching, whole-pattern fitting, statistical embedding, and iterative expert review was used to analyze the raster datasets. Olivine, pyroxenes, merrillite, and secondary calcite were identified providing constraints on primary magmatic processes and subsequent terrestrial alteration. Texture reconstructions of confirmed olivine grains using the extended Williams-Imhof-Matthies-Vinel (E-WIMV) orientation distribution method revealed non-random LPOs across the meteorite slice. Comparison of co-registered Raman spectra with the reconstructed textures demonstrates a systematic relationship between crystallographic orientation and the relative peak intensities of the olivine doublet

between 810-870 cm^{-1} . Spectra associated with c-axis-dominated orientations preferentially exhibit enhanced intensity in the higher-wavenumber peak, whereas a- and b-axis orientations preferentially favor the lower-wavenumber peak. These results suggest that Raman spectroscopy may resolve information about preferred orientation in Martian basalts and could provide a means of inferring magmatic fabrics and deformation histories using the Mars Perseverance rover measurements from the SuperCam and SHERLOC instruments.

1.0 Introduction

Crystallographic preferred orientation in igneous mineral assemblages preserved within Martian meteorites can reveal the direction of basalt flows, the nature of anisotropic crystal growth, and illuminate the dynamics of viscous magmatic flow. Quantification of lattice preferred orientations (LPOs) typically involves electron backscatter diffraction (EBSD) or synchrotron-based X-ray microdiffraction techniques that require extensive sample preparation and are often difficult to apply to highly mosaicized materials, such as are typical of shocked Martian assemblages. Determining mineral LPOs directly on Mars presents an even greater challenge, as current rover payloads lack dedicated instruments capable of measuring crystallographic orientations at microscopic scales within intact rock exposures. The NASA Mars 2020 Perseverance rover is equipped with two Raman spectrometers, SuperCam and SHERLOC, capable of remotely probing the mineralogy and chemistry of rocks exposed along stratigraphic outcrops, cliff faces, and crater walls within Jezero Crater, Mars (Kyle Uckert et al., 2021; Wiens et al.,

2021b). Although Raman spectroscopy is primarily employed for mineral identification, orientation-dependent variations in Raman peak intensities may also provide information about crystallographic preferred orientation, making it particularly useful where underlying rock units are obscured by younger materials and exposed only along one dimension. (Baer et al., 2006; Benn & Allard, 1989; Correa-Gomes et al., 2001; Grosche et al., 2020; Hrouda et al., 2019; Waters, 1960; Wen et al., 2018; Wentworth & Macdonald, 1953) By quantifying LPOs of suites of individual mineral grains, it may be possible to extrapolate and trace back larger-scale igneous flow directions, relate landslide aprons to their source regions, or to characterize uplift in otherwise horizontal strata from the assemblage of mineral orientations. (Devoe et al., 2023; Y. Li et al., 2026; Wang et al., 2015b) To achieve this, orientation-dependent Raman spectra of common Martian minerals must first be calibrated against independently determined crystallographic orientations.

Martian shergottite-nakhlite-chassignite (SNC) meteorites represent the closest materials available for direct laboratory investigation of the Martian crust. They form a unique group of achondritic meteorites that are geochemically and isotopically linked to Mars and provide direct insight into Martian magmatism, differentiation, shock metamorphism, and crustal evolution. Their ejection ages, noble gas compositions, and relatively young crystallization ages indicate that they originated from the Martian surface and were delivered to Earth by impact events. Shergottites represent the dominant class of Martian meteorites, accounting for more than 75% of all known SNC meteorites. They are igneous basalts or gabbros

composed primarily of pyroxene, olivine, and maskelynite, together with accessory Fe-Ti oxides (ilmenite and titanomagnetite), sulfides (troilite), and phosphates (merrillite), that crystallized relatively recently (~170-575 Ma) from heterogeneous mantle reservoirs, showing evidence of both extrusive and intrusive origins. Calcite may occur as a secondary alteration mineral formed following the meteorite's arrival on Earth. Their geochemical variability indicates long-term differentiation and variable convective mixing within the Martian mantle, while their compositional diversity suggests fractional crystallization, mantle heterogeneity, and localized crustal assimilation during magma ascent. The lattice preferred orientation of these minerals can provide insight into magma flow dynamics, impact deformation, cooling histories, and whether the rock records magma solidification as lava flows, sills, dykes, or cumulates. Remote detection of analogous fabrics on Mars could therefore provide new insights into the volcanic and tectonic evolution of the Martian crust. (Agee et al., 2015; Beck et al., 2004; Borg & Draper, 2003; Bridges & Warren, 2006; Herd et al., 2002; McSween, 1994; Nyquist et al., 2001; Treiman, 1993; Udry et al., 2020)

In this study, we investigate the mineralogy and crystallographic textures of the olivine-bearing Martian shergottite Northwest Africa (NWA) 13276 using co-registered unpolarized Raman spectroscopy, synchrotron powder X-ray microdiffraction (XRD), and Laue microdiffraction rasters. Specifically, we address two fundamental challenges in planetary mineral characterization: identifying mineral phases in large diffraction raster datasets and determining whether Raman

spectroscopy can recover crystallographic information from Martian rocks. These objectives require integrating mineral identification, crystallographic texture analysis, and Raman spectroscopy at identical spatial locations within the meteorite. Mineral phases were identified using a semi-supervised, human-in-the-loop workflow that combines diffraction peak matching, whole-pattern profile fitting, statistical embeddings, and iterative expert review (Y. Huang et al., 2026). The integration of multivariate statistical and semi-supervised methods enabled thousands of diffraction patterns across the raster to be classified, substantially reducing manual interpretation while maintaining expert oversight for ambiguous cases. NWA 13276 contains euhedral to subhedral primary olivine-pyroxene assemblages, with accessory merrillite and apatite, and secondary terrestrial calcite. High-density co-registered Raman point-count grids and synchrotron XRD rasters were acquired for NWA 13276, while oriented terrestrial olivine, augite, and diopside reference crystals were analyzed to calibrate orientation-dependent Raman peak intensities. Co-registering Raman spectroscopy with synchrotron XRD provides an independent mineralogical and crystallographic reference for every Raman spectrum, revealing systematic relationships between Raman peak intensities and crystallographic orientation. Texture reconstructions of confirmed olivine grains were performed using the extended Williams-Imhof-Matthies-Vinel (E-WIMV) orientation-distribution method to determine lattice preferred orientations across the meteorite slice (Matthies et al., 1988). The resulting crystallographic orientations were directly compared with their corresponding Raman spectra to evaluate whether variations in the diagnostic olivine

doublet between 810 and 870 cm^{-1} preserve information about crystal orientation. Raman spectra were classified according to independently reconstructed a-, b-, and c-axis orientations, providing a comprehensive set of orientation-dependent unpolarized Raman spectral signatures. We then evaluate whether these relationships can be used to infer LPOs, magmatic fabrics, and deformation histories from Raman observations acquired by the SuperCam and SHERLOC instruments on the Mars *Perseverance* rover. To our knowledge, this is the first study to calibrate orientation-dependent Raman signatures in a Martian meteorite using co-registered, high-density Raman and synchrotron powder X-ray diffraction point-count grids, combined with quantitative texture reconstruction, and supported by a semi-supervised, human-in-the-loop mineral identification workflow.

2.0 Methods

2.1 Martian Shergottite NWA 13276 and Instrumentation

NWA 13276 is an olivine-bearing Martian shergottite containing euhedral to subhedral crystals ranging from approximately 15 μm to 1 mm in diameter. Primary mineral phases consist predominantly of olivine, augite, pigeonite, diopside, and maskelynite, together with accessory merrillite and apatite, and secondary terrestrial calcite. A ~ 1 mm thick polished section was mounted to a glass slide for transport and placed on a flat stainless steel sample stage for co-registered Raman spectroscopy, synchrotron powder X-ray microdiffraction, and Laue microdiffraction measurements. Powder X-ray diffraction was used for mineral identification and texture reconstruction, whereas Laue diffraction was used to evaluate crystal

mosaicity and identify minerals that retained coherent single-crystal diffraction. Co-registration between the Raman and XRD rasters was ensured using microscope images and a laser-position proxy recorded immediately before, during, and after each measurement sequence. Cross-instrument spatial alignment was statistically verified through mineral identification agreement between overlapping regions of the Raman and XRD rasters. High-resolution images of the analysis regions, including the starting and ending positions of each raster, were acquired to facilitate accurate dataset registration. Photographic records of the co-registered rasters superimposed over the meteorite slice are shown in **Figure 1**.

The Raman raster consisted of a 20 x 30 point grid acquired at a 200 μm step size, totaling 600 measurements. Because Raman acquisition times were substantially longer than X-ray diffraction measurements, the Raman raster was collected at a lower spatial sampling density while covering the same region analyzed by synchrotron XRD. The powder XRD and Laue diffraction rasters consisted of 80 x 120 point grids acquired at a 50 μm step size, totaling 9,600 measurements each. This geometry produced a 4 x 6 mm raster area, which was selected to provide representative grain statistics while maintaining high spatial resolution.

Raman measurements were acquired using a Horiba LabRAM HR Evolution single stage spectrometer equipped with an air-cooled solid-state laser emitting at 532 nm (100 mW maximum output) and filtered through a long range 532 nm notch filter. Laser power at the sample was ~ 10 mW. Spectra were collected at a spectral resolution of $\sim 1\text{ cm}^{-1}$ with a grating with 1800 lines/mm, at an aperture distance of

50X (NA=0.5), and using an open-electrode CCD detector cooled to -60° C. Samples were placed on an automated Märzhäuser XY mapping stage (resolution 0.1 μm , reproducibility 1 μm) and measured using scan and point counting techniques at ambient temperature and pressure [4]. A high purity Si-chip standard was used for spectral wavenumber calibration. Raman spectra are presented with no additional processing beyond offset correction or min-max normalization. Measurements were collected between 100 and 1200 cm^{-1} to encompass the fundamental vibrational modes required for identification of the expected mineral assemblages.

Point grid powder X-ray microdiffraction and Laue X-ray microdiffraction measurements were conducted at beamline 12.3.2 of the Lawrence Berkeley National Laboratory Advanced Light Source. The superbend source operated over a polychromatic energy bandpass of 5-20 keV, with monochromatic measurements acquired at 10 keV ($\lambda = 1.239842 \text{ \AA}$). The focused X-ray beam had a spot diameter of $\sim 1 \mu\text{m}$ with a maximum penetration depth of $\sim 100 \mu\text{m}$. Diffraction patterns were collected using a Dectris Pilatus 1M TIF detector (179 x 168.387 mm active area) configured with a detector angle of $40^\circ 2\theta$ and a sample-to-detector distance of 186 mm. The translational stage rastered across the incident X-ray beam using 50 μm step increments.

Additionally, bulk sample capillary XRD measurements were conducted at beamline BL2-1 of the SLAC Stanford Synchrotron Radiation Lightsource to verify bulk meteorite phase assemblages. The 1.3 Tesla bending magnet source operated over an energy range of 5.5-17.500 keV and was configured at a wavelength of

0.729678 Å. The focused beam had an energy resolution of approximately 5×10^{-4} $\Delta E/E$, a spot size of 0.20 x 0.45 mm², and an angular acceptance of 1.5 mrad.

Diffraction data were collected using a Dectris Pilatus100K detector. The resulting bulk diffraction pattern was used to verify the overall phase assemblage identified from the co-registered Raman and synchrotron powder diffraction rasters.

2.2 Raman Mineral Identification

Raman spectra were manually identified using characteristic vibrational bands of the expected mineral assemblages in Martian shergottites and by comparison with terrestrial reference spectra, including spectra from the RRUFF database (Lafuente et al., 2015b). Phase identification emphasized the complete spectral response between 100-1200 cm⁻¹ rather than individual diagnostic peaks alone. Mineral assignments were made through comparison of peak positions, relative intensities, peak shapes, and the presence or absence of characteristic vibrational modes. Olivine was identified primarily by the characteristic SiO₄ symmetric and asymmetric stretching doublet between ~810-870 cm⁻¹ along with corresponding lower-frequency lattice modes when available (Heymann & Cellucci, 1988b; Kolesov & Geiger, 2004; Mouri & Enami, 2008). Pyroxenes were distinguished by their characteristic Si-O stretching and bending modes near 960-1012 cm⁻¹, ~665 cm⁻¹, and 324-390 cm⁻¹ (E. Huang et al., 2000; Wang, 2001). Merrillite, apatite, and calcite were identified using their characteristic phosphate and carbonate vibrational bands at 964-975 cm⁻¹ and 1087 cm⁻¹, respectively (Berlanga et al., 2019b; Jia et al., 2020; Rutt & Nicola, 1974). Spectra exhibiting contributions from multiple mineral phases were classified as

mixed spectra rather than assigned to a single mineral. Mixed spectra typically occurred near grain boundaries or where the Raman sampling volume intersected adjacent mineral grains. Some spectra exhibited strong fluorescence baselines that completely obscured Raman peaks or had shock-induced peak broadening (possibly associated with maskelynite) that complicated peak assignments (Adcock et al., 2017; Darling et al., 2021). These spectra were labeled as unknown within the Raman raster. Mineral abundance histograms and nearest-neighbor statistics were computed to quantify mineral abundances, spatial relationships, and mineral assemblage associations. Mineral assignments were reviewed iteratively across the complete raster to maintain consistency in phase identification and resolve ambiguous spectra where possible. The manually identified Raman raster served as an independent mineralogical dataset for comparison with the semi-supervised XRD classifications and subsequent texture analysis.

2.3 Semi-supervised XRD Mineral Identification

2.3.1 Crystallographic Parameters-Based Pipeline

The powder XRD raster included 9,600 diffraction patterns, making complete manual identification impractical. Mineral identification was therefore performed using a hierarchical semi-supervised workflow that combines deterministic diffraction analysis with iterative expert review. The workflow consisted of two complementary stages: 1) a physics-based mineral identification pipeline that screened every diffraction pattern using crystallographic constraints, and 2) a semi-supervised expansion procedure that iteratively expanded mineral identifications across the raster

through statistical similarity metrics and expert confirmation. The workflow was designed to minimize false-positive mineral assignments before statistical expansion of the labeled dataset. Preprocessing involved background subtraction, minimal smoothing where necessary, and normalization. Three versions of each diffraction pattern were retained throughout the analysis: the raw diffraction patterns for direct inspection, background-corrected patterns for template matching and peak detection, and normalized patterns for statistical analyses. Retaining multiple representations ensured that normalization procedures used for statistical learning did not obscure physically meaningful diffraction features. Peak detection employed local maxima, peak widths, and baseline-to-peak intensity thresholds. Reference peak positions were also obtained from published CIFs and DIFS peak tables (Brown & Prewitt, 1973; Cameron et al., 1973; Gualtieri, 2000; Hazen, 1976; Hughes et al., 2008; Markgraf & Reeder, 1985). These were used for d-spacing matching and estimating a common 2 θ zero shift. Both global raster d-spacing shifts and mineral-specific shifts were employed to optimize template matching against diagnostic mineral peaks. Primary diffraction peaks were weighted more strongly than secondary reflections, and missing primary peaks incurred penalties during candidate ranking. Non-negative Least Squares (NNLS) whole pattern fitting estimated positive component weights by fitting each diffraction profile as a linear combination of mineral reference patterns. This non-negative constraint allowed identification and quantification of crystalline phases in a mixed sample while handling overlapping diffraction peaks. Mineral identifications were required to satisfy both crystallographic constraints and whole-

pattern agreement before being considered candidate phase assignments. The highest confidence olivine identifications were passed to the semi-supervised expansion pipeline described in the following section. **Figure 2** summarizes the data processing and analysis workflow.

2.3.2 Semi-supervised Human-in-the-loop Expansion

The deterministic mineral identification pipeline produced an initial set of high-confidence candidate mineral assignments while intentionally minimizing false-positive identifications. These manually confirmed patterns served as seed examples for a semi-supervised expansion procedure that iteratively extended mineral identifications across the raster while maintaining expert oversight. Rather than replacing manual mineral identification, the statistical analyses were designed to prioritize diffraction patterns for review and reduce the amount of expert review required. Manually confirmed olivine diffraction patterns were used as the initial labeled population. Each pattern was represented using multiple complementary statistical descriptions to capture similarities in diffraction profile shape, peak positions, and relative intensities. Cosine similarity was employed to identify diffraction patterns exhibiting highly similar normalized profiles, while principal component analysis (PCA) reduced the dimensionality of the dataset and summarized the dominant sources of diffraction variability. Uniform Manifold Approximation and Projection (UMAP) was then used to preserve local neighborhoods within the PCA-reduced feature space, allowing statistically similar diffraction patterns to cluster together while maintaining continuous transitions between related diffraction profiles.

Candidate mineral identifications proposed by the statistical learning methods were reviewed manually and either accepted or rejected before being incorporated into the labeled dataset. The newly confirmed mineral patterns were then used as additional seed examples for subsequent iterations. This semi-supervised process was repeated until successive iterations produced few additional high-confidence mineral identifications and the spatial distributions became internally consistent with neighboring diffraction patterns. Multiple independent similarity metrics were employed because each captures different aspects of diffraction-pattern similarity and spatial distribution. Cosine similarity emphasizes overall profile shape, PCA summarizes the dominant sources of variance, and UMAP preserves local statistical neighborhoods. The final semi-supervised mineral assignments were compared directly with the independently identified Raman raster to evaluate spatial agreement between the two techniques and to identify regions requiring additional review prior to quantitative texture analysis. This workflow maintains a transparent, interpretable, crystallographically constrained, iterative approach that avoids black-box classification while remaining robust to large diffraction datasets, complex mineral assemblages, and low signal-to-noise diffraction patterns.

2.4 Statistical Active Learning and Evidence Fusion

Statistical learning and active learning methods were employed to characterize relationships between diffraction patterns beyond deterministic peak matching alone. The objective was not to replace crystallographic analysis, but rather to identify statistically similar diffraction patterns, reduce the dimensionality of the dataset,

prioritize candidate mineral identifications for manual review, and integrate multiple independent lines of evidence into a unified ranking procedure. Principal component analysis was used as the initial dimensionality reduction method because powder diffraction patterns contain thousands of correlated intensity measurements. PCA transforms these correlated variables into a smaller set of orthogonal principal components (PCs) that preserve the dominant sources of variance within the diffraction dataset. The first 30 principal components were retained because they explained approximately 95% of the total dataset variance while excluding higher-order components dominated by measurement noise. The retained dimensionality was guided by the elbow of the scree plot and the asymptote of the cumulative explained variance curve (**Figure 3**). Sources of variation included mineralogy, peak positions, relative intensities, lattice preferred orientation, crystallinity, mixed-phase contributions, and background variations. Component loadings were examined to identify which diffraction peaks contributed most strongly to each principal component and to evaluate the crystallographic sources of the observed variance as detailed in **Figure 4**. UMAP was applied to the first 15 PCs of the PCA-reduced dataset to preserve local statistical neighborhoods while projecting the diffraction patterns into a 2-dimensional embedding suitable for visualization. PCA preprocessing reduced measurement noise and computational complexity while preserving the dominant crystallographic information prior to nonlinear embedding. The resulting UMAP embedding (**Figure 5**) preserves local neighborhood structure while reducing the influence of weak higher-order components. Neighboring points in

UMAP space suggest diffraction patterns exhibiting similar crystallographic characteristics. The filaments indicate gradual transitions between clusters instead of discrete jumps. Following UMAP embedding and prior to application of cosine similarity metrics, diffraction profiles were L2 normalized to emphasize profile shape rather than absolute intensity. Cosine similarity compares diffraction profile shape independently of absolute intensity, making it particularly well suited for identifying diffraction patterns exhibiting similar peak distributions despite variations in overall scattering intensity (as is often the case with materials exhibiting preferred orientations). The complementary statistical metrics were subsequently integrated through an evidence-fusion strategy. Candidate mineral identifications were ranked using a multi-evidence fusion strategy combining deterministic diffraction analysis, statistical similarity metrics, and spatial context. Each diffraction pattern received an evidence count corresponding to the number of independent analytical methods supporting a given mineral assignment. Agreement between multiple independent criteria increased confidence in candidate mineral identifications and prioritized diffraction patterns for expert review. None of the statistical methods independently assigned mineral identities: rather, they were used to organize, prioritize, and validate diffraction patterns for subsequent expert interpretation. This approach distinguishes the statistical active learning and evidence-fusion workflow from automatic classifiers by maintaining crystallographic interpretability throughout the mineral identification process.

2.5 Texture Analysis and Raman-Texture Correlation

Texture analysis was performed on confirmed olivine diffraction patterns using the Materials Analysis Using Diffraction (MAUD) software package (Lutterotti et al., 1999). Olivine LPOs were evaluated from azimuthally resolved synchrotron diffraction intensities across the meteorite raster. Orientation distribution functions (ODFs) were reconstructed using the extended Williams-Imhof-Matthies-Vinel (E-WIMV) algorithm from the integrated diffraction intensities. Pole figures and inverse pole figures for the olivine [200], [020], and [002] reflections were subsequently calculated from the reconstructed ODFs to quantify crystallographic preferred orientations across the meteorite raster. Because diffraction measurements were acquired at a single macroscopic sample orientation using a fixed-geometry area detector, pole-figure coverage was incomplete and the resulting pole figures represent model-constrained reconstructions of the measured orientation distribution. Pole figure intensities were expressed in multiples of uniform distribution (MUD) contours, allowing direct comparison between reconstructed texture strength and a randomly oriented aggregate. Peak MUD values, area-weighted mean MUD values, and peak-to-mean ratios were calculated for each reconstructed pole figure. Dominant crystallographic axes were assigned using both absolute peak MUD values and peak-to-mean MUD ratios. The peak-to-mean ratio quantified the sharpness of the reconstructed pole figure relative to its background intensity, whereas the uniqueness ratio compared the strongest reconstructed crystallographic axis to the second strongest axis. These complementary metrics distinguish strongly textured orientations from weakly textured or ambiguous reconstructions.

For every confirmed olivine diffraction pattern, the corresponding co-registered Raman spectrum was extracted from the aligned Raman raster. Raman spectra were baseline corrected and normalized prior to comparison with the reconstructed crystallographic orientations. Reconstructed orientations were grouped into dominant *a*-axis, *b*-axis, *c*-axis, and mixed-orientation populations. Mixed orientations represent diffraction patterns in which no single crystallographic axis exhibited a unique dominant texture according to the selected classification criteria. Relative intensities of the diagnostic olivine doublet between 810-870 cm⁻¹ were measured for each spectrum and compared among the reconstructed orientation populations. Relative peak intensities were quantified using the ratio of the local maximum intensities of the lower- and higher- wavenumber members of the olivine doublet. Statistical comparisons between orientation populations were performed using nonparametric resampling methods appropriate for the observed data distributions.

3.0 Results and Discussion

3.1 Mineralogy and Spatial Distribution of NWA 13276

We determined the composition of Martian shergottite NWA 13276 and analyzed the crystallographic orientation of confirmed single phase olivines in a 9,600 point grid μ XRD raster coregistered with Laue μ XRD and a 600 point grid Raman raster (**Figure 6**). Raman spectra and XRD patterns are available in the **Supplement**. Both XRD and Raman raster phase abundances point to its olivine-phyric nature, consisting of >60% pure phase olivine or olivine mixtures

(predominantly forsterite, with modestly varying iron content). This is in agreement with (Borg & Draper, 2003; Nyquist et al., 2001; Yamazaki et al., n.d.). The next most abundant minerals were diopside, augite, calcite, merrillite, and apatite, in order of greatest to least abundance. Phase pure olivines, as confirmed through XRD, consisted of 1,590 measurements. Additionally 4,856 additional patterns were identified as olivine mixtures, primarily co-occurring with pyroxenes.

Although Laue diffraction measurements were collected across the entire raster, coherent Laue patterns were only obtained from secondary calcite. The primary igneous minerals exhibited pervasive mosaicism that largely precluded quantitative Laue orientation analysis. The contrast between coherent calcite and mosaicism in primary minerals supports terrestrial calcite formation after the meteorite arrived on Earth. Significantly more calcite was detected in the XRD measurements than in the Raman measurements, despite calcite's strong Raman signature. This difference likely reflects the coarser spatial sampling of the Raman raster and the heterogeneous distribution of calcite rather than limitations in Raman sensitivity. In XRD and Raman, calcite was found intimately mixed with olivine and pyroxene phase fractions and its formation is not associated with any one mineral phase over another.

Merrillite and apatite were identified by both Raman spectroscopy and XRD, indicating preservation of primary Martian phosphate phases. These phosphates record the evolution of magmatic phosphorus reservoirs and provide constraints on the petrogenesis of the shergottite. The absence of coherent Laue diffraction from

merrillite, in contrast to secondary calcite, indicates that the phosphate phases experienced the same pervasive mosaicism as the surrounding primary igneous minerals, and thus a pre-impact origin to Mars.

Most minerals are well distributed throughout the raster and commonly occur adjacent to olivine, reflecting the high modal abundance of olivine within the meteorite (**Figure 7**).

3.2 Semi-supervised XRD Mineral Identification

Traditional automated mineral identification methods often assume that diffraction patterns can be classified independently using whole-pattern fitting or peak matching alone. However, synchrotron μ XRD measurements collected from intact meteorites contain substantial variability arising from crystallographic preferred orientation, mixed-phase sampling, partial grain illumination, mosaicity, and minor instrumental peak shifts. These effects produce diffraction patterns that may differ considerably despite originating from the same mineral phase, limiting the reliability of fully automated classification. To address these challenges, an iterative semi-supervised workflow that combines Rietveld-refinement-like diffraction analysis, statistical pattern recognition, and expert-guided manual validation to progressively refine mineral identifications across the raster was employed.

Initial candidate olivines were identified using a combination of hierarchical diffraction-peak template matching, full-pattern comparison with synchrotron-calibrated mineral phase reference patterns, and diagnostic d-spacing searches. Candidate diffraction patterns were evaluated using multiple complementary criteria

that included agreement with diagnostic reflections and whole-pattern similarity, while obtaining physically reasonable diffraction peak shifts. This initial screening substantially reduced the search space while maintaining sensitivity to diffraction patterns exhibiting preferred orientation or mixed mineral assemblages. The manually validated olivine identifications served as conservative seed labels for subsequent semi-supervised analysis. Principal component analysis and Uniform Manifold Approximation and Projection were calculated from the complete raster to characterize the statistical structure of the diffraction dataset and to identify neighborhoods containing patterns similar to the confirmed olivines. Candidate expansion was performed using 3 independent criteria: proximity within PCA space, cosine similarity between normalized diffraction profiles, and spatial adjacency within the raster. PCA captured dominant modes of diffraction-pattern variability while preserving global variance. Each of the top 5 principal components captured a crystallographic preferred orientation for olivine. Cosine similarity measured full-profile agreement independent of overall intensity scaling. Spatial neighborhood analysis exploited the expectation that adjacent mineral raster positions commonly sample the same mineral grain or subgrains. These complementary approaches reduced dependence on any single statistical metric in light of a complex diffraction dataset, while preferentially identifying patterns supported by multiple independent lines of evidence.

Candidate diffraction patterns identified by the individual search strategies were subsequently integrated through an evidence-fusion framework. Mineral

identification was not merely assigned from statistical similarity. Instead each candidate accumulated independent “evidence” from diffraction peak matching, cosine similarity, PCA proximity, UMAP neighborhood clustering, and spatial continuity within the raster. The combined metrics were used to generate review priority scores instead of probabilistic classifications. Thus, statistical analysis served to prioritize patterns for manual inspection rather than replacing expert interpretation. This approach minimized propagation of classification errors while allowing the confirmed mineral library to expand iteratively. All candidate olivine patterns were manually reviewed through direct comparison with reference diffraction patterns, diagnostic peak positions as found in DIF files, and neighborhood raster measurements. Each pattern was assigned to one of four categories: confirmed mineral, mixed phase, uncertain, or rejected. Accepted identifications were incorporated into a master annotation database, which subsequently served as the seed population for the next iteration of statistical expansion. Candidate generation, manual validation, and database updating were repeated until successive iterations produced few additional high-confidence mineral identifications, indicating convergence of the semi-supervised workflow. Approximately 1590 high-confidence pure phase olivines were identified.

The iterative human-in-the-loop strategy was selected in preference to purely supervised or unsupervised machine-learning approaches because no sufficiently larger, accurately labeled diffraction dataset exists for olivines at various preferred orientations, and less so for Martian meteorites. Fully supervised classifiers require

representative training data spanning the full range of preferred orientations, mixed phases, and diffraction artifacts, whereas purely unsupervised clustering lacks mineralogical constraints necessary for robust phase identification. By combining crystallographic constraints with statistical similarity and expert validation, the present workflow preserves physical interpretability while exploiting the efficiency of statistical pattern recognition. The resulting confirmed mineral population forms the basis for the lattice preferred orientation reconstructions and Raman orientation analysis presented in the following sections.

3.3 Statistical Structure of the Diffraction Dataset

PCA was applied to the normalized synchrotron X-ray diffraction patterns to characterize the dominant sources of variance within the raster prior to semi-supervised mineral classification. Unlike supervised classification methods, PCA identifies orthogonal directions of maximum variance without prior mineral labels. This allows evaluation of whether diffraction patterns naturally organize according to physically meaningful crystallographic information. Each diffraction pattern was represented as a vector of normalized diffraction intensities over the analyzed 2θ interval, and projected into a reduced-dimensional feature space defined by the principal components. The scree plot (**Figure 3**) demonstrates that the diffraction dataset possesses relatively low intrinsic dimensionality when applied to the full 9600 point grid diffraction raster. The first principal component (PC1) explains approximately 28% of the total variance, followed by PC2 (21.4%), PC3 (7.8%), PC4 (6.5%), and PC5 (4.7%). These first five principal components account for ~68% of

the variance, while the first fifteen components explain ~90%. Retaining 30 PCs preserved nearly 97% of the total variance, indicating that the majority of diffraction pattern variability can be represented within a substantially reduced feature space while minimizing information loss. The rapid decrease in explained variance beyond the first several components indicates that the dominant sources of variability arise from a relatively small number of systematic crystallographic differences rather than the high-dimensional random noise.

Projection of the diffraction patterns into PCA space revealed that manually confirmed olivine diffraction patterns occupy coherent regions distinct from much of the remaining dataset (**Figure 3**). Although the olivine population does not form a single compact cluster, it occupies several connected subpopulations within the first few principal component projections. These structured branches indicate that olivine diffraction patterns exhibit systematic internal variability rather than random dispersion. Because the confirmed olivine set spans multiple neighboring manifolds while remaining well separated from much of the remaining raster, PCA provides an effective statistical representation for identifying additional olivine candidates during the semi-supervised workflow. The existence of multiple olivine subpopulations is consistent with the expectation that diffraction intensities vary as a function of crystallographic orientation, partial grain illumination, mixed phased sampling, and minor lattice distortions, despite all spectra originating from the same mineral phase. The distribution of Euclidian distances from the centroid of the confirmed olivine population further supports the statistical coherence of the manually identified

olivines (**Figure 8**). Confirmed olivines occupy significantly shorter distances from the olivine centroid than the unlabeled diffraction patterns, while exhibiting a relatively narrow distribution compared to the broader population of raster measurements. Nevertheless, partial overlap exists between the two distributions, indicating that additional unlabeled spectra possess statistical characteristics similar to confirmed olivines. Rather than treating this overlap as a classification ambiguity, these neighboring patterns formed the basis for iterative candidate expansion and manual validation during the semi-supervised identification workflow described above.

The physical origin of the leading principal components was evaluated from their loading vectors (**Figure 4**). Unlike score plots, which describe the statistical relationships among diffraction patterns, loading vectors identify the specific diffraction angles contributing most strongly to each principal component. PC1 exhibits large positive loadings near 25.8° , 29.1° , and 41.4° 2θ , corresponding to strong forsterite reflections, including the inferred [130], [112], and [222] reflections. Of these, the 29.1° feature provides the clearest olivine-specific contribution, whereas the 41.4° region overlaps major augite and diopside reflections and therefore represents broader mafic-silicate variability. PC2 retained many of the same diffraction features but with opposite loading signs for several neighboring peaks, particularly near 29.1° 2θ , indicating that this component primarily describes changes in relative diffraction-peak intensities rather than simple differences in olivine phase abundance. Such intensity variations are expected for spot diffraction measurements

collected from individual crystals exhibiting varying crystallographic orientations and degrees of preferred orientation. Higher order principal components PC3-PC5 progressively incorporate weaker olivine reflections and additional diffraction regions shared with pyroxenes, calcite, and merrillite. These also likely capture secondary sources of variability including preferred orientation, mixed-phase diffraction patterns, partial grain sampling, lattice strain, and minor instrumental peak shifts. The persistence of narrow, reflection-centered loading extrema across the first five PCs demonstrates that the PCA decomposition is controlled by physically meaningful diffraction features rather than broad background structure or statistical noise. PCA loading peak assignments are tabulated in **Table 1**.

These results demonstrate that the synchrotron diffraction dataset possesses an inherent statistical organization arising from mineralogy and crystallography. PCA therefore provides not only an efficient dimensionality reduction technique for subsequent semi-supervised learning, but also a physically interpretable representation of diffraction pattern variability. The correspondence between dominant principal component loadings and diagnostic diffraction reflections confirms that the statistical structure of the dataset is controlled primarily by the specific mineral phase, providing the foundation for the subsequent UMAP analysis and iterative mineral identification.

Uniform Manifold Approximation and Projection was applied to the first fifteen principal components retained from the PCA analysis. Whereas PCA identifies orthogonal directions of maximum variance within the dataset, UMAP is a nonlinear

manifold-learning algorithm designed to preserve local neighborhood relationships during dimensionality reductions. Consequently, diffraction patterns with similar statistical characteristics remain proximal within the embedding, while dissimilar patterns are separated into distinct manifolds. The UMAP coordinates themselves possess no direct physical interpretation, instead, the topology of the embedding reflects the similarity relationships among diffraction patterns. The NWA 13276 diffraction dataset is organized into several well-defined manifolds rather than a single continuous distribution (**Figure 5**). The manifolds are connected by narrow transitional branches and contain multiple dense subclusters, indicating that diffraction patterns vary through discrete but related crystallographic populations and do not exhibit random high-dimensional scatter. The existence of these coherent manifolds demonstrates that the dominant statistical relationships within the diffraction dataset are structured and reproducible, consistent with systematic mineralogical and crystallographic variability across the meteorite.

When the manually confirmed olivine diffraction patterns were projected onto the UMAP embedding, they occupied coherent neighborhoods within several of these manifolds instead of being randomly distributed throughout the dataset (**Figure 5**). Of importance is that the confirmed olivines do not collapse into a single compact cluster. Instead they populate multiple neighboring branches that remain statistically distinct while collectively defining the olivine population. This observation agrees with the PCA analysis and suggests that olivine itself exhibits several internally consistent diffraction pattern orientations, mixed phase samplings, and other lattice or

illumination artifacts that modify the relative intensities of individual diffraction peaks while preserving the overall mineralogical identity. The distribution of confirmed olivines throughout multiple adjacent manifolds also explains why iterative candidate expansion based solely on Euclidean distant or nearest-neighbor searches would incompletely sample the olivine population. Candidate identification benefited from combining PCA proximity, cosine similarity, spatial continuity, and UMAP neighborhood relationships, thereby recovering olivine spectra spanning the full statistical diversity of the mineral rather than a single dominant cluster.

The physical significance of the UMAP embedding was evaluated by projecting the UMAP coordinates back onto their original raster positions. Despite UMAP being constructed solely from diffraction pattern similarity without incorporating any spatial information, both UMAP coordinates exhibit large scale spatial coherences across the meteorite raster (**Figure 5**). UMAP1 displays a broad gradient extending from the upper to lower portions of the raster, whereas UMAP2 varies predominantly along a transverse direction with localized domains of similar values. The absence of random spatial fluctuations indicates that neighboring diffraction patterns are statistically similar, as expected for contiguous mineral grains. An embedding dominated by noise or mathematical artifacts would produce spatially uncorrelated patterns when projected back into raster space.

An additional perspective on the statistical organization of the confirmed olivines is provided by assigning each spectrum to the principal component exhibiting the largest standardized score magnitude. Mapping the dominant PC assignments

back on to the raster reveals that individual olivine grains and grain clusters are characterized by distinct combinations of the leading principal components (**Figure 9**). Neighboring olivines commonly transition between PC1-, PC2-, PC3-, PC4-, and PC5-dominated behavior while remaining spatially coherent: this may be a consequence of the mosaicism of the olivine grains. This is instead of exhibiting a single dominant mode of variability. Averaged diffraction patterns for each dominant PC class demonstrate that the statistical groupings correspond to systematic changes in the relative intensities of the major olivine reflections, particularly near $\sim 26^\circ$, 29° , and $41^\circ 2\theta$, while retaining the characteristic olivine diffraction signature (**Figure 10**). These results indicate that the leading PCs partition variations in diffraction intensity rather than mineral identity, supporting the interpretation that the statistical subpopulation primarily reflects crystallographic orientation within the olivine population.

The PCA and UMAP analysis demonstrate that the statistical structure of the diffraction dataset is governed by physically meaningful crystallographic relationships rather than arbitrary statistical clustering. PCA identifies the dominant diffraction features responsible for the observed variance, while UMAP preserves local neighborhood structure among those diffraction patterns. The strong correspondence between statistical neighborhoods and spatially coherent regions within the meteorite provides independent evidence that the embedding captures real mineralogical and crystallographic variability. These statistically coherent olivine

populations subsequently formed the basis for the lattice preferred orientation reconstructions and Raman orientation analysis.

The observation that the principal component subpopulations differ primarily in the relative intensities of common olivine reflections, rather than the appearance or disappearance of reflections, suggests that the statistical clustering is dominated by crystallographic orientation effects. This hypothesis is evaluated directly through quantitative lattice preferred orientation reconstruction as detailed in section 3.4.

Cosine similarity provides a direct measure of pairwise agreement between individual diffraction patterns. It compares normalized diffraction profiles by evaluating the angle between intensity vectors in high-dimensional diffraction space. Because the metric depends on the relative distribution of intensities rather than their absolute magnitudes, it is largely insensitive to variation in overall diffraction intensity arising from crystal size, orientation, illuminated volume, or synchrotron beam fluctuations. Consequently, patterns sharing similar diffraction peak positions and relative peak intensities exhibit high cosine similarity even when absolute intensities differ substantially. In the semi-supervised workflow, cosine similarity served as an independent statistical criterion for expanding the manually confirmed olivine population. Each confirmed olivine diffraction pattern was compared against the complete raster, and candidate spectra exhibiting high whole-pattern similarity were identified for subsequent manual review. Unlike PCA or UMAP, which summarize relationships among the entire dataset, cosine similarity evaluates each diffraction pattern individually against known reference pattern. This complementary

behavior allowed patterns occupying the periphery of PCA or UMAP neighborhoods to be recovered when their overall diffraction profiles remained highly consistent with confirmed olivines.

The use of cosine similarity was particularly suitable because crystallographic preferred orientation frequently modifies diffraction intensities without substantially changing diffraction peak positions. Two olivine diffraction patterns acquired from differently oriented grains may therefore occupy different locations within PCA or UMAP space while still exhibiting strong whole-pattern similarity. Conversely, mixed-phase spectra generally display reduced cosine similarity because additional reflections alter the overall diffraction profile. Cosine similarity therefore preferentially identifies diffraction patterns preserving the characteristic olivine signature while remaining tolerant of moderate orientation-dependent intensity variations.

Rather than serving as a standalone classifier, cosine similarity constituted one component of the evidence fusion framework used during iterative mineral identification. Candidate spectra identified through cosine similarity were evaluated together with PCA proximity, UMAP neighborhood membership, diffraction peak machine, and spatial continuity. The agreement of multiple statistically independent criteria substantially reduced false-positive identifications while allowing recovery of olivine spectra spanning the full range of crystallographic variability observed across the meteorite raster.

3.4 Olivine Texture and Lattice Preferred Orientations

Crystallographic preferred orientation in NWA 13276 was evaluated from the azimuthally resolved diffraction intensities of confirmed olivine patterns and through extended Williams-Imhof-Matthies-Vinel (E-WIMV) orientation distribution functions (ODFs). The measured diffraction patterns provide an initial, model-independent indication of crystallographic anisotropy. Two-dimensional diffraction images were azimuthally integrated into discrete detector azimuth (η) transects and background subtracted, preserving variations in reflection intensity around individual Debye-Scherrer rings. Expected olivine reflection positions and Miller indices were assigned from a forsterite calibrant (Hazen et al. 1975), allowing the azimuthal behavior of individual reflections to be compared directly with the reconstructed texture. In orthorhombic olivine, reflections of the form ($h00$), ($0k0$), and ($00l$) have reciprocal-lattice vectors parallel to a^* , b^* , and c^* directions, respectively, and thus provide direct measurements sensitive to the corresponding crystallographic axes. The principal reflections used for this comparison were (200) for the a -axis, (020) for the b -axis, and (002) and (004) for the c -axis. Additional pure axial reflections were retained where their reference intensities were sufficient for reliable measurement. Mixed-index reflections, including (110), (120), and (021), were not substituted for missing principal-axis reflections because their reciprocal-lattice vectors contain contributions from more than one crystallographic direction.

For each azimuthal profile, the expected position of each reflection was determined from the calibrant and its integrated intensity was measured within a local

2 θ interval after residual background estimation. Integrated reflection intensities were normalized to the corresponding relative intensity of the randomly oriented calibrant:

$$I_{hkl}(\eta) = (I_{hkl}(\eta))/(I_{ref_{hkl}})$$

This normalization reduced the large differences in intrinsic diffraction intensity among reflections. The resulting I_{hkl} values describe relative enhancement or suppression of crystallographically sensitive reflections under the measured scattering geometry and are not equivalent to crystallographic-axis abundances.

Detector coverage and edge masks were explicitly incorporated into the analysis. One of the detector gaps intersects $\sim 28\text{-}31^\circ$ 2 θ over portions of the measured azimuthal range and can consequently diminish the (200) reflection at some η values. Reflections intersecting a detector gap were treated as missing observations rather than assigned zero intensity. Similarly, reflections for which detector coverage was present but the measured signal did not satisfy the peak-detection criterion were designated as insufficiently constrained and were not interpreted as evidence for the absence of that crystallographic orientation. Axis-sensitive scores were consequently calculated only from reflections measurable at a given azimuth. This distinction is particularly important for the a -axis because (200) is intrinsically weaker than several of the available c -axis reflections.

The azimuthally resolved diffraction patterns displayed pronounced variation in the relative reflection intensities. Pattern 1762 provides a representative example (**Figure 11**). Olivine reflection positions remain approximately constant with detector azimuth, but their intensities vary substantially among η transects. The calibrant-

normalized (200) intensity exhibits strong modulation while the measured (020), (002), and (004) intensities have a weaker response over the azimuthal transects. Similar azimuthal intensity variations occur throughout the raster. Such systematic azimuthal modulation is the expected diffraction manifestation of crystallographic preferred orientation: crystallites satisfying the Bragg condition are not uniformly distributed around the diffraction ring. The direct axis-sensitive representation also demonstrates why missing reflections cannot be interpreted as zero orientation intensity. For example, for pattern 1762, *a*-axis sensitive reflections are measurable only over a subset of azimuthal sectors because of incomplete detector coverage, whereas *c*-axis sensitive reflections are measurable over a larger fraction of η . Connecting measurements across these gaps would imply diffraction information that was not experimentally observed. The discontinuities in **Figure 11c** preserve the actual angular coverage of the diffraction measurements and do not interpolate through detector gaps.

To compare the three principal axis-sensitive signals across the olivine population, valid diffraction intensities for each pattern were summarized across detector azimuth and normalized according to:

$$f_a = S_a / (S_a + S_b + S_c), \quad f_b = S_b / (S_a + S_b + S_c), \quad f_c = S_c / (S_a + S_b + S_c)$$

where S_a , S_b , and S_c are the median calibrant-normalized intensities of the valid *a*-, *b*-, and *c*-axis-sensitive reflections, respectively. These normalized values

represent relative diffraction-intensity fractions under the experimentally sampled scattering geometry and should not be interpreted as volume fractions of grains having a-, b-, or c-axes in a particular sample direction. The resulting ternary distribution is strongly asymmetric and dominated by a-axis-sensitive diffraction, with measurements forming a continuum toward mixed a-c and, less commonly, b-axis-sensitive responses (**Figure 12a**). This distribution demonstrates pervasive crystallographic anisotropy within the high-confidence olivine population rather than anisotropy restricted to a small number of isolated measurements.

Co-registered Raman measurements were incorporated directly into this diffraction representation by coloring each ternary point according to the relative intensity ratio of the olivine Raman doublet, I_1/I_2 [use whatever exact definition you use elsewhere—e.g., I_{820}/I_{850}]. The Raman ratio varies continuously throughout the XRD axis-sensitive space rather than defining sharply separated crystallographic populations (Figure 12a). Nevertheless, grouping measurements according to their dominant full-pattern direct-XRD axis-sensitive signal reveals systematic differences in the Raman response (Figure 12b). The a-axis-sensitive population spans the broadest range of Raman doublet ratios and includes the highest values, whereas the smaller b- and c-axis-sensitive populations are concentrated at generally lower ratios. The substantial overlap among all three populations demonstrates that the Raman doublet ratio is sensitive to crystallographic orientation but does not provide a unique axis assignment from an individual spectrum.

A second, more restrictive comparison was performed using independently aggregated azimuthal-enhancement measurements (**Figure 12c**). Rather than reducing the complete diffraction response to the pattern-level median, this analysis identifies axis-sensitive enhancement from the azimuthally resolved diffraction intensities and requires a minimum of two XRD measurements supporting each Raman footprint. The resulting subset contains 46 co-registered Raman measurements and samples a broad region of a-b-c axis-sensitive space. As in the full-pattern comparison, Raman doublet ratios vary continuously across the ternary distribution, with no discrete Raman populations corresponding uniquely to the three crystallographic axes.

Grouping this subset according to the dominant independently aggregated direct-XRD azimuthal-enhancement signal produces overlapping Raman doublet-ratio distributions for the a-, b-, and c-sensitive populations (Figure 12d). The a-sensitive population again encompasses the widest range of ratios, while b- and c-sensitive measurements occupy smaller populations with substantial overlap. Agreement between the full-pattern and independently aggregated azimuthal analyses indicates that the relationship is not an artifact of a single method of reducing the diffraction intensities. Instead, both representations demonstrate that crystallographic anisotropy contributes measurably to the relative intensity of the olivine Raman doublet while also showing that additional crystallographic, compositional, sampling, and instrumental variables contribute to the observed Raman response.

These direct intensity measurements provide an important independent check on the E-WIMV texture reconstruction but are not themselves crystallographic

orientations. The ternary coordinates cannot be converted directly into pole densities or multiples of uniform distribution (MUD). Pole figures require transformation of the measured hkl -dependent reflection intensities and their experimental geometries into an orientation distribution from which the distribution of a crystallographic direction relative to the sample reference frame is reconstructed. The direct intensity analysis precedes rather than replaces the orientation-distribution analysis, thus the preferential orientation inferred from the reconstructed pole figures is independently expressed in the measured diffraction data themselves.

The crystallographic anisotropy observed directly in the azimuthally resolved diffraction patterns was subsequently evaluated using E-WIMV reconstruction of the olivine ODFs. Reconstructed (200), (020), and (002) pole figures describe the distributions of the olivine a -, b -, and c -axis, respectively, relative to the sample reference frame. Supporting reflections, including (110), (021), (101), (111), (120), and (121), were incorporated where required by the texture reconstruction. Because the synchrotron raster was acquired at a single macroscopic sample orientation with fixed detector geometry, pole-figure coverage was incomplete and the resulting pole figures represent model-constrained reconstructions of the measured orientation distribution rather than complete experimental pole figures. Pole density was expressed in MUD, such that 1 MUD corresponds to the density expected for a randomly oriented aggregate and progressively larger values represent increasing concentrations of crystallographic poles. The reconstructed pole figures exhibit strongly non-random orientation distributions throughout the olivine-bearing regions

of NWA 13276 (**Supplement**). Maximum pole densities commonly reach several tens of MUD and locally approach the upper range of the reconstruction. High absolute MUD values occur in all three principal pole figures, demonstrating strong texture, although maximum MUD alone does not uniquely identify the crystallographic axis exhibiting the sharpest preferred orientation. This distinction is evident when orientation classifications based solely on absolute maximum MUD are compared with classifications based on the concentration of each pole relative to its own mean intensity.

Pole figure sharpness was therefore evaluated using the ratio between maximum and mean pole density. This metric quantifies the degree to which a localized pole-density maximum rises above the remainder of the reconstructed orientation distribution. The *c*-axis (002) pole figures display the greatest peak-to-mean ratios, extending to substantially higher values than the majority of the (200) and (020) distributions. Classification using relative pole figure sharpness consequently produces a markedly more coherent crystallographic result than classification using absolute maximum MUD alone.

Of the 1,590 raster positions for which a unique dominant orientation could be assigned, 1,563 (98.3%) were classified as *c*-axis dominant, 26 were mixed or lacked a uniquely dominant axis, and one was *b*-axis dominant, and none were uniquely *a*-axis dominant. The spatial raster of these classifications demonstrates that *c*-axis dominance is not restricted to a single grain or localized portion of the meteorite but occurs throughout spatially separated olivine-bearing regions (**Figure 6**). The contrast

between this result and the direct axial-reflection ternary analysis further emphasizes that direct analysis quantifies reflection enhancement under the experimental scattering geometry, whereas E-WIMV reconstructs the crystallographic orientation distribution responsible for the observed intensity variation. The positions of the dominant pole maxima further constrain the geometry of the reconstructed fabric. Dominant axis pole maxima are concentrated near the sample normal, with a mean inclination of 14.4° , median of 15.0° , and standard deviation of 7.6° . Most measurements occur near the 15° near-normal boundary, while only a small number approach orientations parallel to the sample plane. The azimuthal distribution is similarly non-random, with a pronounced concentration near approximately 100 - 110° . NWA 13276 therefore records not only a preferred crystallographic axis but also a coherent orientation of that axis relative to the meteorite section.

The strong and spatially persistent olivine LPO may preserve a composite history of crystallization and subsequent modification. Olivine fabrics in igneous rocks can develop through preferential alignment during magmatic flow, anisotropic crystal growth, crystal accumulation, and solid state deformation. Experimental deformation studies similarly demonstrate that olivine develops systematic LPOs under shear, although the resulting fabric depends on stress state, deformation geometry, temperature, pressure, water content, and active slip systems. The presence of a strong fabric therefore does not by itself uniquely identify the mechanism responsible for its formation. Part of the motivation of this work involved utilizing textural information recorded by Martian meteorite LPOs to constrain preferred

orientation-inducing mechanisms. The shock history of a Martian meteorite provides an additional complication. Shock and post-crystallization deformation may rotate, broaden, or partially overprint a pre-existing magmatic or deformational fabric without necessarily erasing it. Consequently, the pervasive *c*-axis LPO observed in NWA 13276 is interpreted conservatively as evidence that a coherent crystallographic fabric survived the meteorite's subsequent shock history. Distinguishing whether this fabric originated principally during crystal growth, magmatic transport or accumulation, or later deformation requires integration with petrographic relationships and comparisons with experimentally and naturally produced olivine fabrics. Regardless of whether the preserved LPO originated primarily during crystallization, magmatic flow, or subsequent deformation, its presence provides a natural experiment for evaluating orientation-dependent Raman scattering. Such Raman scattering has direct applications to remotely measured Martian rocks, where in the absence of direct texture analysis capabilities, measured Raman spectra may act as a proxy for constraining texture through its sensitivity to crystallographic orientation.

3.5 Raman Signatures of Crystallographic Orientation: Implications for Mars

Olivine is characterized by a diagnostic Raman doublet between ~ 810 - 870 cm^{-1} , associated with the coupled symmetric and asymmetric stretching vibrational modes of the SiO_4 tetrahedra. The positions of these bands vary systematically with Mg-Fe composition and have therefore been widely used to estimate olivine composition (Breitenfeld et al., 2018b; Kuebler et al., 2006). Similarly, their relative

amplitudes have long been known to vary depending on crystal orientation (Chopelas, 1991; Ishibashi et al., 2008; Servoin & Piriou, 1973). SuperCam has identified Martian olivine through this doublet, and has used sufficiently resolved spectra to constrain the olivine Fo# at Jezero Crater, Mars from the peak positions (Beyssac et al., 2023; Lopez-Reyes et al., 2025). Raman peak intensity is dependent on the Raman tensor and measurement geometry, and thus provides sensitivity to the crystallographic orientation (Ishibashi et al., 2008; Wenk et al., 2004; Zhang & Karato, 1995).

Ishibashi et al. (2008) quantified the orientation dependence of the olivine doublet in unpolarized Raman spectra of compositionally homogeneous $\text{Fo}^{89}\text{Fa}^{11}$ olivine independently oriented by EBSD. The ratio of the ~ 822 to $\sim 854 \text{ cm}^{-1}$ bands was greatest near the $[100]$ direction, corresponding to enhancement of the lower-wavenumber component, and decreased toward $[010]$, where the higher-wavenumber component became dominant; spectra approaching $[001]$ exhibited more comparable doublet intensities. Importantly, Ishibashi et al. demonstrated that Raman intensity varies continuously with the complete crystallographic orientation relative to the incident laser rather than defining discrete spectral responses associated with the three principal crystallographic axes. Their empirical orientation solution therefore incorporated additional Raman bands near 917 and 959 cm^{-1} together with the olivine doublet.

The automated E-WIMV reconstruction of the 1,590 confirmed olivine patterns established the raster-scale texture distribution, which is dominated by a

strong *c*-axis component. To resolve orientation differences within this broadly *c*-axis dominated population at higher fidelity, a spatially restricted region containing co-registered Raman and XRD measurements was selected for detailed manual refinement and texture reconstruction (**Supplement**). Individual XRD patterns associated with each Raman measurement were inspected and refined, producing higher-quality pole figures that resolve *c*-axis dominated orientations as well as mixed *a*-*c*, *b*-*c*, and more complex orientation components (**Figure 13**). These refined orientations were used for comparison with the corresponding Raman spectra. Raman spectra were then grouped according to the relative intensities of the low- and high-wavenumber doublet members of the olivine doublet. Spectra lacking a confidently identifiable doublet, including mixed or high-background baseline spectra were retained as an uncertain class rather than forced into an orientation-dependent category.

The manually reconstructed subsection is dominated by olivines exhibiting strong *c*-axis preferred orientations, consistent with the broader raster scale texture analysis (**Figure 13**). Within this population, however, the relative Raman doublet intensity is variable. Both low- and high-wavenumber dominant spectra occur among measurements associated with *c*-axis dominated pole figures. The high-wavenumber member nevertheless exhibits a weak tendency toward greater relative intensity among the *c*-axis oriented population. Thus, crystallographic orientation measurably contributes to the Raman response, but the relationship is neither one-to-one nor sufficiently strong to assign a unique crystallographic orientation from an individual

unpolarized Raman spectrum: this ambiguity may be a consequence of the mosaicism of the sample, with potentially rotated subdomains within an otherwise oriented crystal, or of multiple crystallites being sampled due to the penetration depth of the Raman probe.

This result modifies the stronger orientation relationship suggested by initial comparisons of oriented reference crystals and selected meteorite spectra. Instead of defining a deterministic spectra classifier in which one member of the Raman olivine doublet uniquely identifies the *c*-axis, the co-registered diffraction measurements indicate a probabilistic relationship. Variability in Raman intensity within a single orientation class is expected because the measured response depends on the complete crystal orientation relative to incident and scattered light, not solely on which principal crystallographic axis is nearest the measurement direction. Surface roughness, mixed mineral contributions, variations in the fraction of an individual grain sampled by the laser, fluorescence baseline and background intensity, compositional variation, and instrumental geometry can further modify the observed intensity ratio.

The NWA 13276 measurements reproduce the enhancement of the lower-wavenumber doublet component associated with a-axis contributions reported by Ishibashi et al. (2008), but differ in the behavior associated with b- and c-axis-dominated textures. In NWA 13276, c-axis-dominated reconstructions preferentially exhibit enhancement of the higher-wavenumber component, whereas mixed a- and b-axis contributions more commonly enhance the lower-wavenumber component. This

difference likely reflects the substantially different crystallographic and sampling conditions of the two studies. Ishibashi et al. examined chemically homogeneous, individually oriented Fo⁸⁹Fa¹¹ single crystals with orientations independently determined by EBSD, whereas NWA 13276 is a highly mosaicized, compositionally variable Martian assemblage in which E-WIMV reconstructs orientation distributions from diffraction intensities and individual Raman measurements may sample multiple crystallographic subdomains. The NWA 13276 classifications additionally represent dominant or mixed orientation components rather than ideal measurements exactly parallel to [100], [010], or [001].

The approximately equal and uncertain Raman populations reinforce this interpretation (**Figure 13**). Spectra with nearly equivalent doublet intensities occur within the same crystallographically textured region as clearly asymmetric spectra, while several measurements lack a sufficiently resolved olivine doublet for meaningful intensity comparison. The Raman doublet ratio is therefore best interpreted as an orientation-sensitive spectral parameter, rather than a direct orientation measurement. Raman spectroscopy cannot readily replace diffraction-based texture reconstruction, but instead the independently measured crystallographic textures demonstrate that orientation constitutes an additional physical control on olivine Raman intensity that should be considered alongside composition and spectral quality. Repeated measurements across an exposed surface may consequently contain statistical information about crystallographic fabric even where an individual spectrum remains ambiguous. This distinction is important for planetary Raman

spectroscopy aboard the *Perseverance* rover, where diffraction measurements of crystallographic orientation are generally unavailable.

3.5.1 Application To Olivine Raman Measurements on Mars

The NASA *Perseverance* rover provides an immediate opportunity to test this relationship on Mars. SuperCam has acquired Raman spectra of olivine-bearing targets throughout Jezero Crater, including the olivine-rich Séítah crater floor formation and olivine-bearing targets encountered on the upper fan and margin. The SuperCam 532 nm Raman system can acquire remote spectra at stand-off distances of several meters and has repeatedly resolved the characteristic olivine doublet where sufficient signal-to-noise ratios are obtained (Wiens et al., 2021b). SuperCam's Raman spectral resolution is better than 12 cm^{-1} and its millimeter-scale analytical footprint commonly encompasses multiple mineral grains, producing different measurement conditions from the laboratory micro-Raman measurements of NWA 13276. Our laboratory measurements provide the fine-scale detail necessary to apply the relationships to the broader SuperCam Raman measurements.

Séítah provides an especially relevant geological comparison because it is an olivine-rich igneous unit interpreted as a cumulate formed through fractional crystallization and slow cooling of magma that was subsequently exposed by erosion. The olivine found occurs as abundant millimeter-scale grains together with low- and high-Ca pyroxenes and other primary mineral phases-similar to the mineralogy found on NWA 13276. Multiple Séítah targets, including Garde, Dourbes, Penne, Brac, Castellet, and Quartier contain olivine. At Garde, olivine is ubiquitous across the

analyzed abrasion patch, while Dourbes contains multiple measurements in which both members of the $\sim 810\text{-}870\text{ cm}^{-1}$ doublet are resolved. Natural surfaces including Penne, Brac, and Castellet also produced olivine signatures, although generally at lower signal-to-noise ratios than abraded surfaces. These observations provide a direct Martian dataset in which the doublet-intensity behavior characterized in NWA 13276 can be tested.

Representative SuperCam Raman spectra of olivine-bearing Martian targets are shown in **Figure 14**. The spectra include Dourbes (Sol 259), Garde (Sols 207, 209, and 210), Penne (Sol 211), and Lake Haiyaha (Sol 853) (Beyssac et al., 2023; Corpolongo et al., 2023; Moreland et al., 2026). The first five measurements represent olivine-bearing targets within the Séítah formation and Lake Haiyaha is an olivine-rich boulder analyzed on the Jezero upper fan. It produced the strongest olivine Raman signal reported by SuperCam during its first 1,000 sols of operation. Across the measurements, the relative intensities of the $\sim 810\text{-}870\text{ cm}^{-1}$ doublet peaks vary with some spectra exhibiting a stronger low-wavenumber peak and therefore suggested to be more *a*- and/or *b*- axis sensitive, some spectra exhibiting an increased contribution from the high-wavenumber peak and therefore suggestive of more *c*-axis sensitivity, and other spectra approaching approximately equal intensities implying a more indeterminate sensitivity. The preservation of this variability under SuperCam measurement conditions demonstrates that the same spectral parameter examined in the NWA 13276 laboratory measurements is observable in Raman data acquired directly from the Martian surface. These differences cannot presently be attributed

uniquely to crystallographic orientation. Previous SuperCam studies have primarily interpreted the positions of the olivine doublet in terms of Mg-Fe compositions and explicitly recognize that its relative intensities vary with crystal orientation. The SuperCam measurements additionally integrate larger sampling volumes than laboratory micro-Raman spectroscopy, and variations in grain size, surface geometry, dust, mineral mixtures, SNR, and instrumental effects can influence the measured doublet. The spectra in **Figure 14** should therefore not be interpreted as direct measurements of *a*-, *b*-, or *c*-axis orientation, but rather their variability demonstrates that orientation-sensitive doublet asymmetry is retained within the existing Martian Raman dataset and can potentially be evaluated statistically using the relationships constrained by the co-registered Raman-XRD measurements of NWA 13276.

The application should be most appropriately made at the population level rather than assigning crystallographic orientations to individual SuperCam Raman spectra. Olivine spectra acquired across the same geological exposure could be classified by their relative doublet intensities and evaluated for spatially coherent changes in the distribution of doublet ratios. A population exhibiting systematically elevated high-wavenumber peaks would be consistent with, but would not independently demonstrate, an increased contribution from olivines occupying orientations comparable to the *c*-axis dominated textures measured in NWA 13276. Conversely, a broad or spatially random distribution of doublet ratios would provide little evidence for a coherent crystallographic fabric. This population-based approach accounts for the probabilistic relationship observed in NWA 13276 while providing a

testable method for evaluating crystallographic texture in existing and future rover Raman datasets.

The SHERLOC Raman instrument aboard *Perseverance* also provides a complementary but different measurement geometry. Its deep-UV Raman system produces microscale spatial maps, but its spectral resolution is insufficient to resolve the $\sim 810\text{-}870\text{ cm}^{-1}$ olivine doublet as two independent peaks in the crater floor data. Corpolongo et al. (2023) reported that the unresolved olivine response at Dourbes occurs near 827 cm^{-1} , while Garde olivine measurements produce a dominant response near 830 cm^{-1} . They noted that changes in this unresolved feature depend partly on the relative positions and intensities of the constituent ~ 820 and $\sim 850\text{ cm}^{-1}$ bands. The SuperCam dataset provides a more direct opportunity to evaluate the doublet intensity relationship developed in this study, while SHERLOC provides complementary higher spatial resolution mineralogical context.

3.5.2 Geological Interpretation of Oriented Martian Outcrops

Raman-sensitive texture becomes potentially valuable when stand-off spectroscopy is considered in the context of outcrop-scale structure. A foliated, layered, lineated, or otherwise directionally textured olivine-bearing exposure provides a stratigraphical or petrological direction against which spatial changes in Raman olivine doublet behavior can be compared. The original motivation of the NWA 13276 measurements was that such relationships could allow Raman measurements along exposed Martian stratigraphies to constrain mineral orientation where direct crystallographic measurements are unavailable. The Séítah formation is

particularly relevant because it is both olivine-rich and contains pronounced tabular and centimeter to decimeter scale layering. The Issole, Bastide, and Brac regions display variations in grain size, layer thickness, mineralogy, and bulk chemistry through the exposed stratigraphy, and these variations have been interpreted in the context of an olivine cumulate sequence. The Bastide region hosting the Garde target is also described as platy layered outcrops, while the Brac outcrop associated with Dourbes contains more massive rocks with centimeter to decimeter scale layering. These structures should not automatically be interpreted as crystallographic foliation: macroscopic layering may reflect magmatic stratifications, variations in mineral abundance or grain size, cooling structures, weathering, fracture development, or later modification. Nevertheless, an olivine-rich exposure displaying both directional rock fabric and a spatially coherent Raman doublet asymmetry would provide a testable hypothesis that mineral-scale crystallographic fabric contributes to the macroscopic structure.

For an igneous olivine-rich rock, such a relationship could potentially distinguish otherwise ambiguous geological processes. Preferential crystallographic alignment associated with crystal accumulation or magmatic flow could preserve information about melt transport and emplacement, whereas solid state deformation could generate or modify LPO after crystallization. This possibility is particularly relevant to Séítah because its mineralogy, coarse grain size, chemical stratification, and olivine accumulation have been interpreted as products of fractional crystallization within a slowly cooled magmatic system. A spatial relationship

between visible layering and an orientation-sensitive Raman response could therefore provide an additional constraint on whether the exposed fabric reflects crystallization and magmatic flow, subsequent deformation, or a process unrelated to crystallographic orientation. Alternatively, a visually foliated surface could lack any coherent Raman orientation signal, indicating that the macroscopic fabrics is controlled primarily by compositional layering, grain shape, alteration, fracture development, or erosion rather than pervasive olivine LPO. The absence of a Raman-fabric correlation would itself constitute useful geological information. The representative Martian spectra in **Figure 14** demonstrate that the olivine doublet can remain sufficiently resolved under SuperCam measurement conditions for its relative intensities to be quantified in favorable targets, especially on abraded surfaces.

Applications of this approach may be especially valuable for inaccessible or one-dimensionally exposed Martian stratigraphies. SuperCam could interrogate targets from meter-scale standoff distances, allowing Raman measurements to be acquired from surfaces that cannot be directly accessed by contact instruments. A sequence of Raman observations along a foliated cliff, crater wall, resistant ridge, or layered outcrop could potentially test whether olivine doublet asymmetry varies coherently with visible structure. Such measurements would not independently reconstruct an ODF or produce a pole figure, but they could identify regions in which crystallographic fabric is a plausible contributor to the observed geology and provide constraints on mineral fabrics where direct crystallographic measurements are unavailable.

4.0 Conclusions

Shergottites are crucial for understanding Martian igneous processes, mantle heterogeneity, and surface geology. Their mineralogical, geochemical, and textural characteristics offer a direct comparison for Martian volcanic terrains. High-density co-registered Raman spectroscopy and synchrotron X-ray microdiffraction measurements of NWA 13276 identified an olivine- and pyroxene-rich assemblage with accessory merrillite and apatite and secondary terrestrial calcite. Laue measurements further revealed a high degree of mosaicism throughout the primary Martian mineral assemblage, while secondary calcite retained coherent single-crystal diffraction. Integrating Raman spectroscopy and XRD therefore enhances our ability to interpret mineralogical and crystallographic information preserved within Martian meteorites and provides a basis for comparison with measurements from Mars rovers and future sample return missions.

Studying the lattice-preferred orientation of olivine-pyroxene mineral assemblages in Martian shergottites can provide insights into both microscopic and larger-scale directionality in Martian igneous rocks. We demonstrate that co-registered Raman spectroscopic rasters and X-ray microdiffraction pattern rasters provide a means of simultaneously characterizing mineralogy and crystallographic texture within an intact meteorite section, and function as an alternative to the traditional electron backscatter diffraction analyses used for most meteorite characterization. Employing a semi-supervised, human-in-the-loop statistical learning workflow that combines crystallographic peak and d-spacing matching, whole-pattern

fitting, PCA, UMAP, cosine similarity, spatial relationships, evidence fusion, and iterative expert validation enabled greater depth of diffraction and spectral interpretation while substantially reducing the manual effort required for high-volume mineral identification. This approach enabled high-volume mineralogical classification while retaining physical interpretability and accommodating preferred orientation, mixed mineral assemblages, mosaicity, and diffraction-pattern variability that complicate conventional automated classification. The resulting 1,590 confirmed single-phase olivine patterns enabled quantitative texture reconstruction across the meteorite raster.

E-WIMV texture reconstructions revealed strong, non-random olivine lattice preferred orientations throughout NWA 13276, with a pervasive *c*-axis component across spatially separated olivine-bearing regions. Comparison of these independently reconstructed crystallographic textures with their co-registered Raman spectra demonstrates that the relative intensities of the diagnostic $\sim 810\text{-}870\text{ cm}^{-1}$ olivine doublet are sensitive to crystallographic orientation. *C*-axis dominated orientations preferentially exhibit enhanced intensity in the higher-wavenumber peak of the doublet, whereas *a*- and *b*-axis contributions preferentially exhibit enhanced intensity in the lower-wavenumber component, with mixed crystallographic orientations producing intermediate spectral responses. These results demonstrate that unpolarized Raman spectroscopy still contains crystallographic information in addition to its established sensitivity to mineralogy and composition.

Ongoing studies integrating Raman spectroscopy and X-ray diffraction will enhance our ability to interpret data from Mars rovers and future sample return missions and enhance our ability to infer lattice preferred orientations from cliffsides and outcrops. Both the *Perseverance* rover's SuperCam and SHERLOC instruments are equipped to detect olivine-bearing mineral assemblages on Mars, and SuperCam can directly resolve the $\sim 810\text{-}870\text{ cm}^{-1}$ olivine doublet in sufficiently high-quality spectra. Representative SuperCam spectra from olivine-bearing targets in Jezero Crater exhibit variability in the relative intensities of this same doublet, demonstrating that the orientation-sensitive spectral parameter characterized in NWA 13276 is observable under Martian measurement conditions. This work expands Raman spectroscopy beyond mineral identification and composition toward the remote characterization of crystallographic texture, providing a pathway to infer lattice preferred orientations, magmatic fabrics, and deformation histories from intact Martian rocks. Applied across cliffsides, crater walls, and layered outcrops, orientation-sensitive Raman spectroscopy could ultimately allow scientists to remotely reconstruct crystallographic preferred orientations and magmatic flow patterns in Jezero Crater and beyond.

Figures

Chapter 1

Figure 1 Process diagram stepping through the challenges addressed by the use of machine learning on Mars surface rovers.

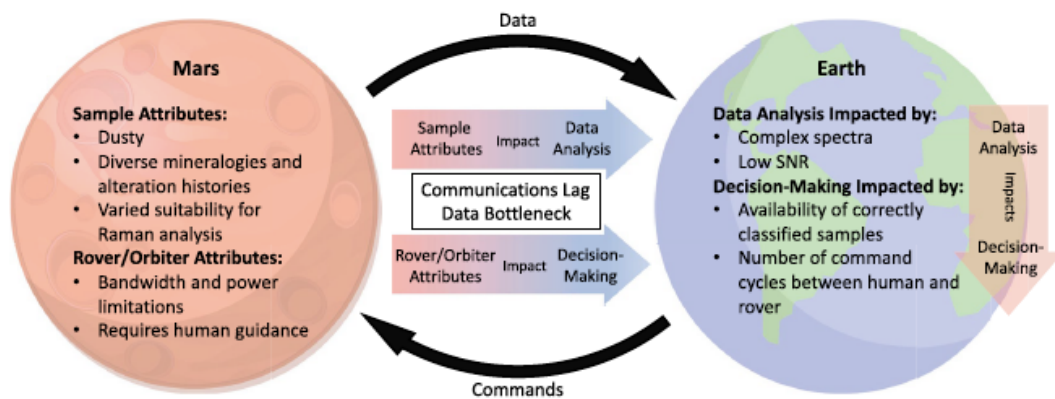


Figure 2 Representative Raman spectra (1 accumulation over a 1-120 s integration) for each pure mineral classification and the three powder mixtures included in the training sets. A range of relevant silicate structures found on Earth and Mars was included: phases with isolated tetrahedra (nesosilicates), single and double chain tetrahedra (inosilicates), sheets (phyllosilicates), and framework silicates (tectosilicates).

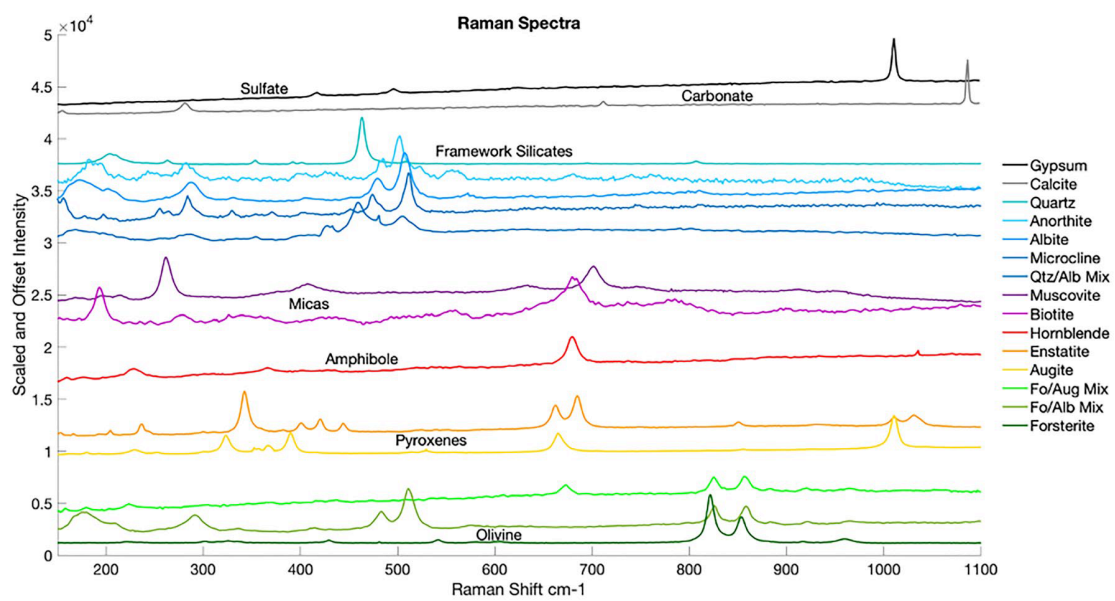
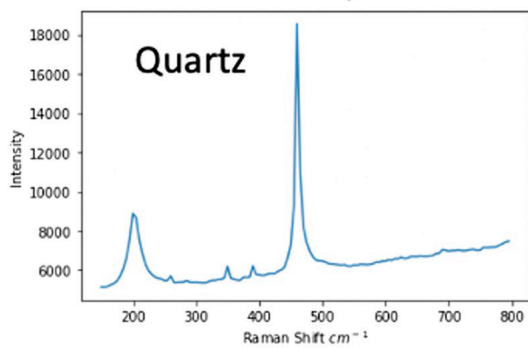


Figure 3 Raw Raman spectrum, trimmed to 150 cm^{-1} to 800 cm^{-1} to highlight Si-O-Si regions (left column), and spectrum passed through the Ricker CWT with top 5 peaks and intensities extracted for independent metrics comparisons with other statistical methods (right column) for quartz, albite, hornblende, and biotite. The Ricker CWT captures all the primary peaks traditionally used to identify silicates, unless they overlap one another, such as doublets and triplets. In the case of albite, which has a doublet in the $504\text{-}509\text{ cm}^{-1}$ region, the more intense peak position is captured. The location of the most intense peak still allows identification of the feldspar endmembers albite, anorthite, and microcline, which have very similar spectra and Si-O-Si doublets.. The CWT pushes some non-peak portions of the data into negative intensities, which allows the peak-finding algorithm to better identify Raman peaks using a signal-to-noise (SNR) ratio threshold. Consequently, this improves the speed at which our CNN model converges. An artifact of the transform is that large peaks appear at the truncated ends of the spectra, and thus the highest and lowest frequency peaks within the transform are dropped before extracting Raman peak information. This edge effect biases the uppermost and lowermost $\sim 50\text{ cm}^{-1}$ of the spectra; the spectral regions that this bias effects is, of course, entirely determined by the spectral window chosen.

Raw Raman Spectrum



CWT Transform and Top 5 Peaks

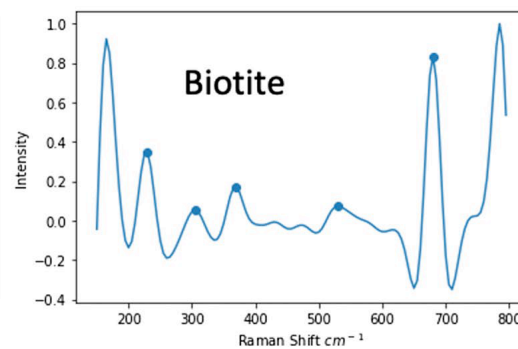
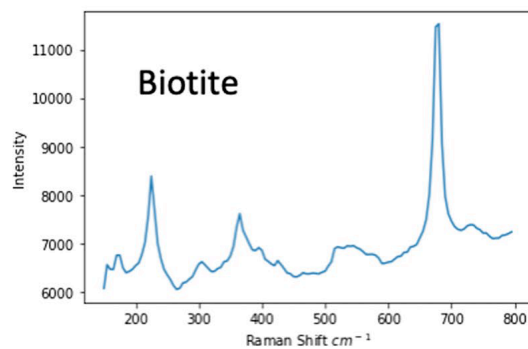
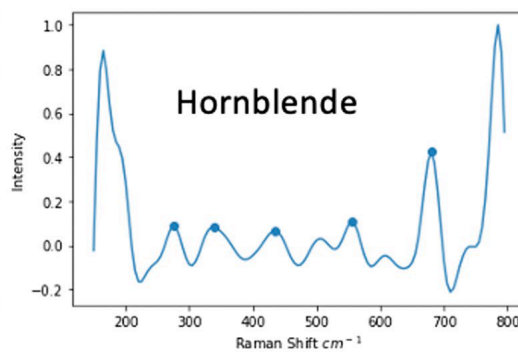
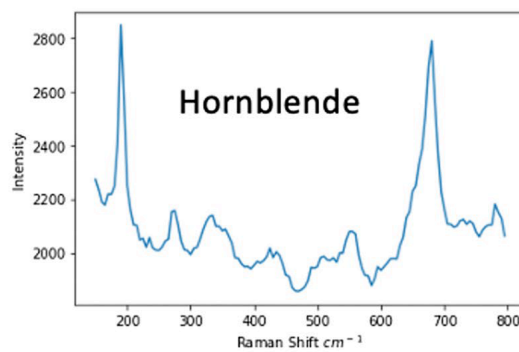
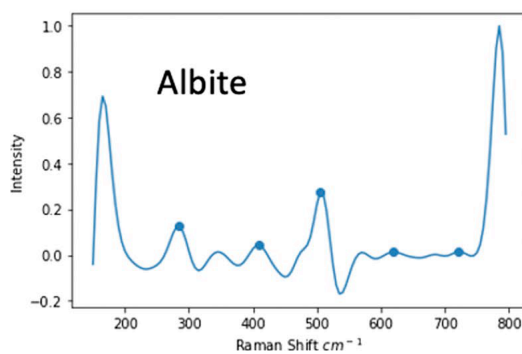
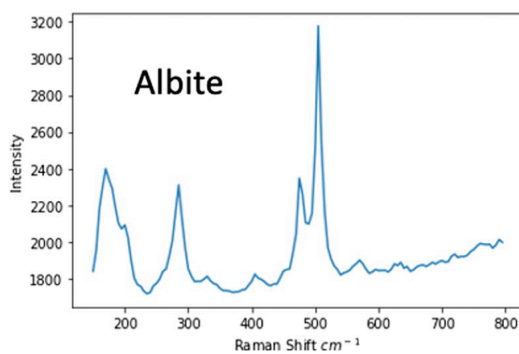
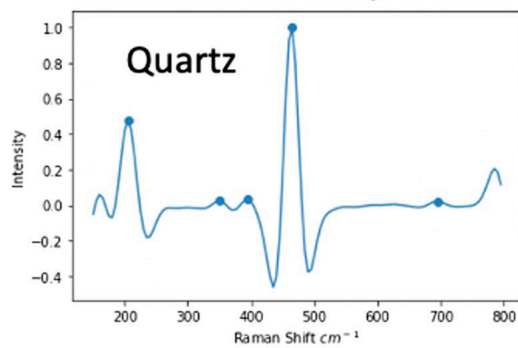


Figure 4 The CNN architecture includes a LeakyRelu activation function, batch normalization, MaxPooling, and decreasing convolutions with each progressive layer. The last two layers of the CNN are fully connected in a dense layer and include batch normalization, TanH and Softmax activation functions, and a random node dropout.

$$5*(21*1*16)*16 + 16*(11*1*32)*32 + 32*(5*1*64)*64 + 2048 + 2048*(14*2048) = 59584768 \text{ learnable parameters.}$$

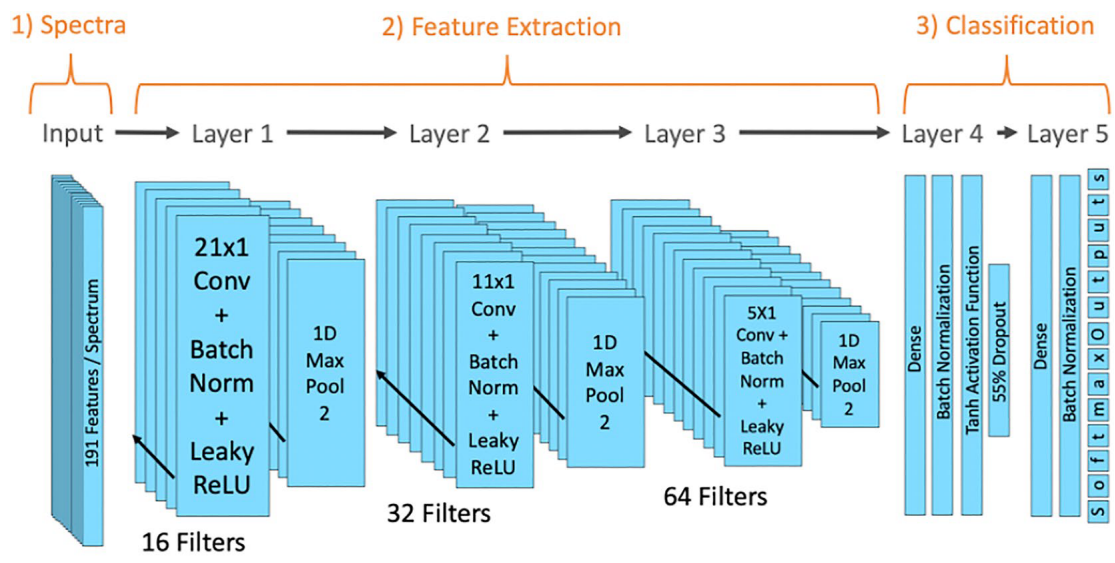


Figure 5 Random sampling of 100 spectra showing within class spectral variation for microcline. Spectra range from excellent, to good, to fair, to poor quality; they also include a range of baselines. Sharp randomly spaced lines are generated by cosmic rays.

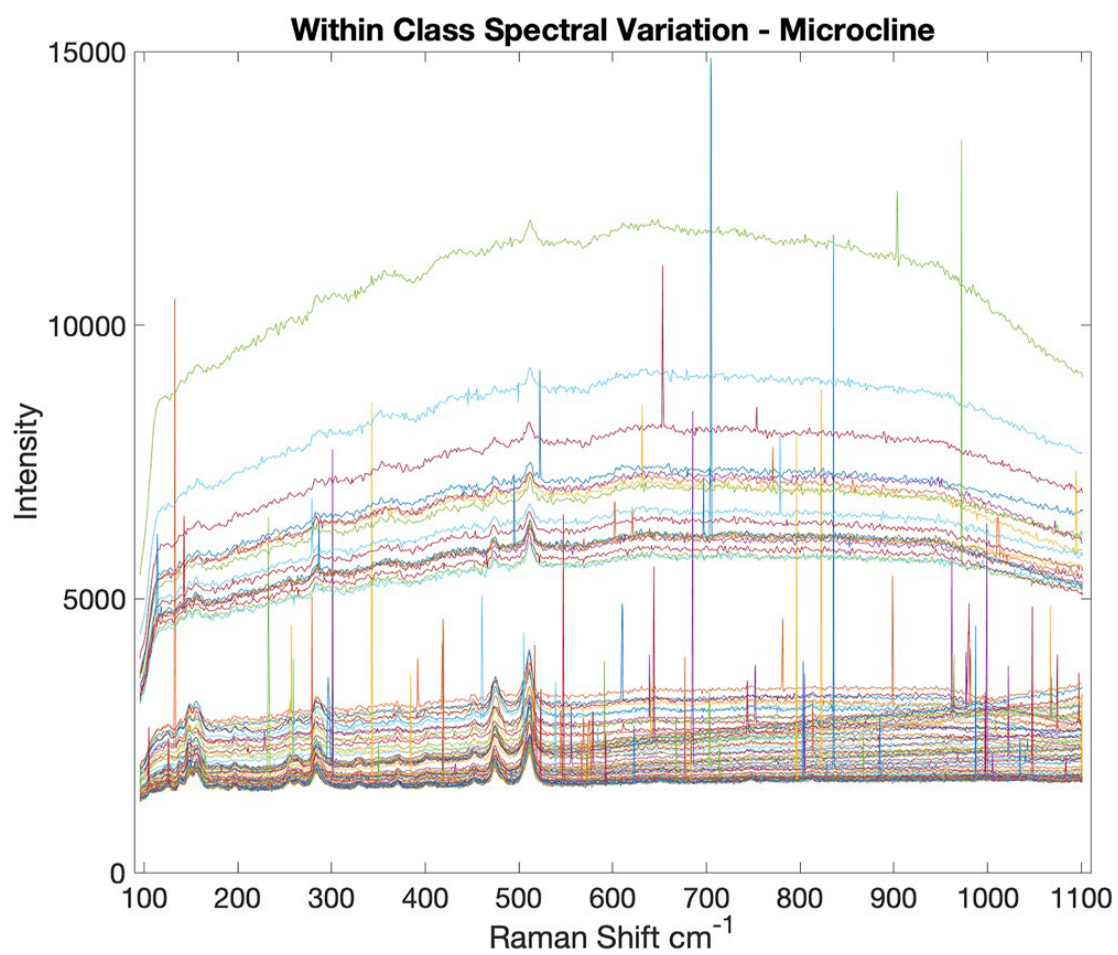


Figure 6 a) An example of an overfitting CNN. Loss and accuracy curves do not converge until epoch 140+. The training set converges at 99% accuracy within 2-3 epochs while the validation set lags behind and does not fully converge until epoch 145. b) Current working CNN learning curves converge quickly and accurately.

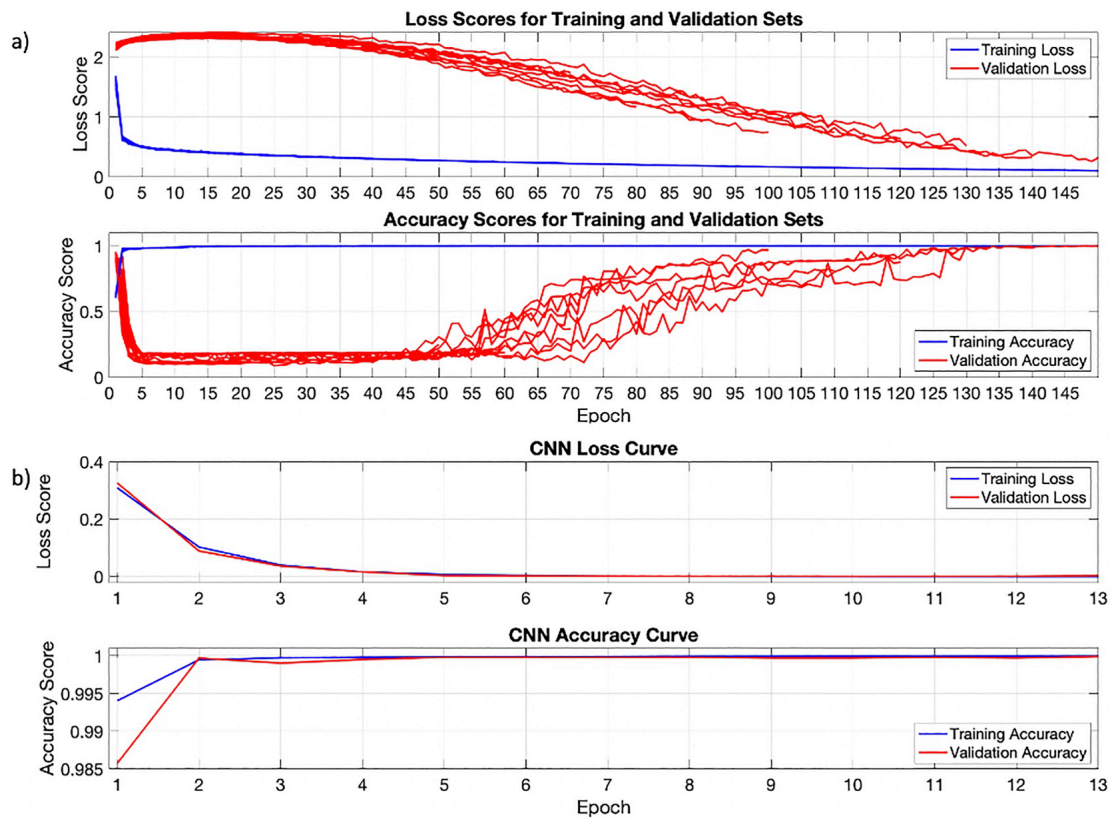


Figure 7 Weighted F1 scores using training sets of varying sizes.

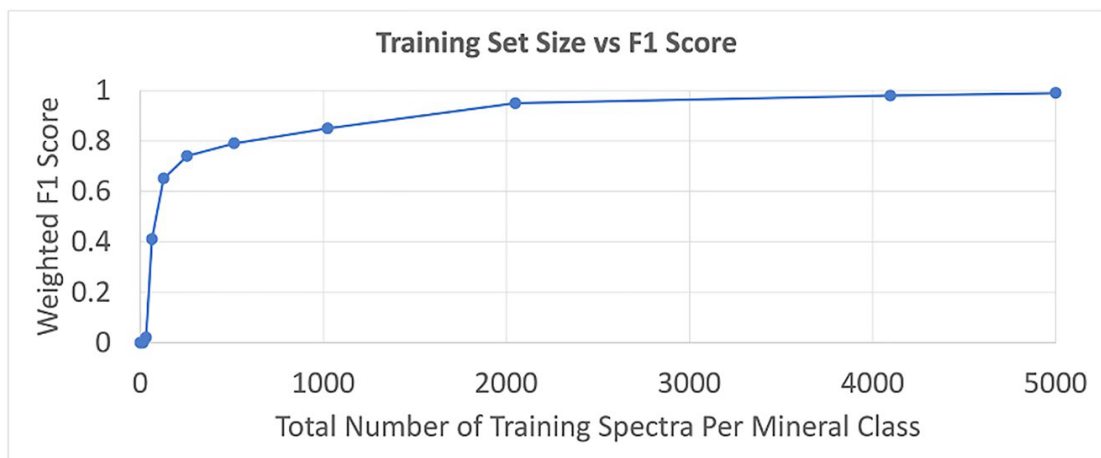


Figure 8 CNN successful classifications with average top three probability assignments. Variability in the amphibole spectra (particularly) is likely to be also affected by the different orientations of randomly positioned samples.

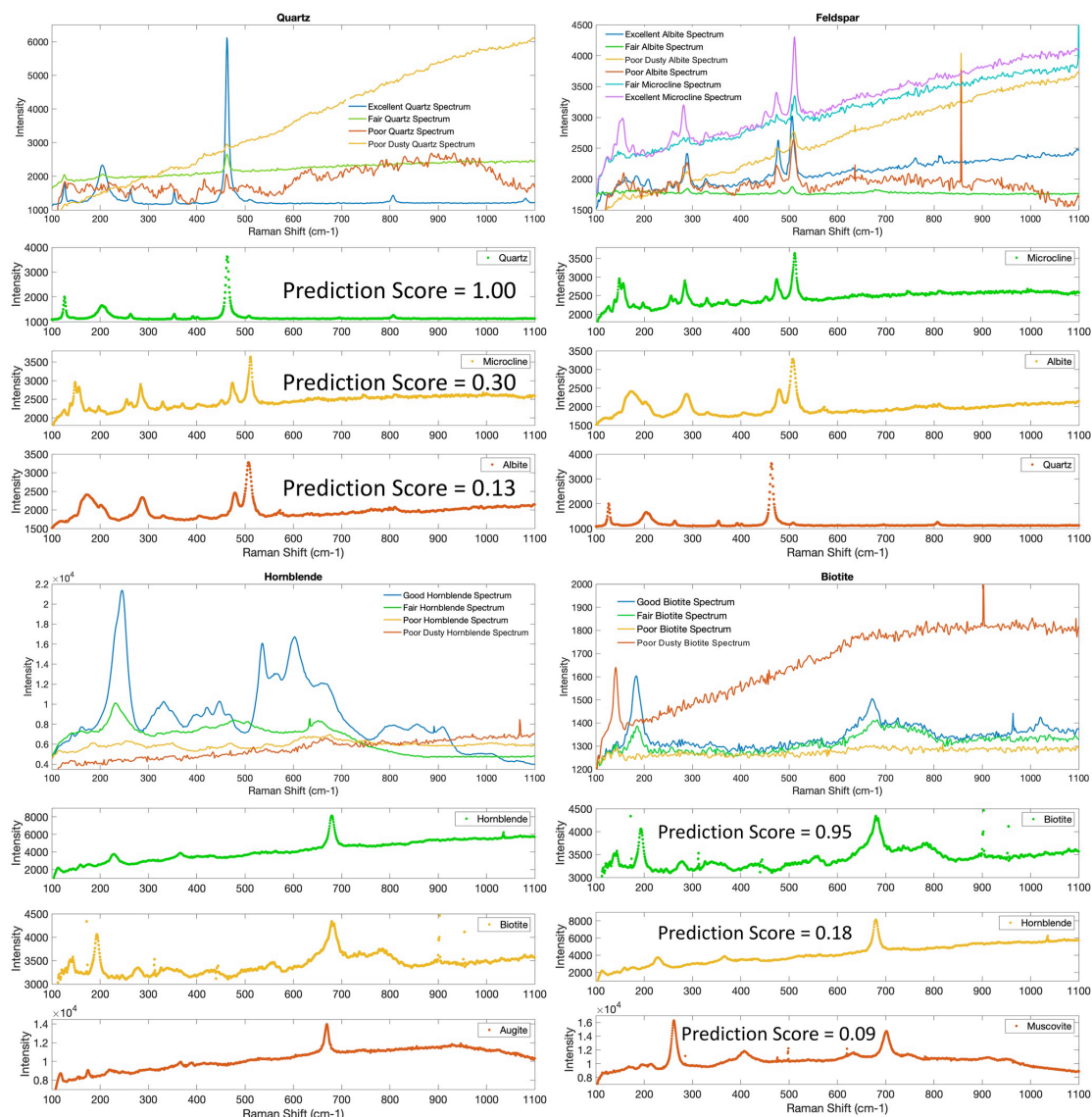
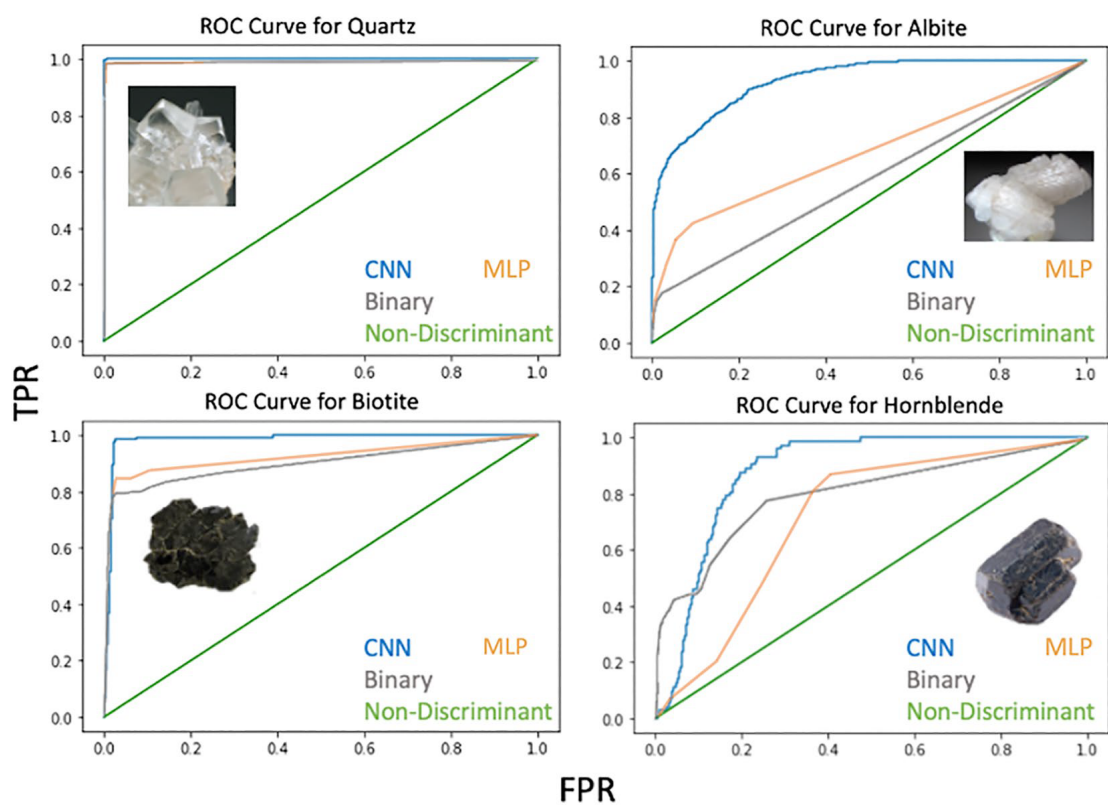


Figure 9 Superimposed ROC curves for the CNN and random forest binary classifiers with FPR on the x axis and TPR on the y axis. The green diagonal is representative of a random classifier that has no ability to discriminate between classes. A perfect classifier makes a right angle at the upper left, similar to the quartz ROC curve.

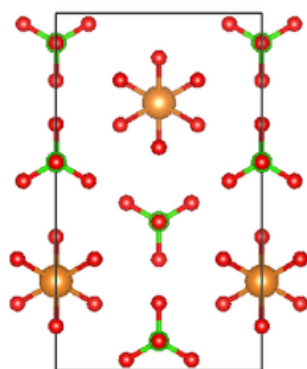


Chapter 2

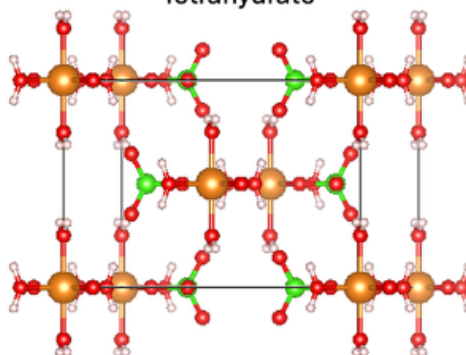
Figure 1 Crystal structures of the experimentally investigated hydration phases of magnesium perchlorate and magnesium sulfate. $\text{Mg}(\text{ClO}_4)_2$ is shown as the hexahydrate, tetrahydrate, dihydrate, and anhydrate, illustrating the discrete structural changes that accompany progressive dehydration. MgSO_4 is shown as epsomite (heptahydrate) and hexahydrate, the crystalline phases observed prior to the development of poorly crystalline and X-ray-amorphous dehydration products at higher temperatures. Crystal structures are derived from published crystallographic models of West (1935), Solovyov (2011), Robertson and Bish (2011), Lim (2011), Baur (1964), and Falkin et al. (1963).



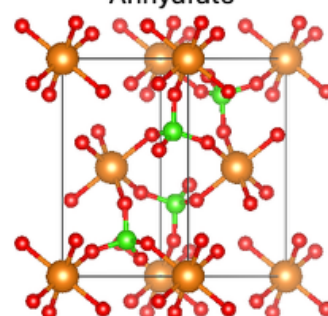
Hexahydrate



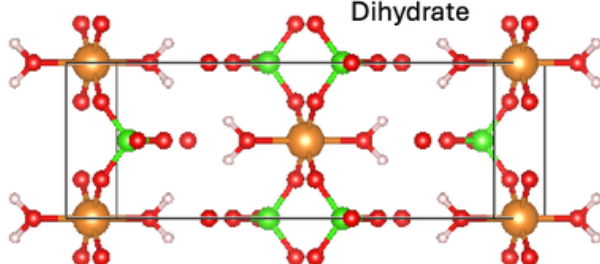
Tetrahydrate



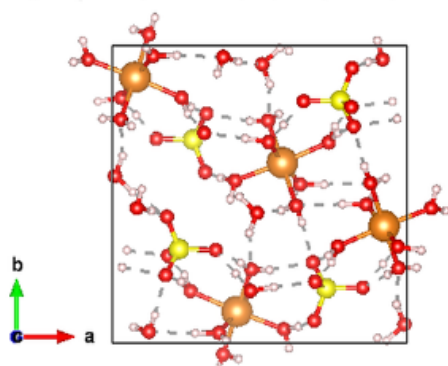
Anhydrate



Dihydrate



Epsomite (heptahydrate)



Hexahydrate

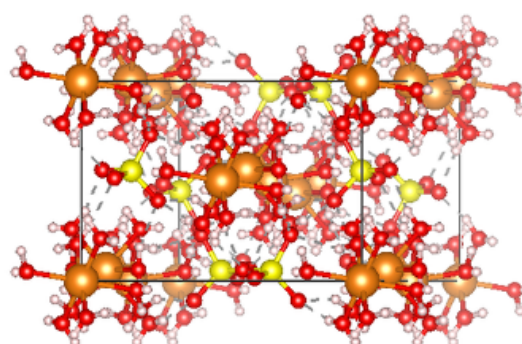


Figure 2 Variable-temperature Raman spectra of $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 phases during dehydration. (a) Locally Min–Max normalized Raman spectra of $\text{Mg}(\text{ClO}_4)_2$ highlighting the evolution of the ν_2 and ν_4 bending modes, ν_1 symmetric stretch, ν_3 asymmetric stretch, and OH stretching region with increasing temperature. (b) Corresponding MgSO_4 spectra highlighting the same vibrational regions. Dotted vertical lines mark the approximate range of peak migration for each vibrational mode, and colored labels indicate the hydration phases identified from complementary X-ray diffraction measurements. Spectra collected below 20 °C were acquired with the portable Raman spectrometer and therefore do not include the OH stretching region. Deconvolved normalized Raman peak spectra are provided in the Supplement.

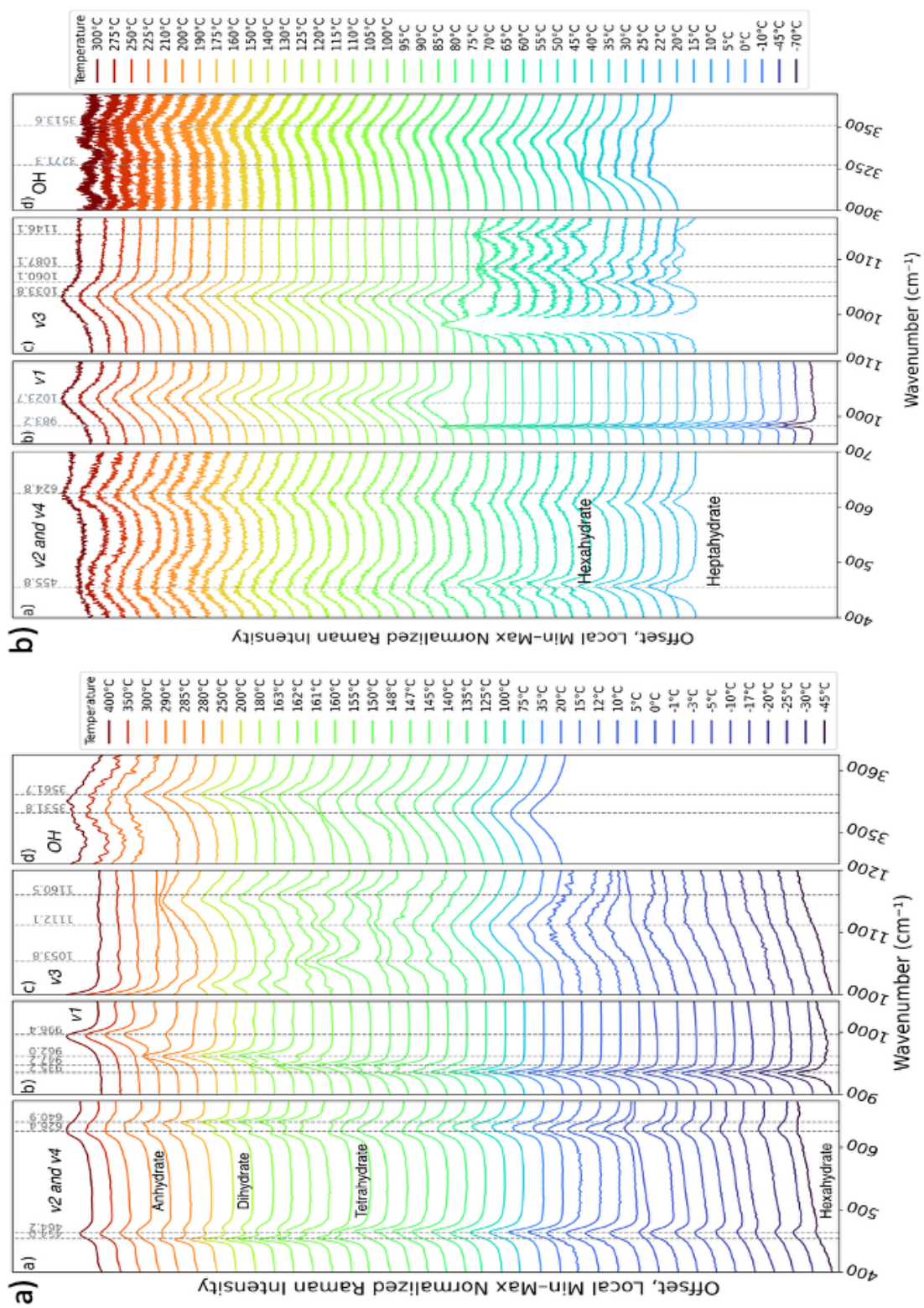


Figure 3 Hydration-dependent evolution of Raman frequencies and tetrahedral force constants for $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 . (a) Temperature dependence of the ν_1 , ν_2 , ν_3 , and ν_4 Raman vibrational modes of $\text{Mg}(\text{ClO}_4)_2$ during dehydration. Colored backgrounds indicate the hydration phases. (b) Corresponding Raman mode evolution for MgSO_4 . The heptahydrate–hexahydrate transition is followed by the development of poorly crystalline and X-ray–amorphous dehydration products at higher temperatures. (c) Four-parameter Wilson GF force constants for $\text{Mg}(\text{ClO}_4)_2$ derived from the Raman frequencies. The Cl–O stretching constant (f_r) increases through successive dehydration reactions, whereas the angular bending (f_θ), stretch–bend coupling ($f_{r\theta}$), and bend–bend interaction ($f_{\theta\theta}$) constants record hydration-dependent changes in tetrahedral bonding and symmetry. Colored stars show force constants calculated from representative SHERLOC (SH) and SuperCam (SC) Raman spectra of Martian perchlorates for comparison with the laboratory trends. The horizontal positions of the rover data points are arbitrary and are shown only to avoid overlap; only the force constant values (N m^{-1}) are physically meaningful. (d) Corresponding Wilson GF force constants for MgSO_4 . In contrast to $\text{Mg}(\text{ClO}_4)_2$, sulfate force constants evolve more continuously during dehydration, consistent with progressive structural disordering rather than discrete symmetry-changing phase transitions. Colored stars indicate force constants calculated from representative SHERLOC and SuperCam sulfate spectra acquired at Jezero crater. Rover data is discussed in Section 4.5.

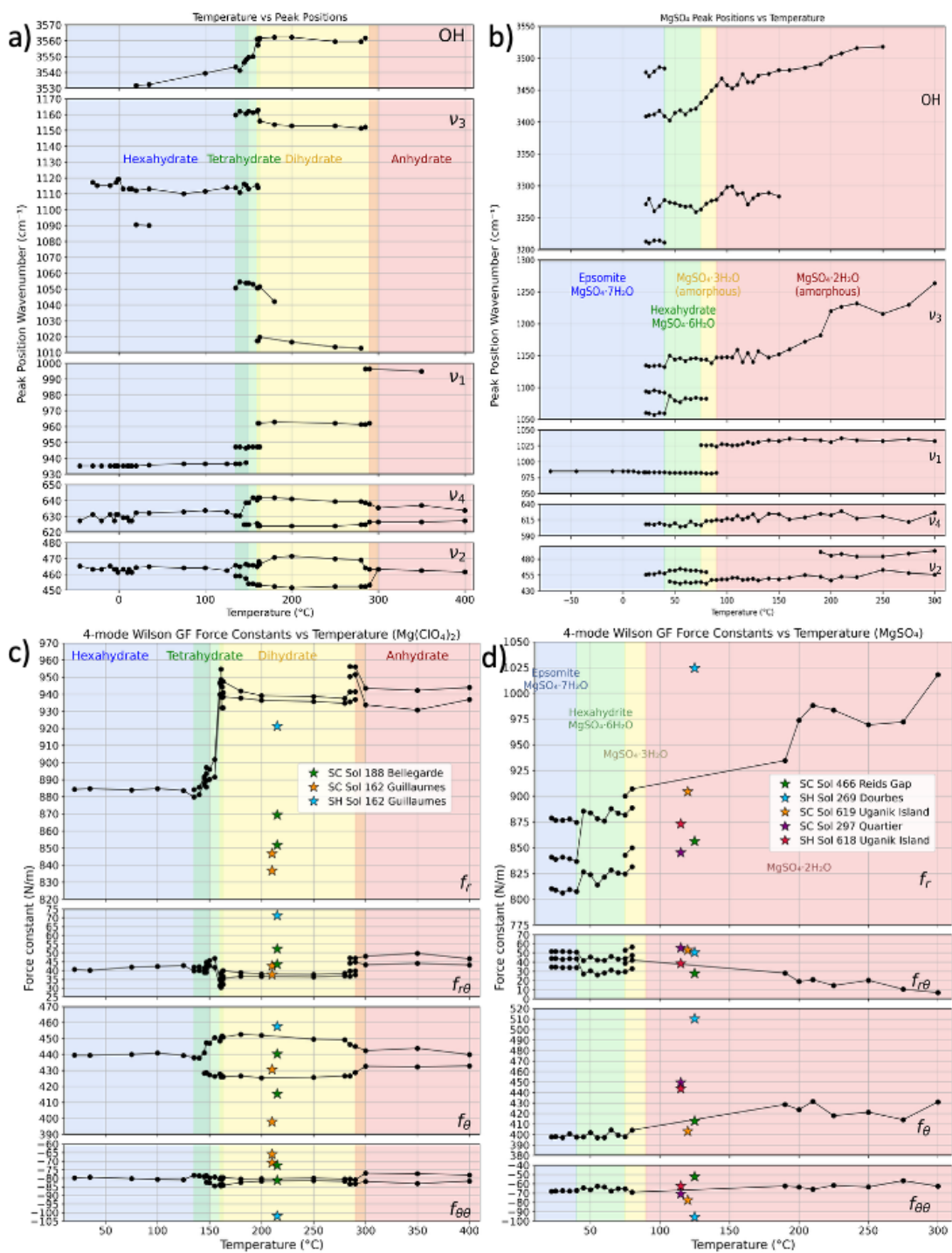


Figure 4 Hydration-dependent Fermi resonance in $\text{Mg}(\text{ClO}_4)_2$ hexahydrate. (a) Lorentzian deconvolution of the ν_1 symmetric stretching region showing the low-frequency $2\nu_2$ overtone ($\sim 923\text{--}929\text{ cm}^{-1}$) as a shoulder on the ν_1 fundamental between -45 and $125\text{ }^\circ\text{C}$. (b) Temperature dependence of the observed ν_1 and $2\nu_2$ peak positions together with the calculated unperturbed vibrational frequencies from the two-level avoided-crossing model. Square symbols denote measurements acquired with the portable Raman spectrometer and circles denote measurements acquired with the Horiba Raman system. (c) Temperature dependence of the separation between the observed ν_1 and $2\nu_2$ modes. (d) Ratio of the overtone ($2\nu_2$) Raman intensity to the ν_1 fundamental intensity, showing systematic variation across the hexahydrate stability field. The Fermi resonance is observed only in the hexahydrate phase and disappears following formation of the tetrahydrate as ν_2 splits and the anharmonic coupling is quenched.

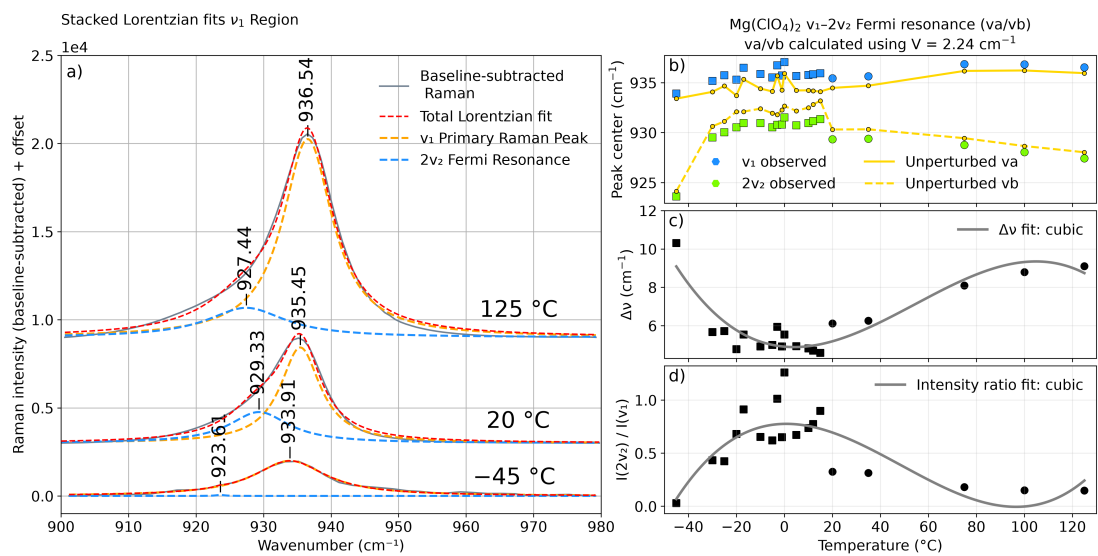


Figure 5 Evolution of low-frequency lattice modes during dehydration of $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 . (a) Temperature-dependent Raman spectra of $\text{Mg}(\text{ClO}_4)_2$ in the 100–425 cm^{-1} region showing representative spectra for the hexahydrate (35 °C), tetrahydrate (155 °C), and dihydrate (180 °C). Progressive shifts, splitting, and intensity changes of the lattice modes reflect dehydration-driven changes in Mg^{2+} coordination, ClO_4^- interactions, and the local crystal framework. (b) Temperature-dependent Raman spectra of MgSO_4 in the 100–400 cm^{-1} region showing representative spectra for the heptahydrate (22 °C), hexahydrate (50 °C), and partially amorphous $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ (180 °C). In contrast to $\text{Mg}(\text{ClO}_4)_2$, the low-frequency sulfate lattice modes evolve more continuously during dehydration, consistent with progressive structural disordering while preserving local sulfate coordination.

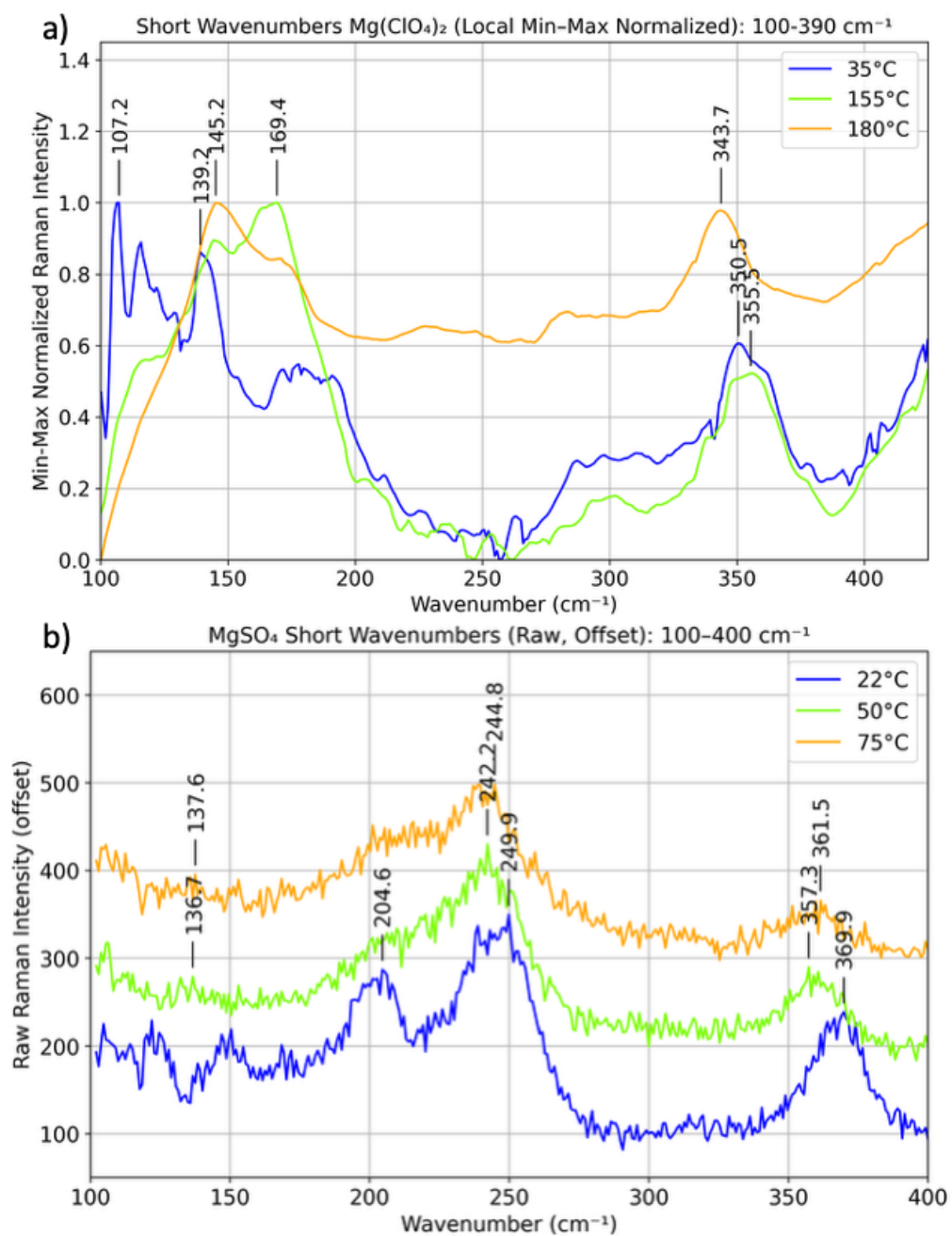


Figure 6 Comparison of representative Raman spectra and powder X-ray diffraction patterns during dehydration of $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 . **(a)** $\text{Mg}(\text{ClO}_4)_2$ Raman spectra collected under vacuum from -70 to 425 °C with representative phase-pure spectra shown at 20 °C (hexahydrate), 155 °C (tetrahydrate), 180 °C (dihydrate), and 300 °C (anhydrate). Corresponding X-ray diffraction patterns were collected at 20 °C, 110 °C, 170 °C, and 300 °C. Each Raman spectrum corresponds to a crystalline hydration phase identified by XRD, demonstrating discrete dehydration through successive hexahydrate, tetrahydrate, dihydrate, and anhydrous phases while preserving long-range crystallinity. Crystal structures are derived from published CIF models for the hexahydrate (West, 1935), tetrahydrate (Solovyov et al., 2011), dihydrate (Robertson and Bish, 2011), and anhydrate (Lim et al., 2011). Full Raman and XRD datasets are provided in the Supplement.

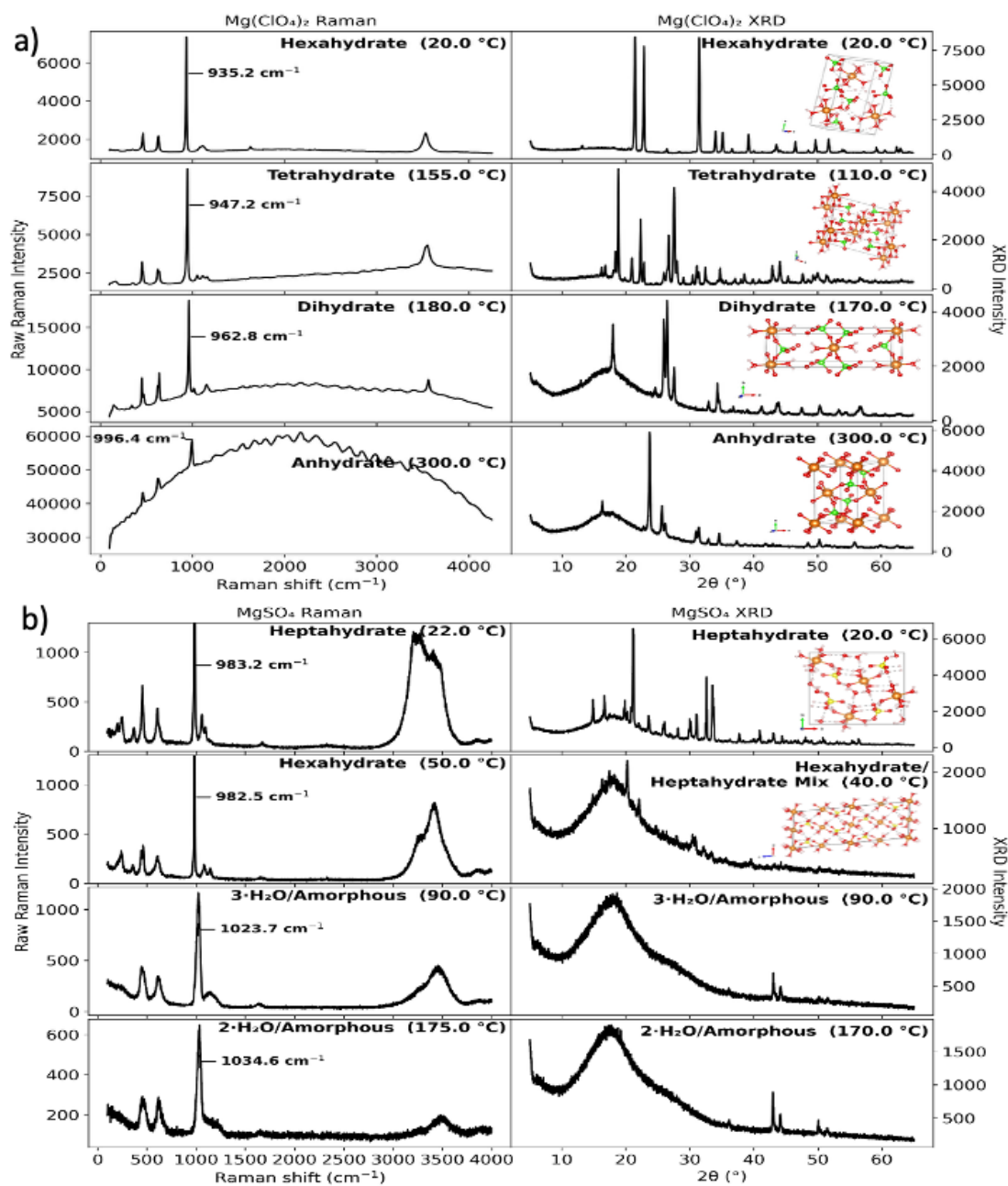
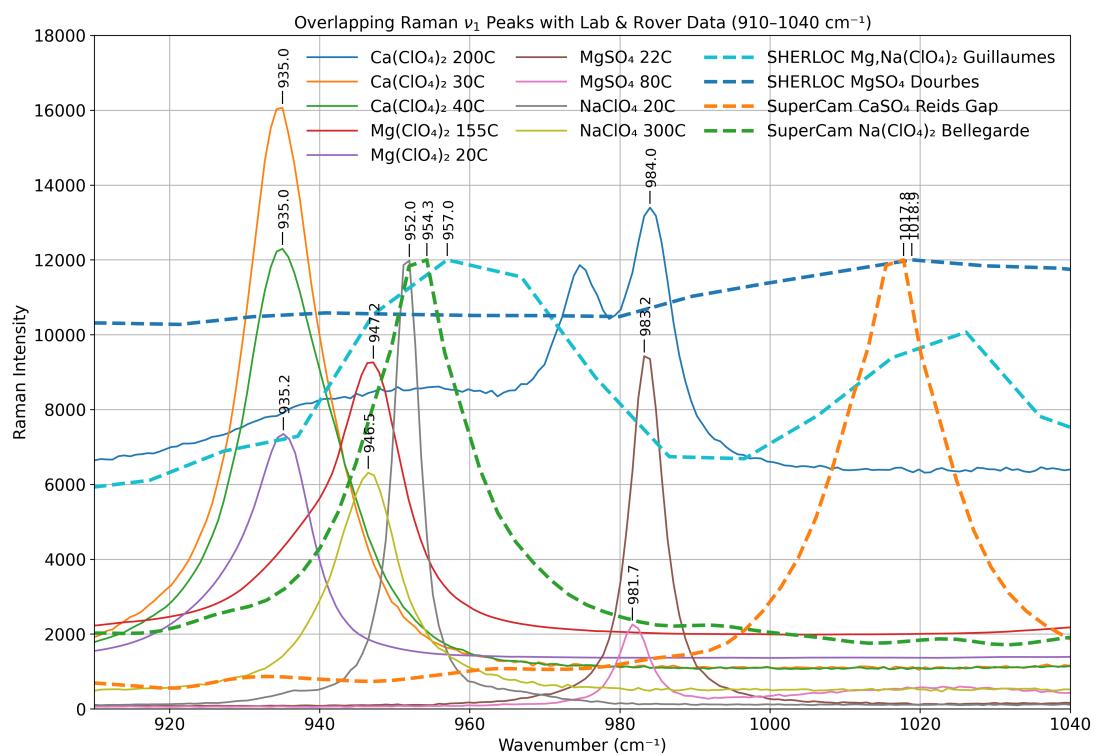


Figure 7 Raman spectra of the ν_1 symmetric stretching region (900–1020 cm^{-1}) for magnesium perchlorate, calcium perchlorate, sodium perchlorate, magnesium sulfate, and representative SHERLOC and SuperCam rover spectra acquired from Martian hydrated salts. Laboratory spectra span multiple hydration states and temperatures. The spectra demonstrate substantial overlap among ν_1 peak positions, including $\text{Mg}(\text{ClO}_4)_2$ hexahydrate ($\sim 935 \text{ cm}^{-1}$), MgSO_4 epsomite ($\sim 983 \text{ cm}^{-1}$), $\text{Ca}(\text{ClO}_4)_2$ hydration phases ($\sim 935\text{--}984 \text{ cm}^{-1}$), and NaClO_4 ($\sim 952 \text{ cm}^{-1}$). The $\text{Mg}(\text{ClO}_4)_2$ hexahydrate additionally exhibits a low-wavenumber shoulder arising from the $2\nu_2$ Fermi resonance. The rover spectra illustrate that similar ν_1 peak positions may correspond to different mineral compositions, hydration states, and local bonding environments. These overlaps demonstrate that reliable mineral identification requires interpretation of the full Raman spectrum, including the ν_2 and ν_4 bending modes, low-frequency lattice vibrations, OH stretching region, Raman peak shapes, and, where applicable, force constant analysis, rather than the ν_1 region alone.



Chapter 3

Figure 1 NWA 13276 Raman and XRD/Laue grids. a) and b) show the starting and ending measurement locations highlighted by the red laser. c) The meteorite slice with the Raman and XRD rasters superimposed (yellow rectangle). d) Zoomed into with the superimposed XRD/Laue analysis raster. The translucent green, blue, grey, and yellow overlay shows automated phase identification using the collected XRD patterns.

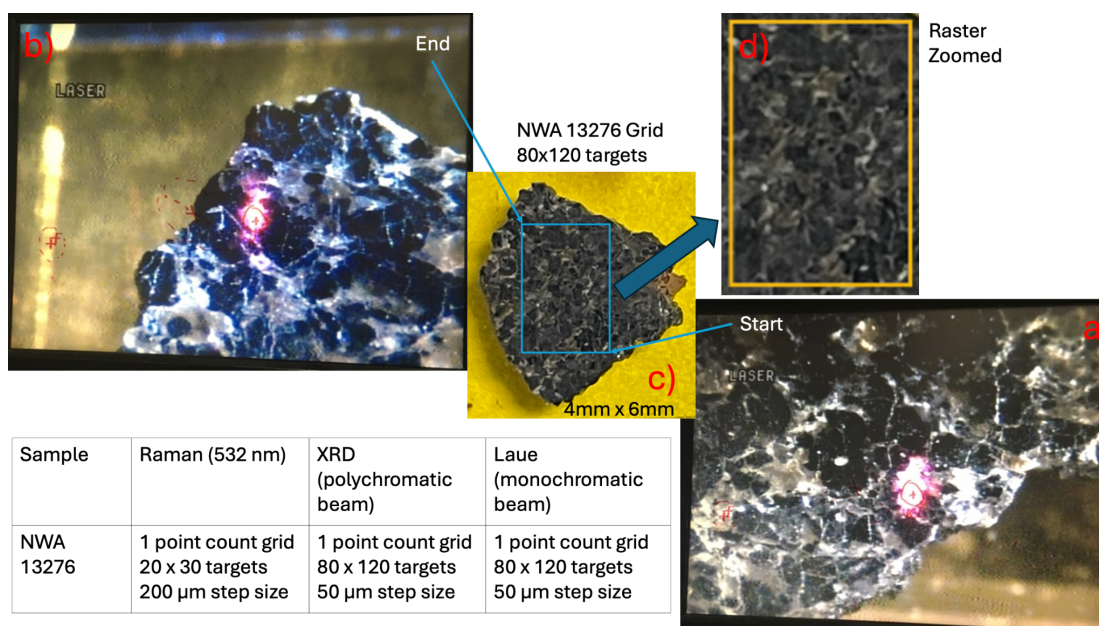


Figure 2 Raman, X-ray diffraction, and Laue diffraction rasters were fed through an expert-guided semi-supervised statistical learning and active learning template matching pipeline for mineral identification and subsequent XRD texture analysis, pole figure creation, and correlation between Raman spectra and crystallographic orientation.

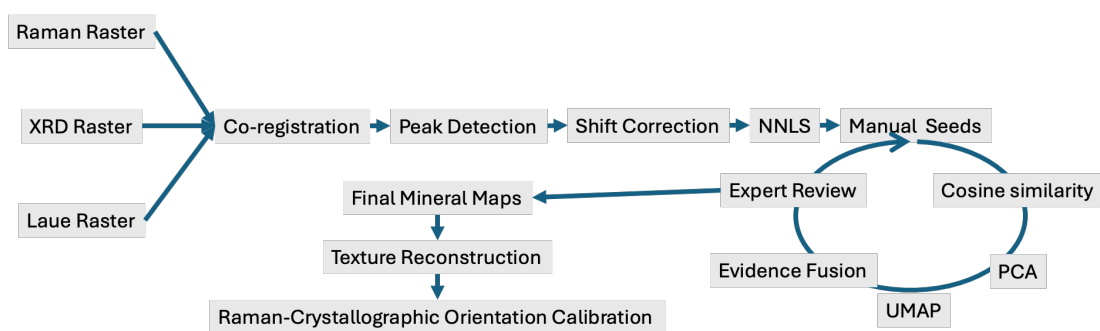


Figure 3 Principal component analysis of NWA 13276 XRD raster. Pairwise score plots show the distribution of all diffraction patterns in the first 5 PCs, with manually confirmed olivine patterns highlighted in orange. Confirmed olivines occupy multiple coherent regions of PCA space indicating systematic variability within the olivine diffraction population likely indicating preferred orientation. The scree plot shows the explained variance of successive principal components, and the cumulative explained variance demonstrates that the first 15 PCs account for 90% of the total variance and 30 PCs retain ~97%.

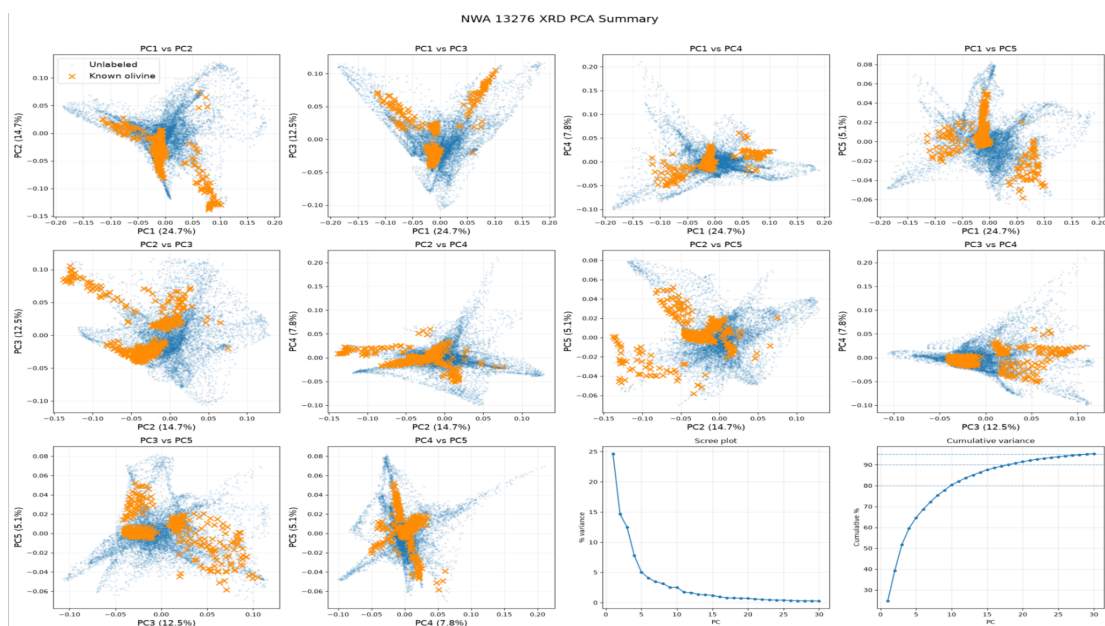


Figure 4 Each loading magnitude identifies the diffraction peaks' contribution to each principal component. Narrow loading extrema coincide with measured olivine, pyroxene, or calcite reflections, and their different preferred orientations found in NWA 13276, confirming that PCA is organizing XRD patterns according to diffraction features and not just statistics. Detailed assignments of the principal loading features are provided in Table 1.

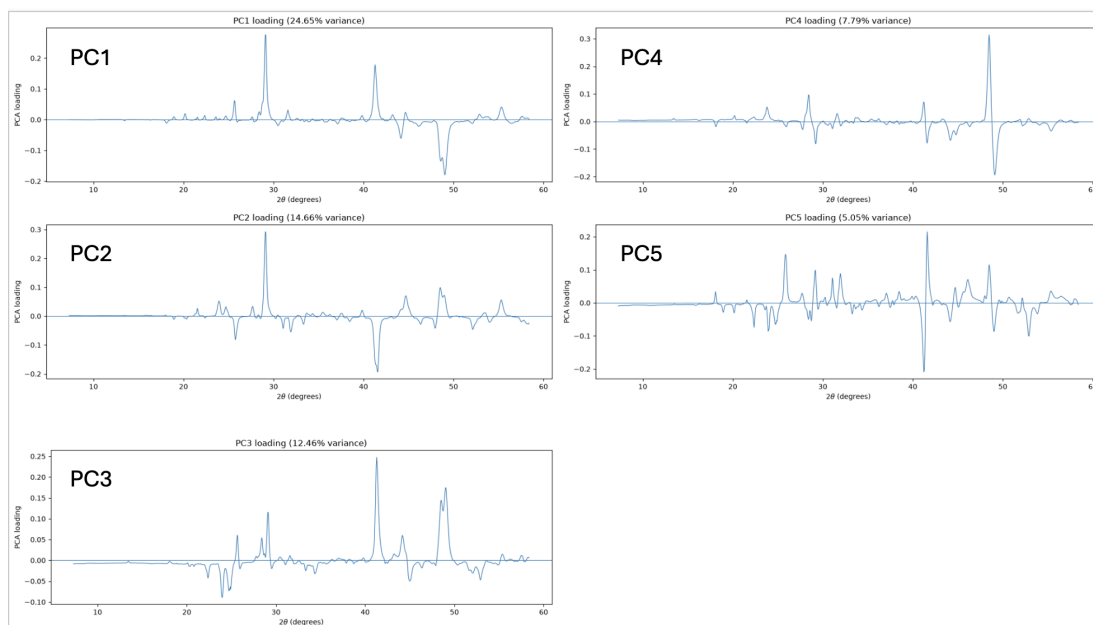


Figure 5 UMAP representation and spatial back-propagation of the NWA 13276 XRD raster. a) Two-dimensional UMAP embedding calculated from the first 15 PCA scores. Several clusters of manually confirmed olivines indicate lattice preferred orientations and to a lesser extent Mg/Fe abundances. The narrow filaments represent gradual statistical transitions between diffraction pattern clusters. b) and c) UMAP1 and UMAP2 coordinates projected back onto the original XRD raster positions. Although no spatial coordinates were supplied to UMAP, both components form coherent spatial domains across the meteorite, demonstrating that statistically related diffraction patterns also exhibit mineral grain-scale spatial organization. These gradients may reflect systematically shifting sample and detector geometry or changing preferred orientation or mineral composition.

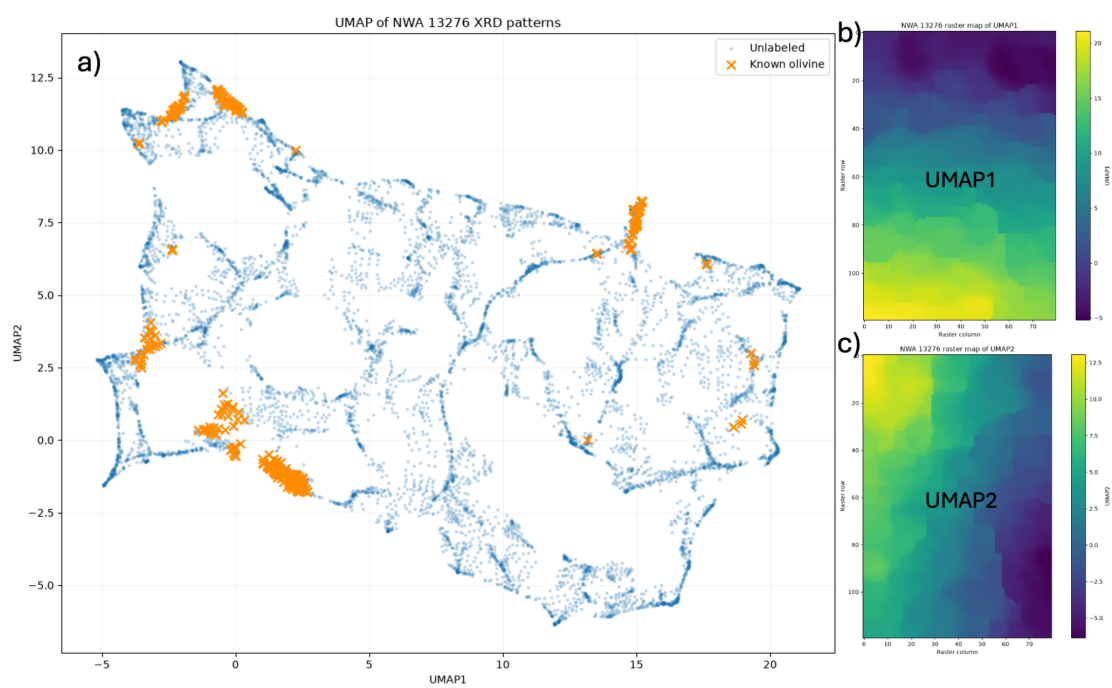


Figure 6 Co-registered Raman, synchrotron μ XRD, and Laue μ XRD rasters of NWA 13276. a) Manually identified Raman mineral raster acquired on a 20 x 30 grid at 200 μ m intervals. Colors indicate single-phase, mixed phase, and uncertain mineral assignments. b) Synchrotron μ XRD raster acquired on an 80 x 120 grid at 50 μ m intervals, showing the spatial distribution of high-confidence olivine identifications. c) Laue μ XRD raster acquired over the same 80 x 120 grid. Coherent single-crystal Laue diffraction is concentrated in secondary calcite. The rest of the primary igneous assemblage is predominantly mosaiced.

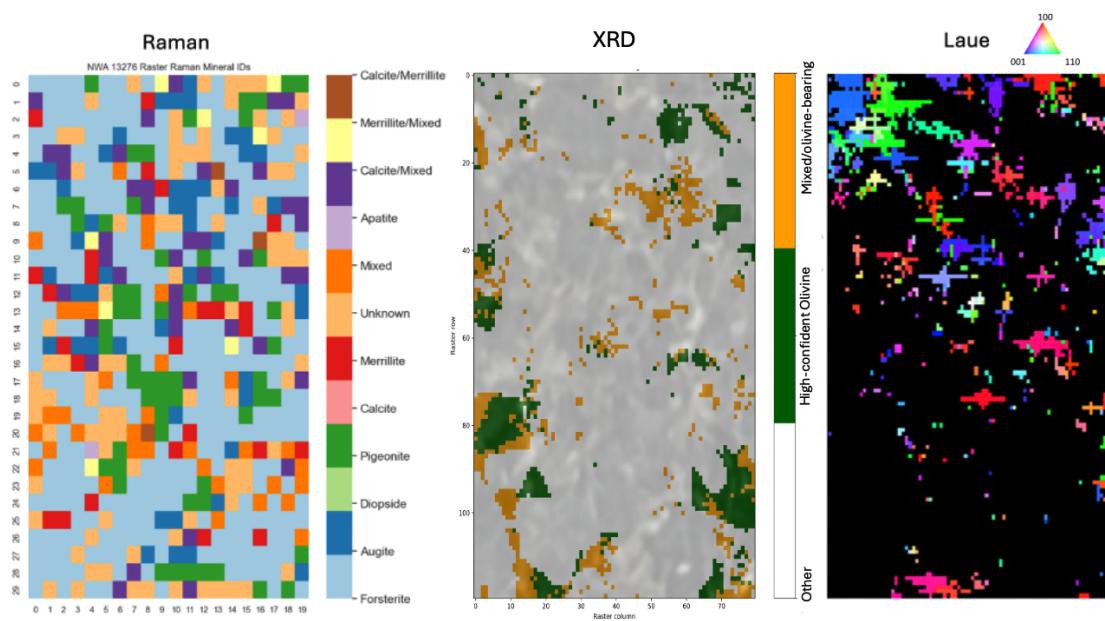


Figure 7 Normalized nearest-neighbor mineral associations in the NWA 13276 Raman raster. Rows represent the mineral classification of each central Raman measurement and columns represent the mineral classifications of neighboring raster positions. Values are normalized neighbor counts and quantify the relative frequency with which each mineral of mixed-phase class occurs adjacent to another class. The high frequency of olivine-containing associations reflects the high modal abundance and broad spatial distribution of olivine across the raster.

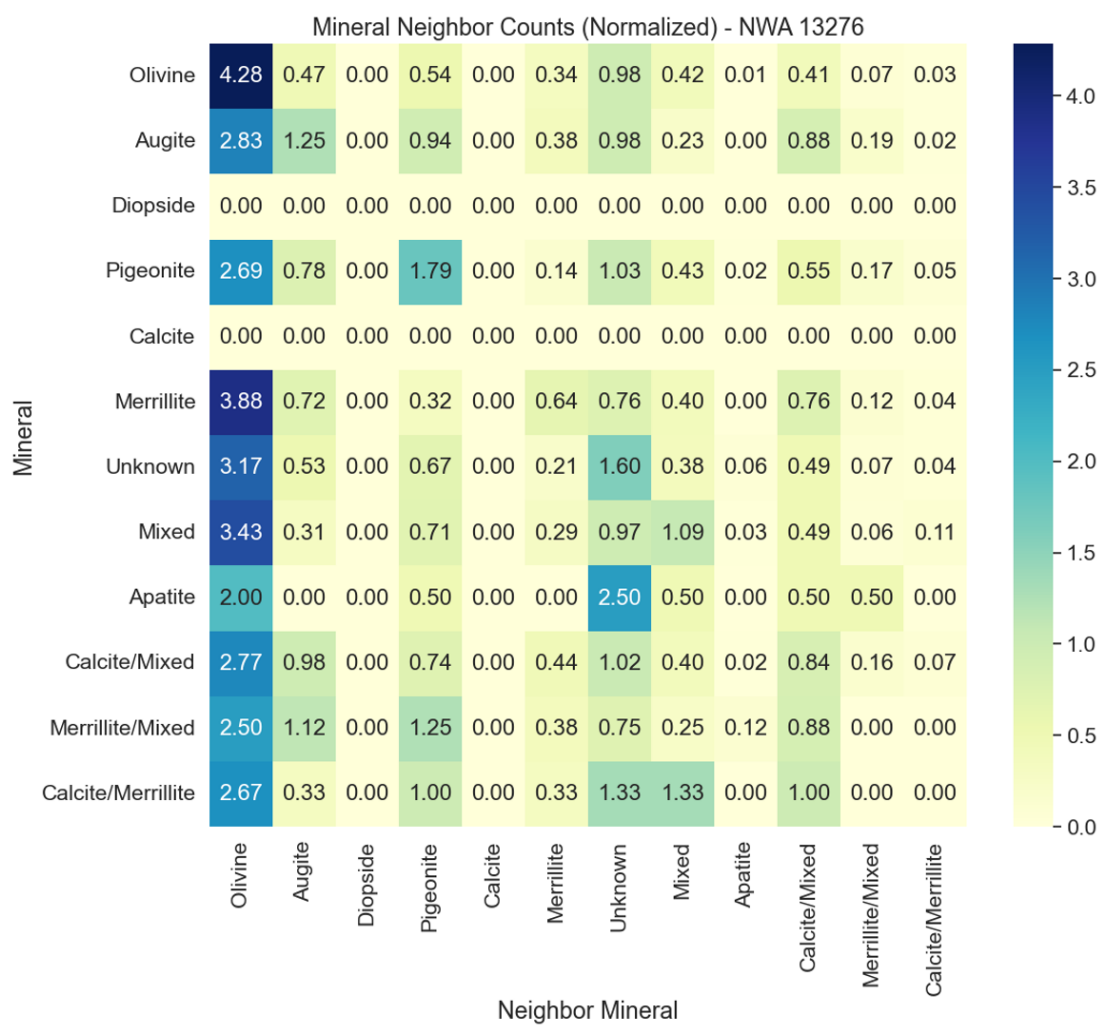


Figure 8 Euclidean distance from the PCA centroid of the manually confirmed olivine population. Histograms compare distances for confirmed olivine patterns (orange) and unlabeled diffraction patterns (blue) within the PCA-reduced feature space. The dashed vertical line marks the median distance of the confirmed olivine population. Confirmed olivines are concentrated at shorter distances, while partial overlap with the unlabeled population identifies statistically similar patterns available for subsequent candidate expansion and expert review.

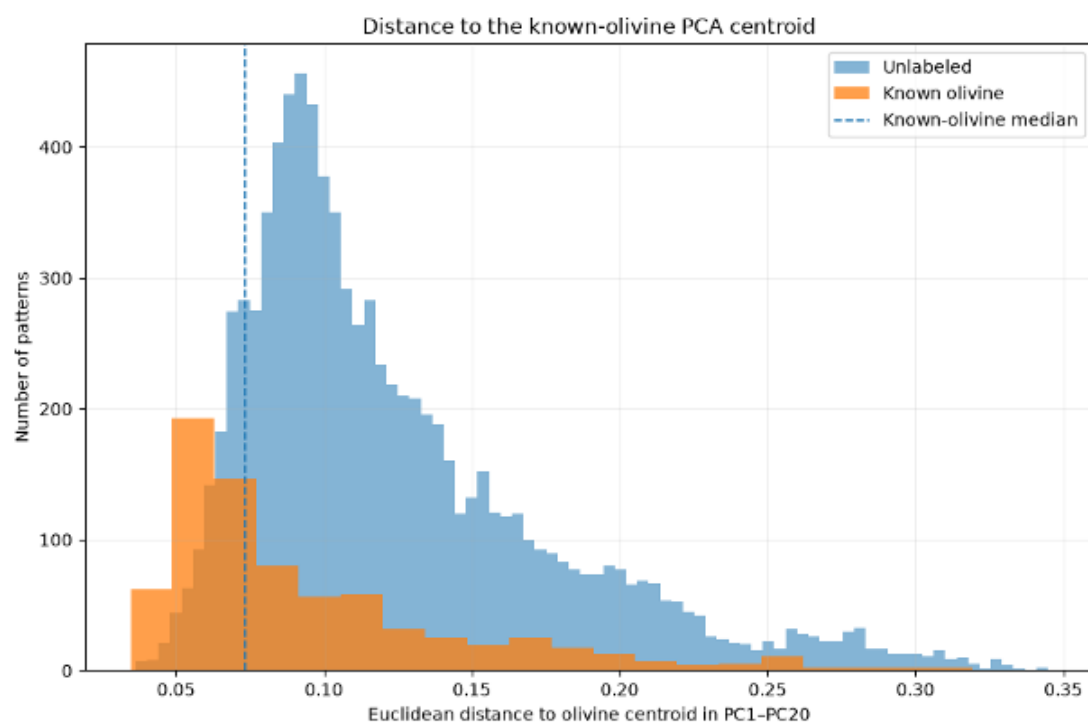


Figure 9 Spatial distribution of first 5 PC behavior among confirmed olivine diffraction patterns in the meteorite. Each confirmed olivine raster position is colored according to the principal component (PC1-PC5) having the largest standardized score magnitude. Patterns not dominated by the first five PCs are classified as “Other.” Spatially coherent domains and transitions between dominant PC classes demonstrate systematic variation within the confirmed olivine population across individual grains and grain clusters.

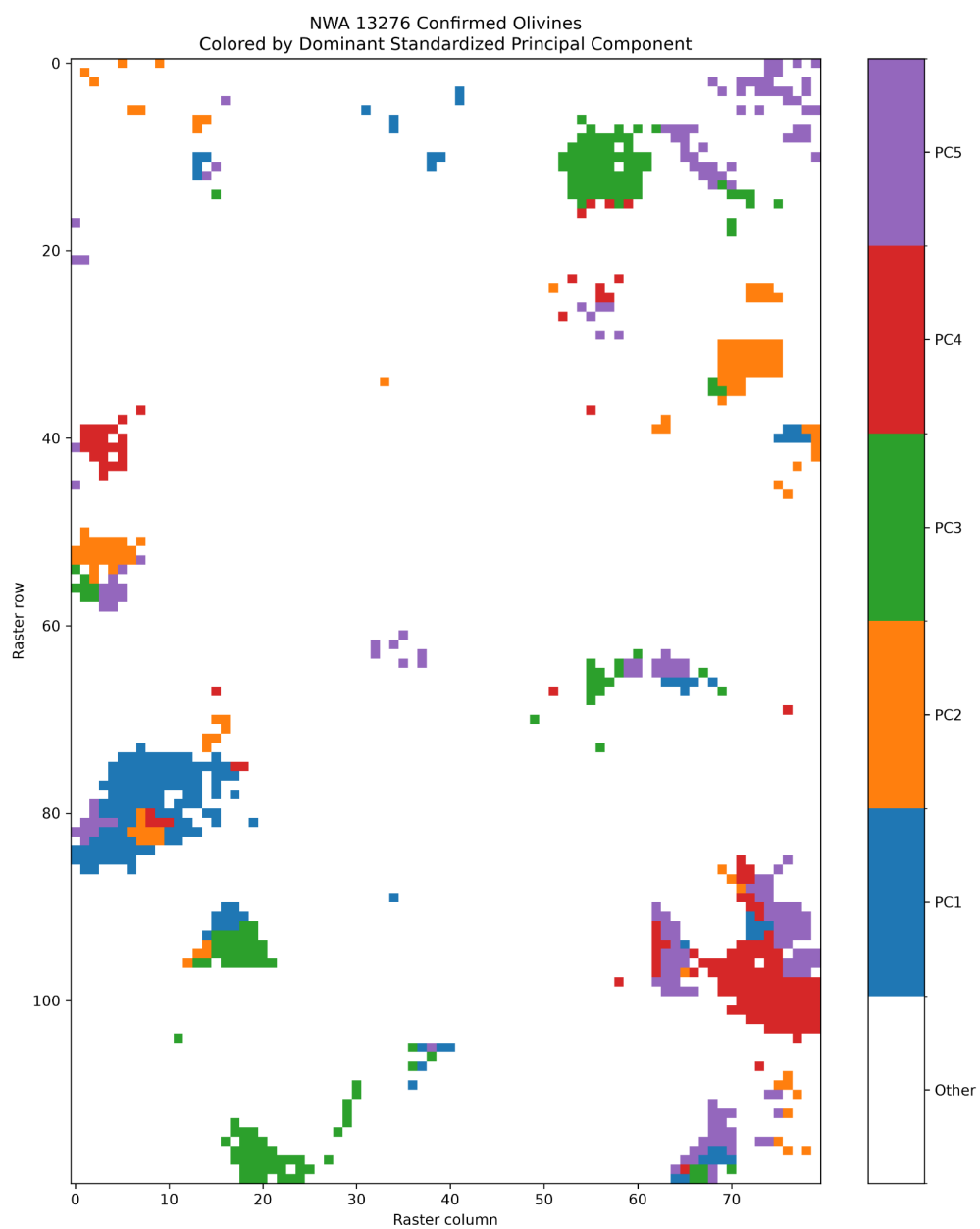


Figure 10 Mean normalized synchrotron μ XRD patterns of confirmed olivines grouped by dominant standardized principal component. Average diffraction profiles for PC1-PC5 classes retain the characteristic olivine diffraction pattern while exhibiting systematic differences in the relative intensities of major reflections. Selected olivine reflections are labeled by Miller index. The persistence of common reflection position across the five groups indicates that the PCA classes primarily partition variations in diffraction intensity (and thus preferred orientation) rather than distinct mineral identities.

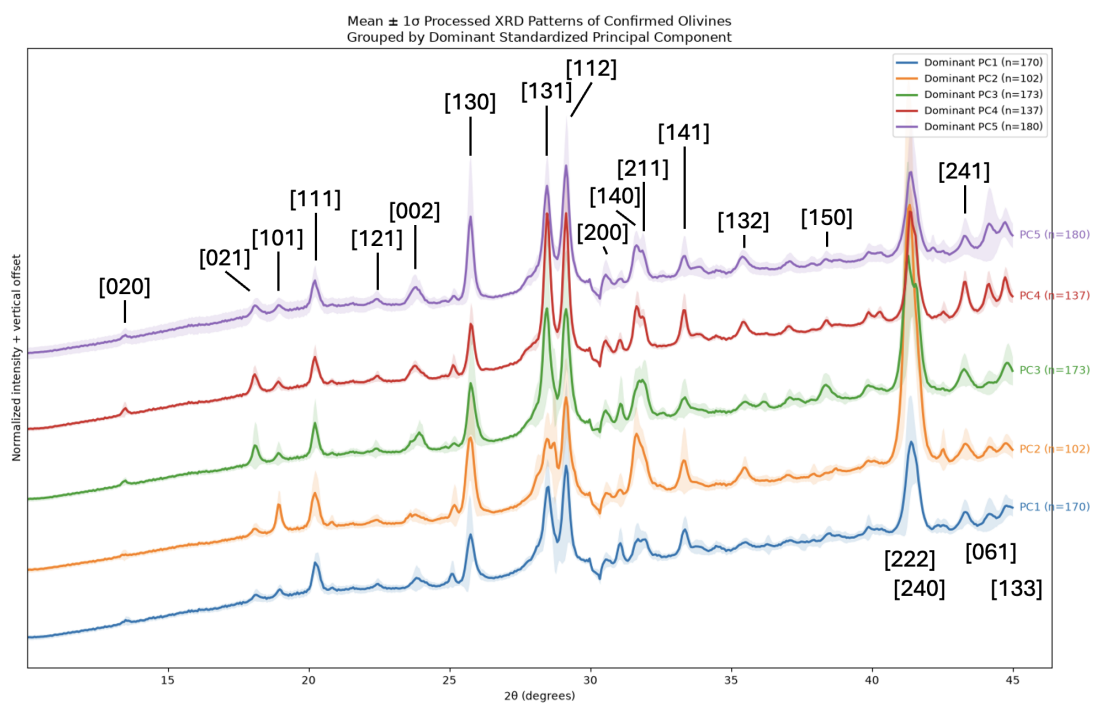


Figure 11 Azimuthally resolved (5° intervals) diffraction behavior of representative NWA 13276. a) Background-corrected diffraction profiles integrated over discrete detector azimuth (η) transects. Expected forsterite reflection positions are marked by Miller indices. Discontinuities and absent measurements reflect detector gaps and incomplete angular coverage. b) Calibrant-normalized integrated intensities of selected olivine reflections as a function of detector azimuth. c) Relative a-, b-, and c-axis sensitive diffraction signals derived from measurable (h00), (0k0), and (00l) reflections. Gaps are retained as missing observations rather than interpolated or assigned zero intensity. The azimuthal modulation of reflection intensity provides a direct, model-independent measurement of crystallographic anisotropy prior to E-WIMV texture reconstruction. Insert) Raw diffraction image displaying Debye-Scherrer rings and the 10 detector panels and the dark gaps between them.

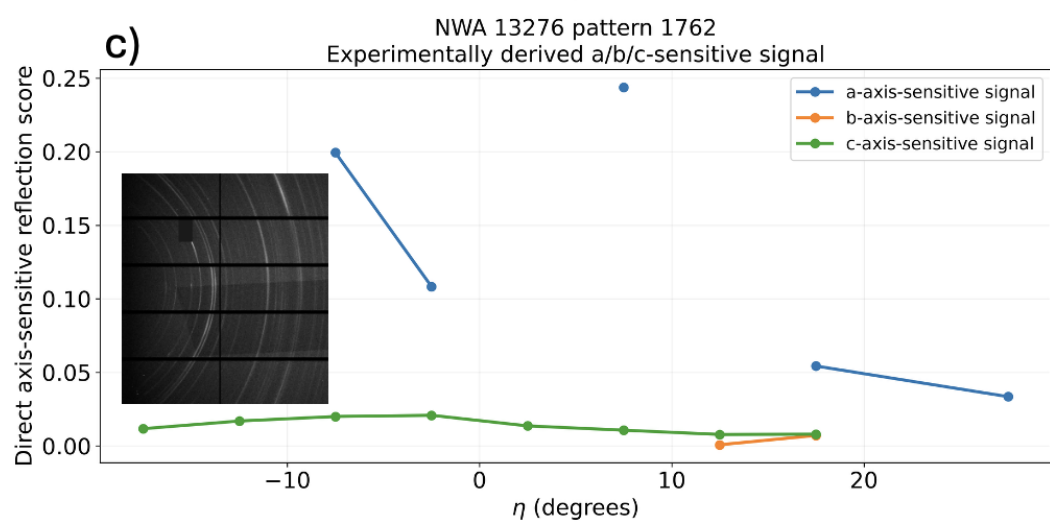
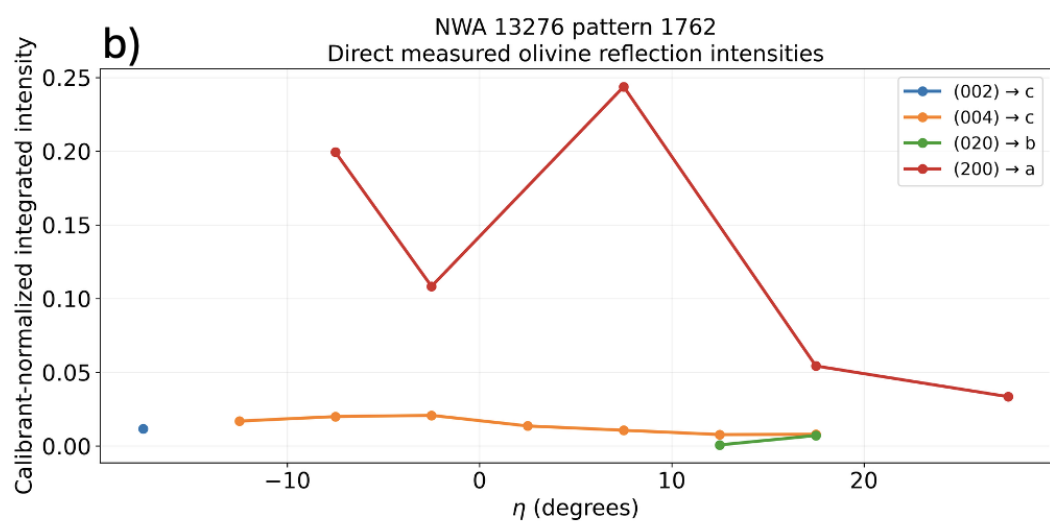
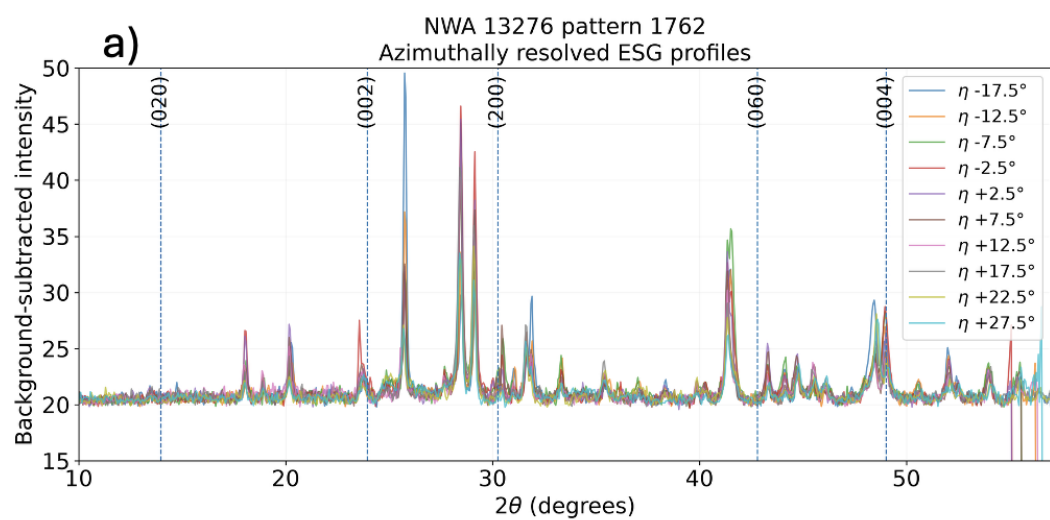


Figure 12 Relationship between direct XRD axis-sensitive reflection intensities and the olivine Raman doublet ratio in NWA 13276. a) Pattern-level relative a-, b-, and c-axis-sensitive diffraction signals for high-confidence olivines, calculated from measurable axial reflections and displayed in ternary space; points are colored by the corresponding Raman olivine doublet intensity ratio. b) Raman doublet ratios grouped according to the dominant pattern-level direct-XRD axis-sensitive signal. c) Independently aggregated η -resolved axis-sensitive reflection enhancements displayed in ternary space and colored by Raman doublet ratio. A minimum number of measurable XRD points per axis was required for inclusion. d) Corresponding Raman doublet ratios grouped by the dominant independently aggregated direct-axis-sensitive signal. Together, the two treatments compare Raman doublet asymmetry against experimentally measured crystallographic anisotropy without requiring E-WIMV orientation reconstruction.

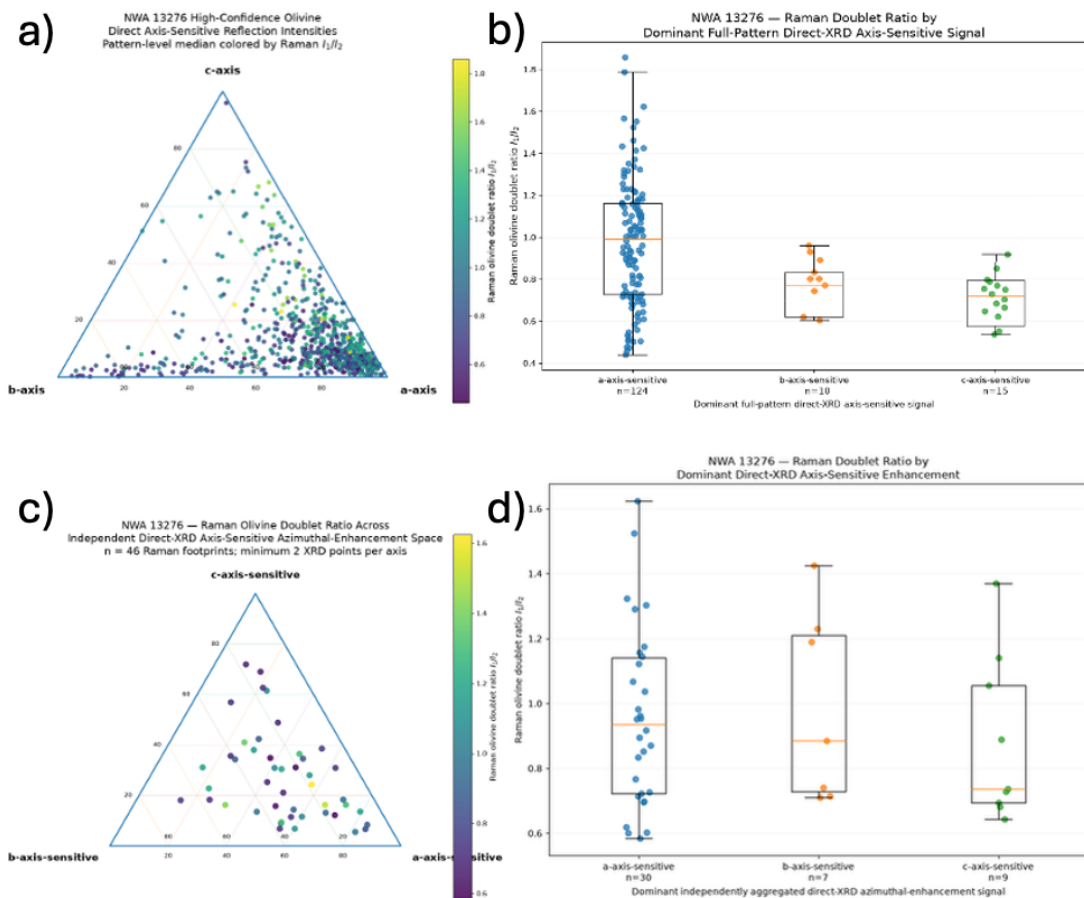


Figure 13 Representative manually refined E-WIMV texture reconstructions and corresponding co-registered Raman spectra from the selected NWA 13276 subset. Each row compares representative synchrotron diffraction data, the corresponding olivine Raman spectrum, and manually refined pole figures for the same co-registered region. Although automated raster-scale E-WIMV reconstruction indicates pervasive c-axis dominance, more detailed manual refinements resolve variable contributions from a-, b-, and c-axis components. Corresponding Raman spectra illustrate changes in relative intensity of the $\sim 810\text{-}870\text{ cm}^{-1}$ olivine doublet across these reconstructed orientation states. Some spectra exhibit stronger low-wavenumber peaks and therefore suggested to be more a- and/or b- axis sensitive, some spectra exhibit an increased contribution from the high-wavenumber peak and therefore suggested to be more c-axis sensitive, and other spectra approaching approximately equal intensities imply a more mixed a-, b-, or c-axis sensitivity.

NWA 13276 — Raman Spectra, Olivine Doublet Behavior, and Corresponding XRD Patterns

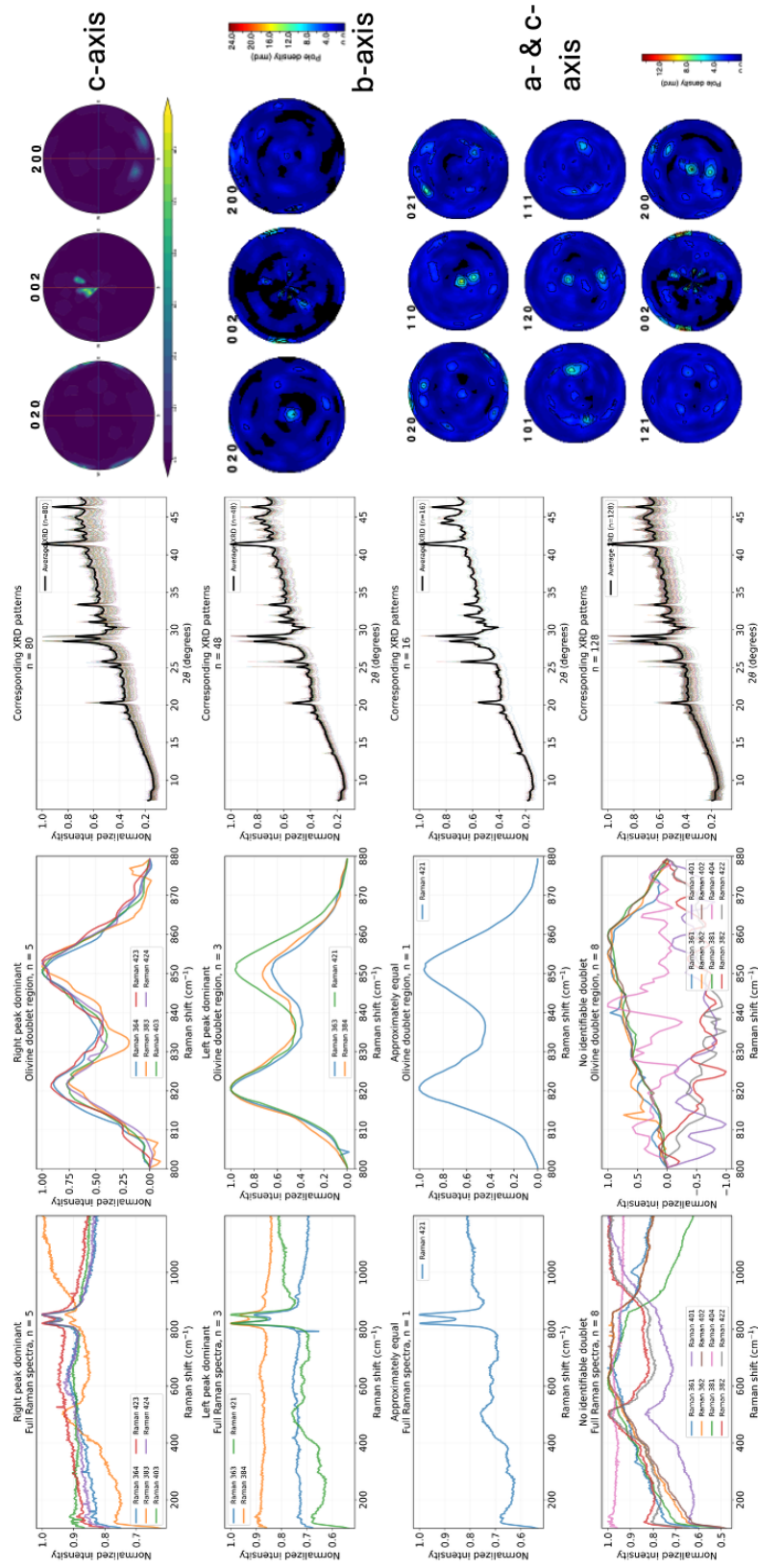
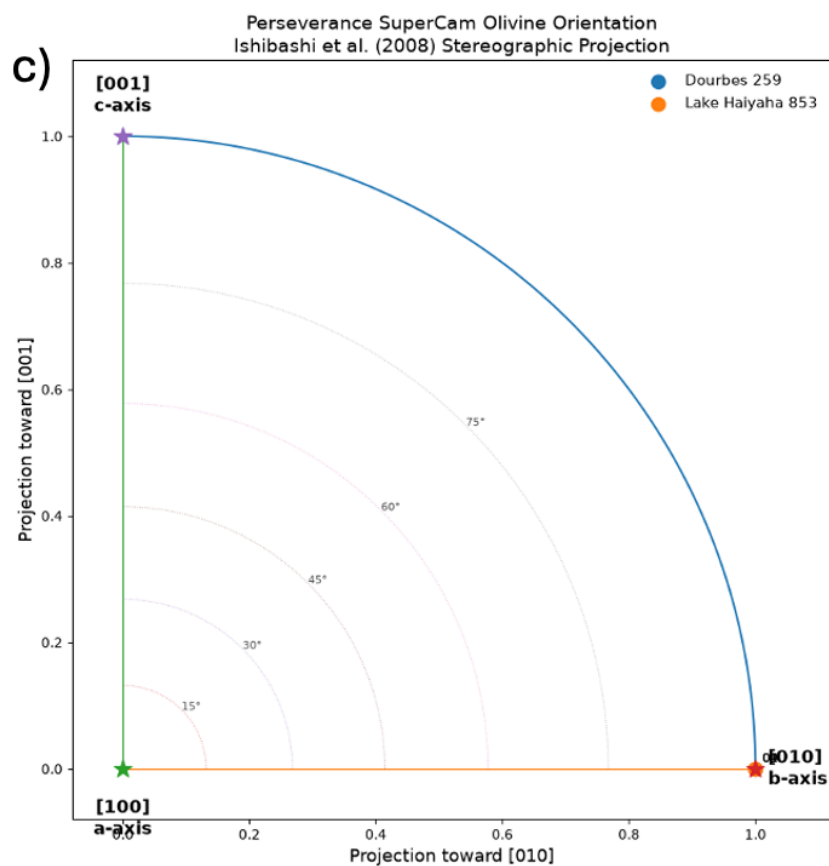
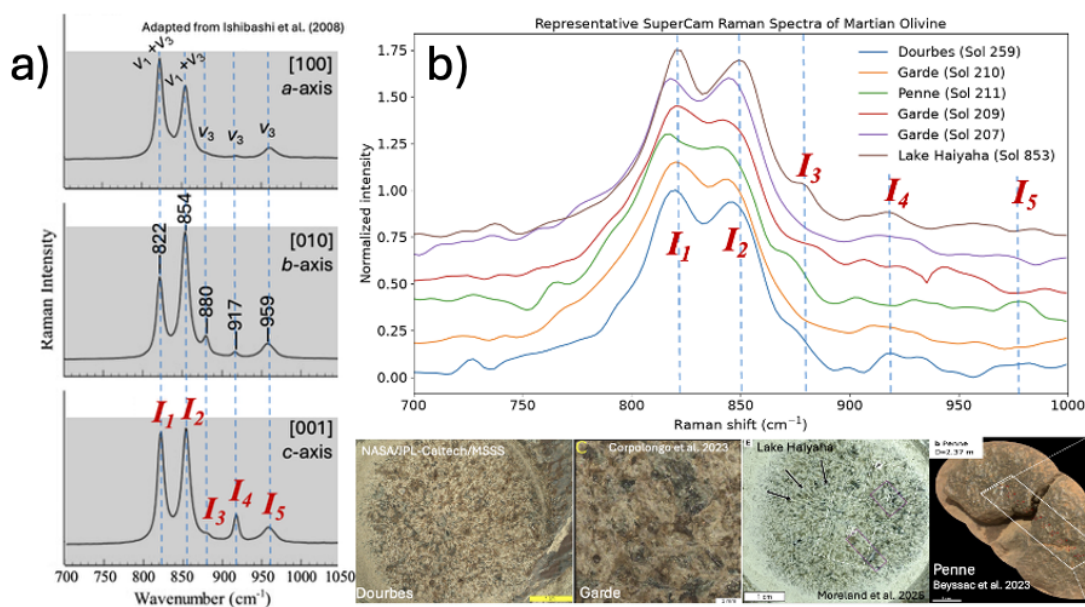


Figure 14 a) Application of orientation-sensitive olivine Raman behavior to Perseverance SuperCam measurements from Jezero Crater, Mars. a) Unpolarized olivine Raman spectra adapted from Ishibashi et al. (2008), illustrating orientation-dependent variation in the diagnostic doublet and associated Raman bands for measurements approaching the [100], [010], and [001] crystallographic directions. Raman features I_I – I_S used for orientation-sensitive comparison are indicated. b) Representative Perseverance SuperCam Raman spectra of Martian olivine. Averaged SuperCam spectra from Dourbes, Garde, and Penne within the Séítah formation, and the olivine-rich Lake Haiyaha boulder on the Jezero upper fan. Spectra are normalized and vertically offset for comparison. All measurements contain the characteristic olivine doublet near ~ 810 – 870 cm^{-1} but exhibit variation in the relative peak intensities. These variations demonstrate that the orientation-sensitive spectral parameter identified in NWA 13276 is preserved in Martian Raman observations, although individual spectra cannot presently be assigned unique crystallographic orientations because of differences in compositions, sampling geometry, grain mixtures/sizes, surface properties, and instrumental response. c) Ishibashi et al. (2008) stereographic projection of the inferred olivine orientations. Both Dourbes (Sol 259) and Lake Haiyaha (Sol 853) plot at or very near the [010] (b-axis) end-member, indicating that those two SuperCam measurements are most consistent with laser illumination approximately parallel to the olivine b crystallographic axis. Images adapted from NASA/JPL-Caltech/MSSS, Corpolongo et al. (2023), Moreland et al. (2026), and Beyssac et al. (2023).



Tables

Chapter 1

Table 1

List of Measured Rocks and Minerals, Their Provenance, the Size of the Spectral Set, and the Allocation of Spectra Toward the Testing or Training Data Sets

Sample	Location	Number of spectra	Data set
Gabbro slab—0% dust	Madagascar	8,952	Test
Gabbro slab—50% dust	Madagascar	9,740	Test
Granite slab—0% dust	Unknown	11,028	Test
Granite slab—0% dust	Unknown	10,000	Test
Hawaiian Basalt Dust	Big Island, HI, United States	—	—
Quartz	Spruce Pine, NC, United States	10,032	Training
Feldspar—Albite	Bancroft, ON, Canada	5,875	Training
Feldspar—Anorthite	Miyaka-jima, Tokyo, Japan	5,600	Training
Feldspar—Microcline	Fremont, CO, United States	5,600	Training
Amphibole—Hornblende	Dresden, SN, Germany	5,054	Training
Mica—Biotite	Bancroft, ON, Canada	7,925	Training
Mica—Muscovite	Ottawa, ON, Canada	5,900	Training
Olivine—Forsterite	San Carlos, AZ, United States	6,140	Training
Pyroxene—Augite	Trento Province, Italy	6,103	Training
Pyroxene—Enstatite	Mpwa, Tanzania	5,600	Training
Carbonate—Calcite	Unknown	5,032	Training
Sulfate—Gypsum	Unknown	5,000	Training
50% Quartz/50% Albite mix	Powder mix from locations above	5,000	Training
50% Forsterite/50% Augite mix	Powder mix from locations above	5,040	Training
50% Forsterite/50% Albite mix	Powder mix from locations above	5,220	Training

Table 2*Gridsearch CNN Parameters and Architecture Exploration With Reported Ranges and Optimized Tuned Values*

Parameter	Range	Tuned value CWT	Tuned value raw
Number of layers (Chollet, 2018; Goodfellow et al., 2016)	Bilayer, Trilayer, Quadlayer	Trilayer (confirms Liu et al., 2017 convention)	Trilayer (confirms Liu et al., 2017 convention)
Filter numbers (Chollet, 2018; Goodfellow et al., 2016)	2, 4, 8, 16, 32, 64, 238	16, 32, 64	16, 32, 64
Filter shape (Chollet, 2018; Goodfellow et al., 2016)	$3 \times 1, 5 \times 1, 11 \times 1, 21 \times 1, 31 \times 1$	$21 \times 1, 11 \times 1, 5 \times 1$	$21 \times 1, 11 \times 1, 5 \times 1$
Activation function (Chollet, 2018; Bishop 2006; Goodfellow et al., 2016)	Sigmoid, TanH, LeakyReLU, Softmax	LeakyReLU , TanH, Softmax	LeakyReLU , TanH, Softmax
LeakyReLU Alpha	0.1–0.5	0.3	0.3
Loss function (Chollet, 2018; Bishop 2006; Goodfellow et al., 2016)	Sparse categorical cross entropy	Sparse categorical cross entropy	Sparse categorical cross entropy
Optimizer function (Bishop 2006; Witten et al., 2011; Goodfellow et al., 2016; Chollet 2018)	SGD, ADAM, RMSProp	RMSProp	RMSProp
Learning rate (Witten et al., 2011; Bishop, 2006)	0.0001–0.1	0.001	0.001
Batch size (Witten et al., 2011; Bishop, 2006)	1–500	8–32	8–32
Drop out rate (Chollet, 2018; Bishop, 2006; Goodfellow et al., 2016)	0.2–0.8	0.55	0.55

Note. Raw and CWT spectra performed well under similar parameters. CNN, convolutional neural network.

Table 3*Weighted F1 Scores Across All Mineral Classes for 0% and 50% Dust Covered Granite and Gabbro*

	K-means clustering	Random forest	Linear SVC	Logistic regression	MLP	CNN
Success Granite 0% Dust Coverage	13.92%	45.82%	54.65%	63.90%	89.00%	99.43%
Success Granite 50% Dust Coverage	14.48%	39.34%	47.16%	33.33%	64.65%	81.18%
Success Gabbro 0% Dust Coverage	12.04%	23.58%	52.00%	58.02%	87.35%	99.40%
Success Gabbro 50% Dust Coverage	10.11%	20.07%	45.94%	51.13%	64.12%	80.39%

Note. Feldspars were grouped into one category. Only quartz, albite, microcline, biotite, and hornblende were identified. The proposed CNN outperformed all models even under challenging dusty conditions. The CNN column values were formatted in bold to guide the reader's attention to the results for the primary technique proposed in this study. All of the values bold or not are weighted F1 scores. CNN, convolutional neural network; MLP, multi-layer perceptron.

Chapter 2

Table 1 Tabulated Raman spectra vibrational modes and Fermi resonance peaks for magnesium perchlorate hydrates and anhydrate at their temperature of appearance, except for the hexahydrate, where the frequencies are reported for its highest temperature presence. *Indicates the dominant peak. ^FIndicates Fermi resonance shoulder from the ν_2 (ClO_4) overtone. The Fermi resonance persists through the hexahydrate phase stability field until ν_2 splits into a doublet and the perchlorate transitions into the tetrahydrate phase. Magnesium perchlorate band assignments from Patel et al. (1983), Agarwal et al. (1985), White & Falk (1986), Bishop et al. (2014), Wu et al. (2016), Ratcliff & Irish (1984), Chi et al. (2007). Tabulated Raman spectra vibrational modes of magnesium sulfate hydrates and possible amorphous phases (indicated by (?)) at their temperature of appearance, except for the heptahydrate, where the frequencies are reported for its highest temperature presence. *Indicates the dominant peak. Magnesium perchlorate band assignments are derived from prior studies (Chaban et al., 2002; Wang et al., 2006, 2009; L. Yang et al., 2020).

Vibrational Bands (cm ⁻¹)	Mg(ClO ₄) ₂ ·6H ₂ O 100°C	Mg(ClO ₄) ₂ ·4H ₂ O 125°C	Mg(ClO ₄) ₂ ·2H ₂ O 160°C	Mg(ClO ₄) ₂ 285°C
ν_2 symmetric bend	464.2	454.0*, 465.6 (doublet)	452.4*, 469.8 (doublet)	462.3
ν_4 asymmetric bend	625-635	623.9*, 641.8 (doublet)	625, 6* (doublet)	626.4*, 635.3 (doublet)
$2\nu_2$ Fermi resonance	929.3 ^F	-	-	-
ν_1 symmetric stretch	935.2	947.2	962.8	994.8
ν_3 asymmetric stretch	1075-1125 (split)	1017-1158 (split)	1016-1157 (split)	1015-1180 (split)
OH Stretch	3531.8	3550.0	3562.2	-
	MgSO ₄ ·7H ₂ O 35°C	MgSO ₄ ·6H ₂ O 40°C	MgSO ₄ ·3(?)H ₂ O 80°C	MgSO ₄ ·2(?)H ₂ O 125°C
ν_2 symmetric bend	455.8	443.3, 462.4* (split)	447.5	452.4*, 491.4 (split)
ν_4 asymmetric bend	608.6	610.2	615.1	624.8
ν_1 symmetric stretch	983.2	982.5	~1023.7	~1033.8
ν_3 asymmetric stretch	1060.1*, 1094.0, 1128.6 (split)	1079.4*, 1143.8 (split)	1143.8	~1090-1320 (very broad)
OH Stretch	3207.3*, 3271.3, 3408.7	3272.4, 3425.6*	3281.0, 3457.1*	3513.6

Table 2 Refined XRD unit-cell parameters for crystalline $\text{Mg}(\text{ClO}_4)_2$ and MgSO_4 hydration phases compared with literature values. Kapton-covered $\text{Mg}(\text{ClO}_4)_2$ measurements are included for phase identification but should be interpreted cautiously because Kapton scattering affects full-profile refinement. No lattice parameters are reported for the $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ /amorphous and $2\text{H}_2\text{O}$ /amorphous compositions because these phases lack sufficient long-range crystallinity for refinement. V = volume. VE = volumetric thermal expansion coefficient.

	a (Å)	b (Å)	c (Å)	V (Å³)	Rwp	VE (1/V(dV/dT))
Mg(ClO₄)₂·6·H₂O (this study 25°C)	7.80	13.51	5.27	555.8	5.238	2.48E ⁻⁴
Mg(ClO₄)₂·4·H₂O (this study 110°C)	11.48	8.00	5.93	504.5	7.67	-1.35E ⁻⁴
Mg(ClO₄)₂·2·H₂O (this study 180°C Kapton)	14.40	5.22	5.45	388.3	6.848	5.72E ⁻⁵
Mg(ClO₄)₂ (this study 300°C Kapton)	4.83	8.39	7.98	282.3	6.63	5.90E ⁻⁵
Mg(ClO₄)₂·6·H₂O (West (1935))	7.76	13.46	5.26	549.4	-	-
Mg(ClO₄)₂·4·H₂O (Solovyov (2011))	11.48	8.00	5.94	504.5	-	-
Mg(ClO₄)₂·2·H₂O (Robertson & Bish (2011))	14.39	5.22	5.44	387.9	-	-
Mg(ClO₄)₂ (Lim (2011))	4.86	8.42	7.87	282.1	-	-
MgSO₄·7·H₂O Epsomite (this study 22°C)	11.90	12.01	6.87	982.0	6.44	1.47E ⁻³
MgSO₄·6·H₂O (this study 40°C)	10.10	7.21	24.42	1760.8	2.98	7.04E ⁻²
MgSO₄·7·H₂O Epsomite (Baur (1964))	11.86	12.00	6.86	976.2	-	-
MgSO₄·6·H₂O (Falkin et al. (1963))	10.11	7.21	24.41	1761.2	-	-

Chapter 3

Table 1. PCA loading peak assignments.

Principal component	Approx. loading feature, 2 θ (°)	Sign	Closest strong reference feature(s)	Likely forsterite hkl	Interpretation
PC1	~25.8	+	Forsterite 25.80°	[130]	Strong olivine contribution
~28.5	+	Forsterite 28.48°; augite/diopside ~28.36–28.54°	[131]	Major olivine/pyroxene overlap region	
~29.1	strong +	Forsterite 29.13°	[112]	Dominant olivine-defining feature	
~31.6–31.9	+	Forsterite 31.62/31.90°; calcite 31.50°	[122], likely [140]/[032]	Secondary olivine intensity variation; possible carbonate overlap	
~41.4	strong +	Forsterite 41.41°; augite 41.39°; diopside 41.41°	[222]	Strong mafic-silicate reflection; not uniquely olivine	
~44.9	+	Forsterite 44.90°; calcite 44.86°	likely [133]	Weaker high-angle discriminator	
PC2	~23.8–24.3	–	Forsterite 23.72–23.84°; augite/diopside 23.92–24.26°	[121], [002]	Relative olivine–pyroxene peak contrast
~25.8	+	Forsterite 25.80°	[130]	Strong olivine contribution	
~29.1	strong –	Forsterite 29.13°	[112]	Opposes PC1-style olivine intensity pattern	
~31.6–32.0	+	Forsterite 31.62/31.90°; calcite 31.50°	[122], likely [140]/[032]	Relative peak-intensity redistribution	
~41.4	strong +	Forsterite/augite/diopside coincident region	[222]	Mafic-silicate intensity contrast	
~44.8–45.0	–	Forsterite 44.90°; calcite 44.86°	likely [133]	High-angle contrast	
PC3	~18.3–20.5	±	Forsterite 18.31, 19.12, 20.37/20.47°	[021], [101], [111]/[120]	Lower-angle olivine structure
~23.7–24.3	–	Forsterite plus augite/diopside overlap	[121]/[002]	Mixed olivine–pyroxene discrimination	

~25.8	+	Forsterite 25.80°	[130]	Olivine-sensitive	
~28.5	–	Forsterite 28.48°; pyroxenes ~28.4–28.5°	[131]	Relative intensity/orientation variation	
~29.1	+	Forsterite 29.13°	[112]	Olivine-sensitive	
~31.2–32.0	+/-	Forsterite, calcite, merrillite overlap	[122]/[140]/[032]	Mixed-phase and orientation-sensitive region	
~41.1–41.5	strong +/- pair	Forsterite/pyroxene overlap near 41.4°	[222]	Strong relative- intensity redistribution	
~44.8–45.0	+	Forsterite/calcite region	likely [133]	Higher-angle secondary variance	
PC4	~23.7–25.8	strong + complex	Forsterite 23.7–25.8°; augite/diopside 23.9– 24.7°; merrillite 25.10°	[121]/[002]/[130]	Strong mixed mineralogical contrast
~28.5–29.1	strong –	Forsterite 28.48/29.13°; pyroxene overlap	[131]/[112]	Inverse weighting of main mafic peaks	
~34.3–35.4	+	Augite/diopside 34.2– 35.4°; forsterite 35.42°	likely [132] for Fo at 35.42°	Greater pyroxene/mixed- phase influence	
~41.4	+	Forsterite/pyroxene overlap	[222]	High-angle mafic- silicate variance	
~44.4–45.0	-/+	Forsterite 44.35– 44.90°; calcite 44.86°	likely [232]/[133]	Secondary phase/intensity contrast	
PC5	~25.8	strong –	Forsterite 25.80°	[130]	Orientation/inten- sity-sensitive olivine feature
~28.5	strong –	Forsterite 28.48°; pyroxene overlap	[131]	Relative intensity redistribution	
~29.1–30.5	+	Forsterite 29.13, 30.15, 30.51°	[112], [200], [041]	Higher-order olivine structural variation	
~31.6–31.9	–	Forsterite 31.62/31.90°	[122], likely [140]/[032]	Orientation-sensitive peak contrast	
~41.4	+	Forsterite/pyroxene overlap	[222]	Mafic-silicate contribution	
~44.4–44.9	strong +	Forsterite 44.35/44.48/44.90°; calcite 44.86°	likely [061]/[232]/[133]	Dominant high-angle secondary variance	

Supplemental Information

Chapter 1 Supplemental Information

Introduction

The following supplementary materials contain Raman band assignments, XRD, and XRF mineralogy for the minerals included in the Machine Learning Raman Open Dataset (MLROD) training set used to train the CNN classifier. Presented are also representative per class CNN metrics using MLROD and receiver operating characteristic curves (ROC) outputs for independent RRUFF spectra. Specifications for *Perseverance* rover Raman spectrometers (SuperCam and SHERLOC) are tabulated alongside the laboratory spectrometer used to acquire MLROD.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
Quartz (cm ⁻¹)	465 vs	205 s	350 m	805 w	695 vw
Band Assignment (Chio et al. 2003; Sharma, Mammone, and Nicol 1981)	ν_s - Si-O-Si 6-membered ring symmetric stretch	lattice (soft) modes, Si-O torsional	lattice distortion mode, Si-O torsional	single mode, doubly degenerate class E	stretching modes
Albite (cm ⁻¹)	505 vs	285 s	410 m/br	760/765 w/br	640 vw
Band Assignment (Berlanga et al. 2019; Freeman et al. 2008; McKeown 2005; Sharma et al. 2002; Sharma, Philpotts, and Matson 1985; Stopar et al. 2005)	ν_s -Si-O-Si 4-membered ring breathing modes	Si-O-Si 4-membered ring rotational-translation modes	Si-O-Si 4-membered ring rotational-translation modes	deformation modes of tetrahedral ring δ (O-T-O)	Al-O-Si bend: T1(o)-O _{bc} (o)-T2(o); Na-OA1 stretch; (Si, Al) tetrahedra deformations; O-Na-O bend
Microcline (cm ⁻¹)	515 vs	470 s	285 s	750 vw	645 vw
Band Assignment (Berlanga et al. 2019; Freeman et al. 2008; Sharma et al. 2002, 1985; Stopar et al. 2005)	ν_s -Si-O-Si 4-membered ring breathing modes	Si-O-Si 4-membered ring rotational-translation modes	Si-O-Si 4-membered ring rotational-translation modes	deformation modes of tetrahedral ring δ (O-T-O)	δ (O-T-O) deformation modes of tetrahedra
Hornblende (cm ⁻¹)	680 vs	225/230 s	365/370 m/br	540 w	885-975 w/br
Band Assignment (Buzgar et al. 2013)	ν_s - symmetric stretching mode Si-O _{bc} -Si.	lattice mode	M-O, where M = Ca and Mg, Fe ²⁺	δ (Si ₄ O ₁₁)	ν_s (O-Si-O) and ν_{as} (Si-O _{bc} -Si)
Biotite (cm ⁻¹)	680 vs	275 m	555 m	790 m/br	340 m/br
Band Assignment (Berlanga et al. 2019; Singha and Singh 2016; Stopar et al. 2005)	δ (Si-O-Si) bending modes	T(M-O)	δ (Si-O-Si) bending modes	ν (Si-O-Si)	T(M-O), M=Mg or Fe translational mode
Muscovite (cm ⁻¹)	700 vs	910 w	630 m	265 vs	405 s
Band Assignment (McKeown, Bell, and Etz 1999; Singha and Singh 2016)	δ (O-Al-O)	tetrahedral breathing mode. Stretching of δ (Si-O-Al) and δ (Si-O-Si)	δ (Al-O-Al) bending and δ (O-Al-O) translation	δ (O-Si-O) translation	δ (O-Al-O) and O-Si-O translations
Forsterite (cm ⁻¹)	855 vs	825 vs	960 m	325 w	425 m
Band Assignment (Kolesov and Geiger 2004; Kuebler et al. 2006; Lam et al. 1990; Mouri and Enami 2008; Wang, Sharma, and Cooney 1993)	ν_1 symmetric and ν_3 antisymmetric stretching of Si-O _{ab} bonds within SiO ₄ -4 anions	ν_1 symmetric and ν_3 antisymmetric stretching of Si-O _{ab} bonds within SiO ₄ -4 anions	ν_3 of T(SiO ₄)	T(SiO ₄)	ν_2 symmetric bend
Augite (cm ⁻¹)	670 vs	220/225 m	370/375 m	530/535 br	1025 w/br
Band Assignment (Buzgar et al. 2013; Huang et al. 2000; Wang et al. 1999)	ν_{11} symmetric stretching SiO in SiO ₄ tetrahedra - ν_s (Si-O _{br})	M-O cation oxygen vibrations	ν_3 and ν_4 M-O cation-oxygen vibrations	δ (O-Si-O) bending mode	ν_{16}/ν_{17} ν_3 (Si-O _{ab})
Enstatite (cm ⁻¹)	675/680 s	340/345 vs	235/240 m	1025 m	410/415 m
Band Assignment (Huang et al. 2000; Wang et al. 1999)	ν_{11} and ν_{12} symmetric stretching SiO in SiO ₄ tetrahedra	ν_3	ν_1	ν_{17}	ν_3 and ν_4
Anorthite	502 vs	285 s	403 s	766 m	743 w
Band Assignment (Berlanga et al. 2019; Freeman et al. 2008; Sharma et al. 2002, 1985; Stopar et al. 2005)	ν_s -Si-O-Si 4-membered ring breathing modes	Si-O-Si 4-membered ring rotational-translation modes	Si-O-Si 4-membered ring rotational-translation modes	deformation modes of tetrahedral ring δ (O-T-O)	δ (O-T-O) deformation modes of tetrahedra
Calcite	1088 vs	285 m	712 w		
Band Assignment (Buzgar et al. 2009; Gunasekaran et al. 2006)	ν_1 symmetric CO ₃ stretching	T(Ca, CO ₃)	ν_4 symmetric CO ₃ deformation	-	-
Gypsum	1008 vs	495 m	417 w		
Band Assignment (White et al. 2008; Buzgar et al. 2009)	ν_1 (SO ₄) symmetric bending	ν_2 (SO ₄) symmetric bending	ν_2 (SO ₄) symmetric bending	-	-

Table S1 Standardized CWT Raman peak positions for the top 5 peak intensities for each mineral trained on the CNN and the respective band assignments. Abbreviations stand for the relative peak intensity (vs-strong, s-strong, m-medium, w-weak, vw-very weak).

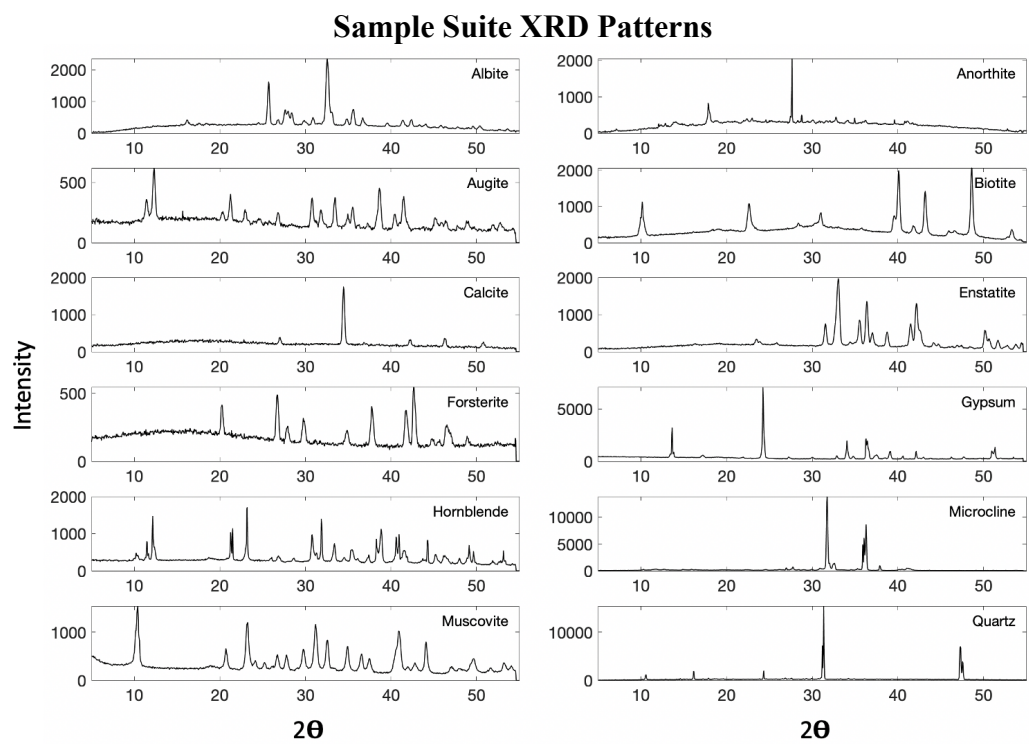


Figure S1 X-ray diffraction patterns for minerals in training set.

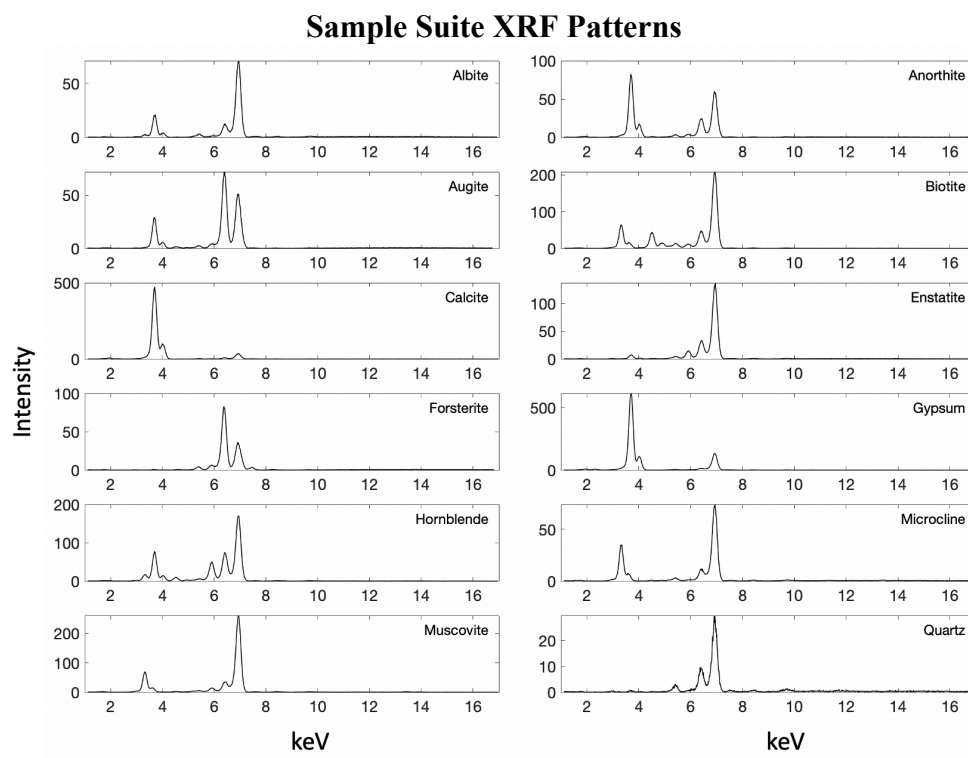


Figure S2 X-ray fluorescence patterns for minerals in training set.

Sample Individual Class Metrics Raw Spectra 0% Dust

Classification/ID Label	Precision	Recall	F1-Score	Support Spectra
0	1.00	1.00	1.00	1555
1	0.99	0.99	0.99	406
2	1.00	1.00	1.00	879
3	0.98	0.98	0.98	88
4	1.00	1.00	1.00	52
5	1.00	1.00	1.00	702
6	0.98	0.97	0.98	5091
7	1.00	1.00	1.00	3537
8	1.00	1.00	1.00	2027
9	0.99	1.00	1.00	400
10	1.00	1.00	1.00	46
11	0.99	0.99	1.00	21
12	0.97	0.98	0.99	87
13	0.97	0.96	0.97	33
14	0.97	0.97	0.97	28
Weighted Average	0.99	.98	.99	Total: 14952

Table S2 Individual mineral class metrics show successful recall and precision in the CNN model. Weighted F1 scores account for training model support spectra imbalance and provide excellent classification results.

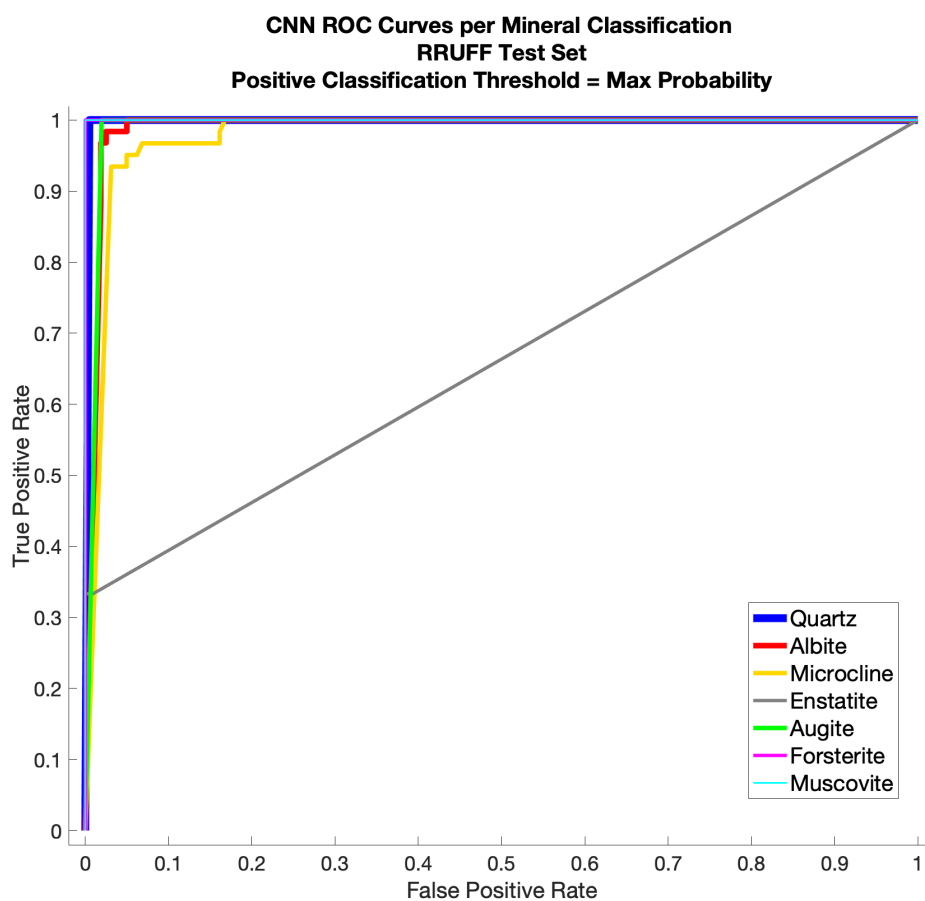


Figure S3 CNN ROC curves for the RRUFF independent test set. The classifications are outstanding, except for a subset of the RRUFF enstatite spectra which may be either misclassified or compositionally more complex than is implied by the enstatite endmember name.

Raman Instruments	Laser Excitation (nm)	Spectroscopic Range	Spectral Resolution	CNN trained on MLROD Spectroscopic Range (cm⁻¹) Inputs
SuperCam (Raman) <i>Perseverance</i> (Wiens et al. 2021)	532 nm	535 - 855 nm; ~150 - 7000 cm ⁻¹	0.3 - 0.4 nm; ~10 cm ⁻¹	-
SHERLOC (Resonance Raman) <i>Perseverance</i> (Uckert et al. 2021)	248.6 nm	250 - 275 nm; ~200 - 4000 cm ⁻¹	0.296 nm; ~40 cm ⁻¹	-
Horiba LabRAM HR Evolution (laboratory spectrometer used to create MLROD)	532 nm	Maximum Chosen: ~535 – 588 nm; ~100 – 1800 cm ⁻¹ Minimum Chosen: ~536 – 565 nm; ~150 – 1100 cm ⁻¹	0.03 nm; ~1 cm ⁻¹	~150 - 1100 cm ⁻¹

Table S3 Comparison of relevant laser and spectrometer specifications between current Mars payloads implementing Raman spectroscopy and the Horiba spectrometer used to create MLROD. To date the MLROD trained CNN algorithm can be used with SuperCam data. The same CNN algorithm can be employed with SHERLOC data with the addition of DUV training sets at 248.6 nm laser excitations and wavelength adjustments in the code.

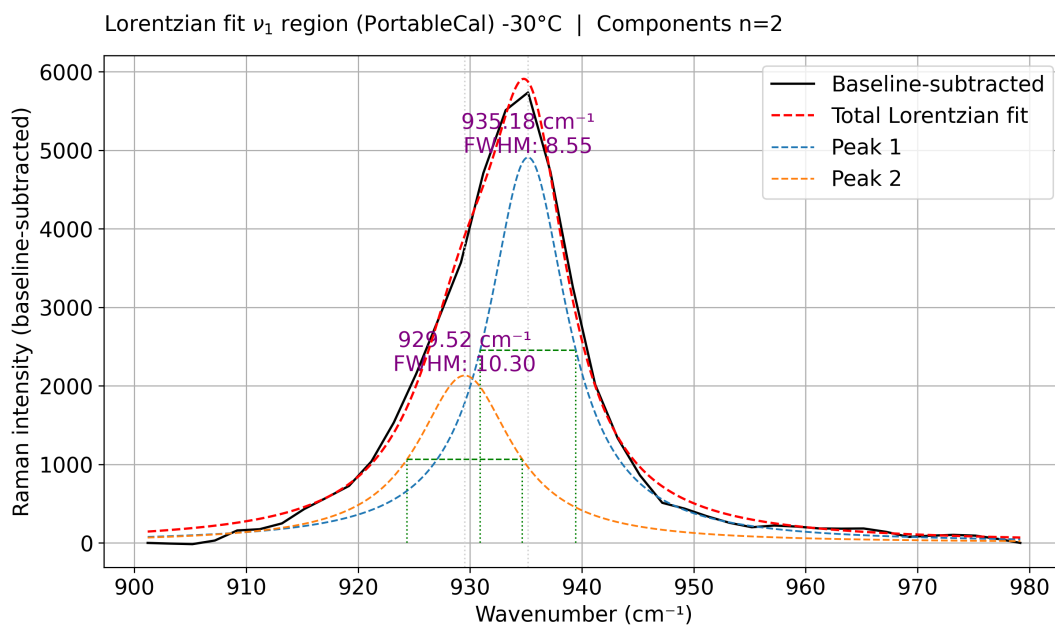
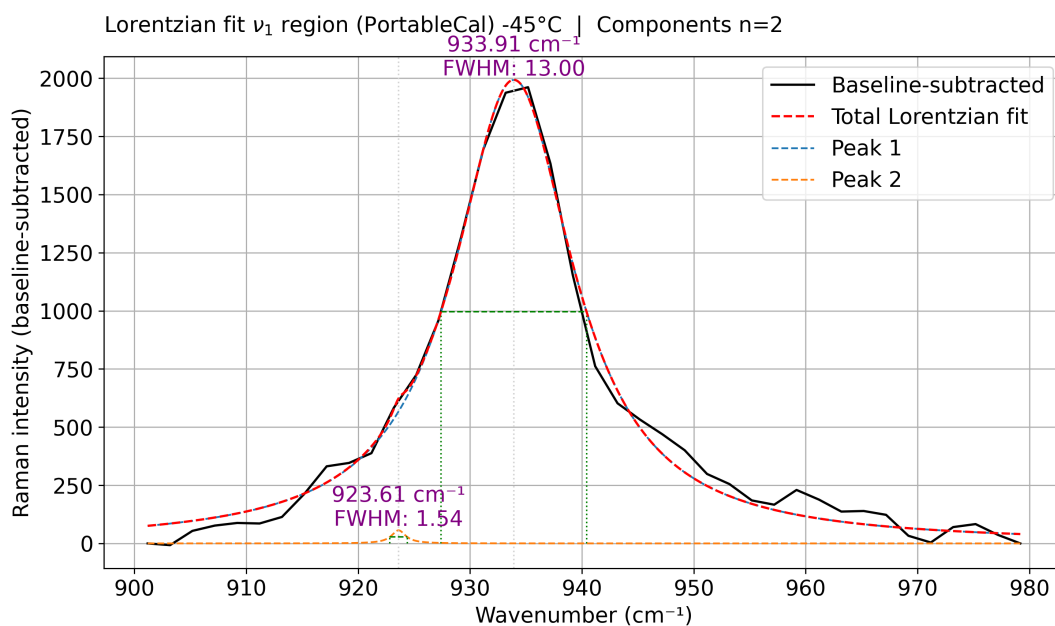
Chapter 2 Supplemental Information

Introduction

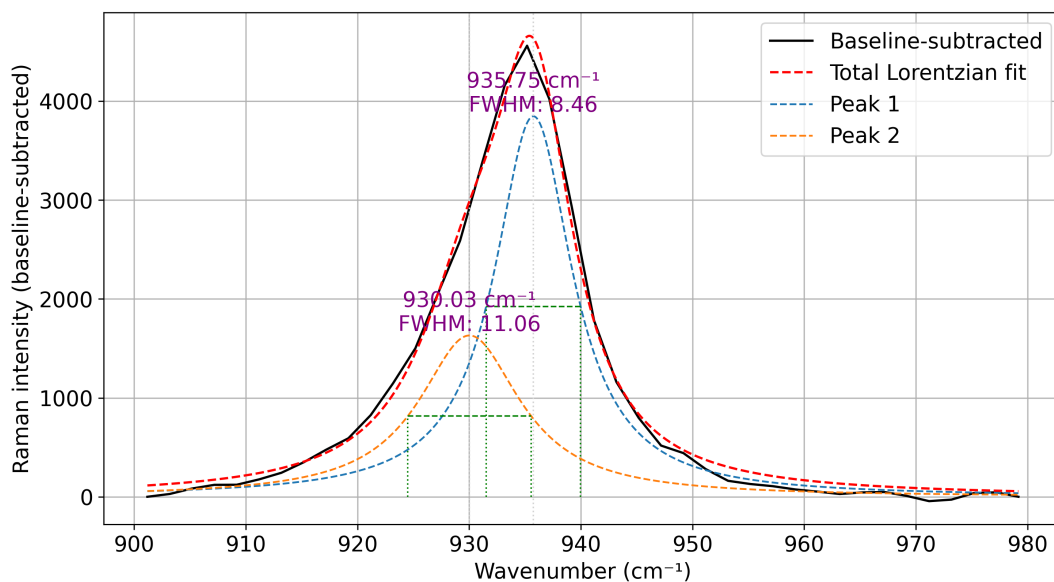
The supporting information contained in this Supplement illustrate the analysis and processing for spectral deconvolution and/or X-ray diffraction refinements, the derivation for Wilson GF and Herzberg 4-mode force constants, and the associated Herzberg force constant plots used to corroborate the main Wilson GF force constants results. Deconvolved Raman ν_1 peak regions for Mg perchlorate and Mg sulfate use Lorentzian peak fits. The Mg perchlorate hexahydrate deconvolutions show the Fermi resonance shoulder. The X-ray diffraction patterns shown include any additional temperature steps that weren't included in the manuscript, all patterns that were not X-ray amorphous, and patterns where a refinement was possible. Some patterns include a small Fe peak in the 44 and 50 2-theta range that corresponds to the sample holder.

S1. Lorentzian Peak Fits Deconvolved Raman Spectra for Mg Perchlorate and Mg Sulfate

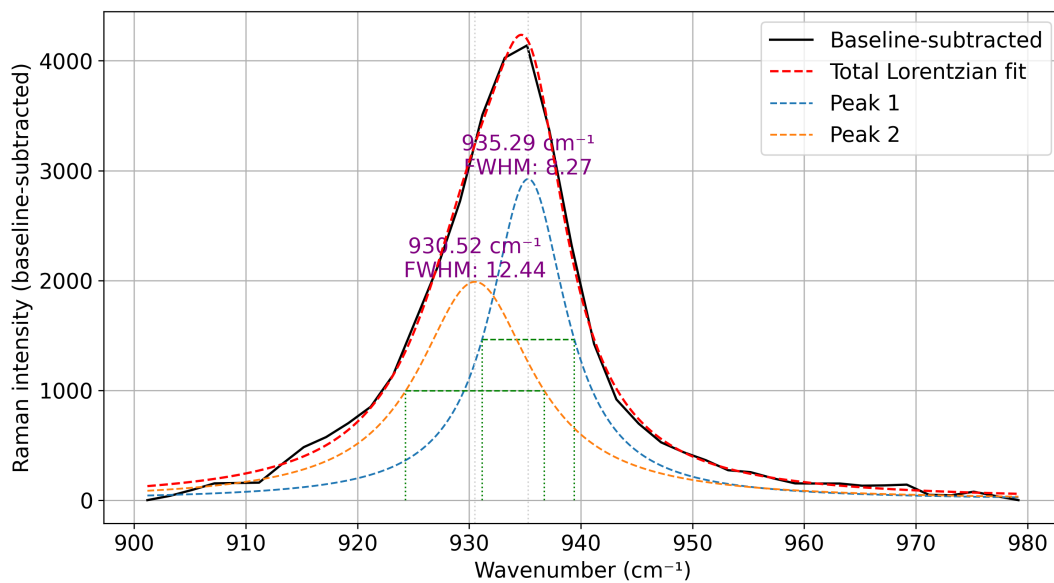
S1.1 $\text{Mg}(\text{ClO}_4)_2 \cdot \text{XH}_2\text{O}$ Plots -45 to 400 °C

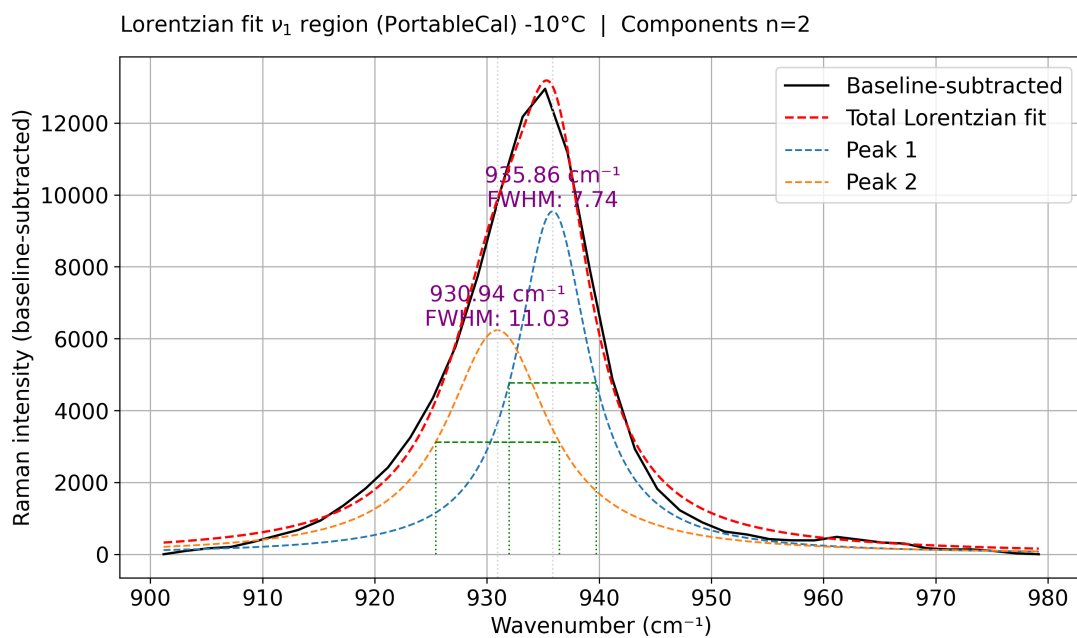
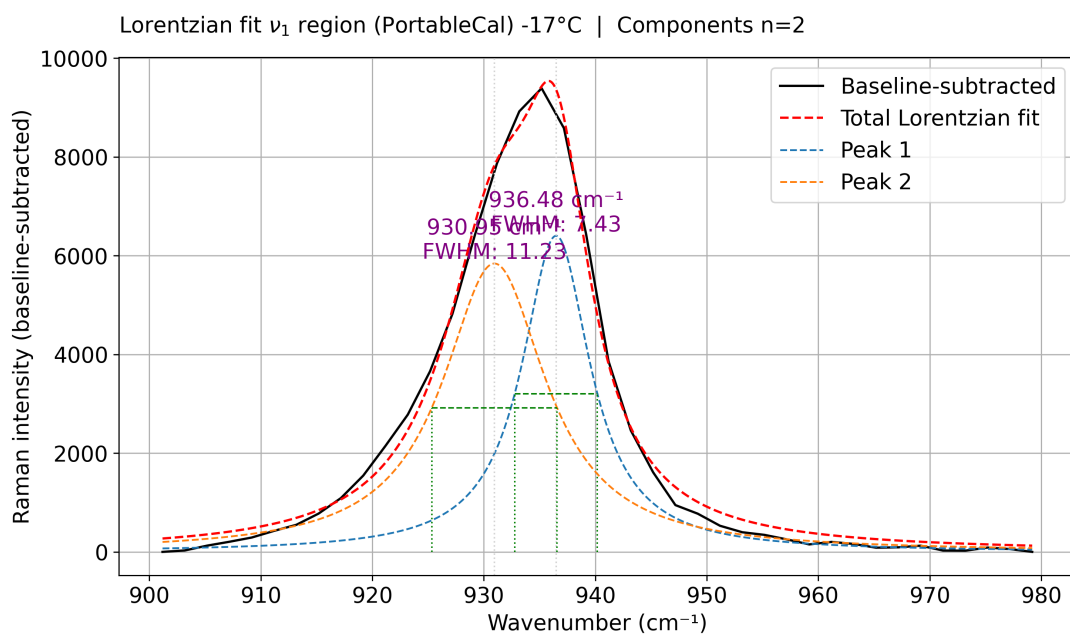


Lorentzian fit ν_1 region (PortableCal) -25°C | Components n=2

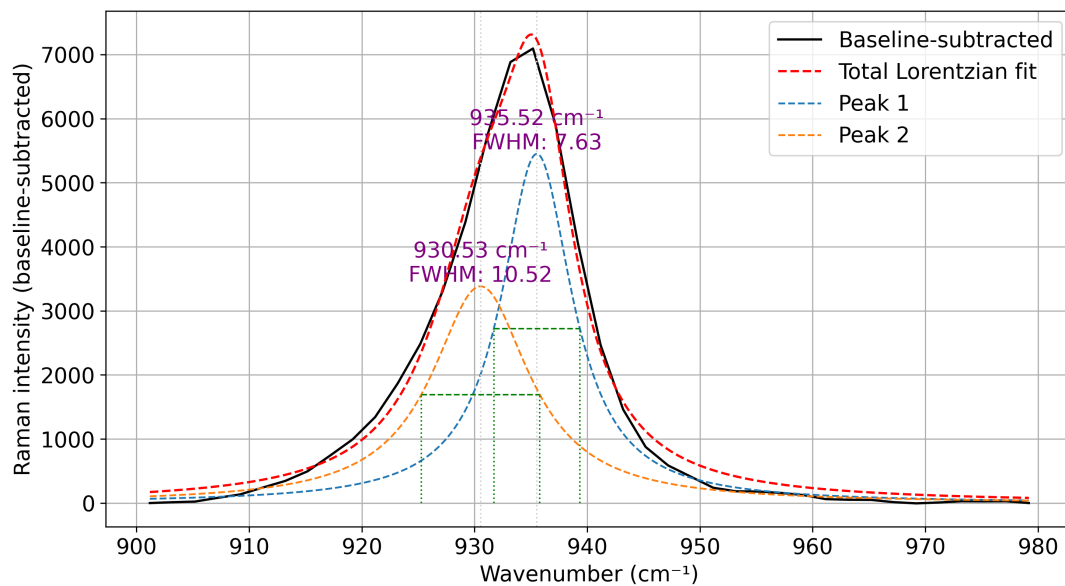


Lorentzian fit ν_1 region (PortableCal) -20°C | Components n=2

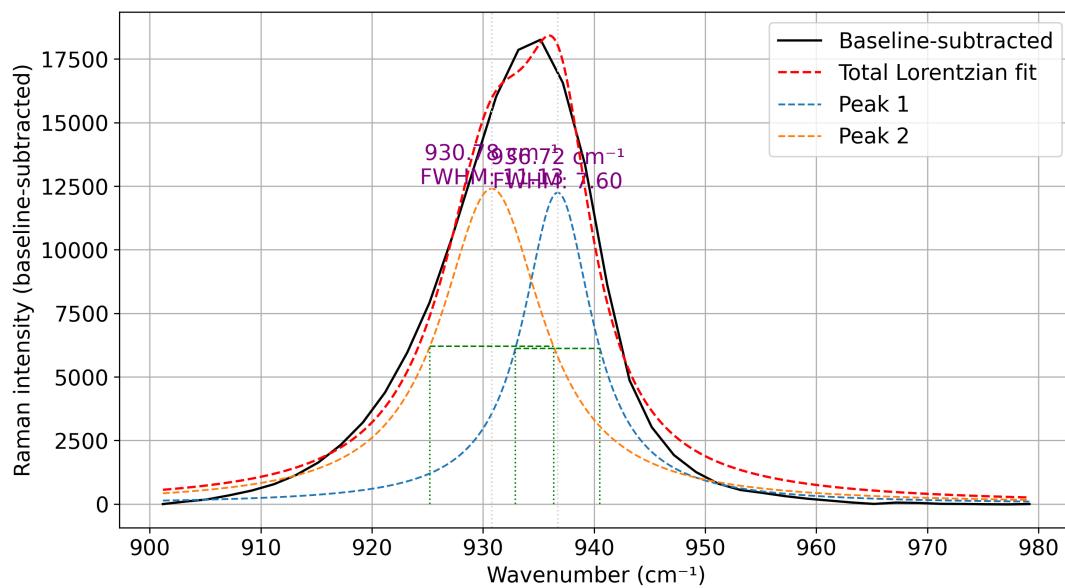




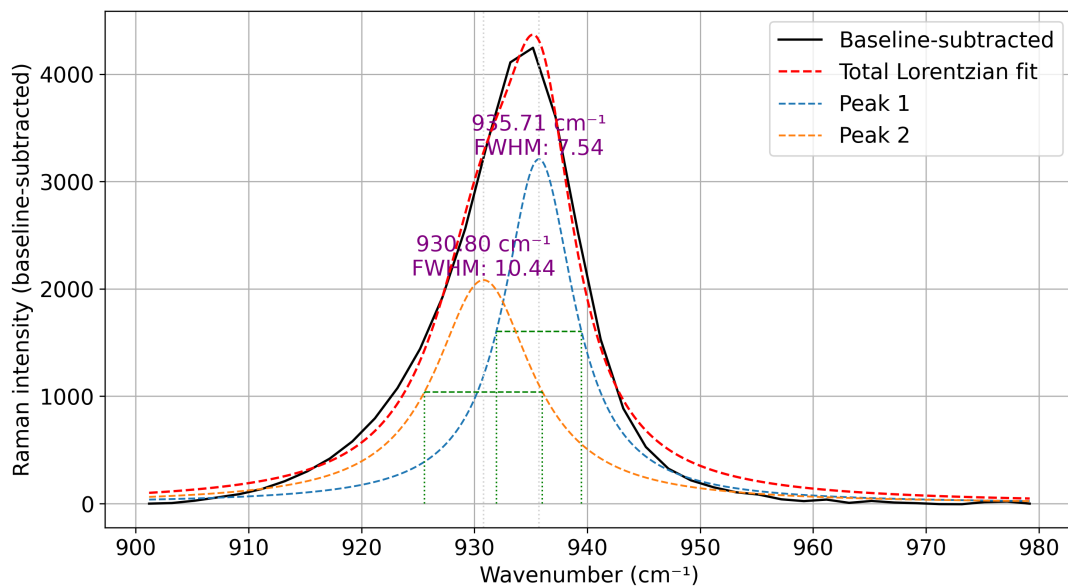
Lorentzian fit ν_1 region (PortableCal) -5°C | Components n=2



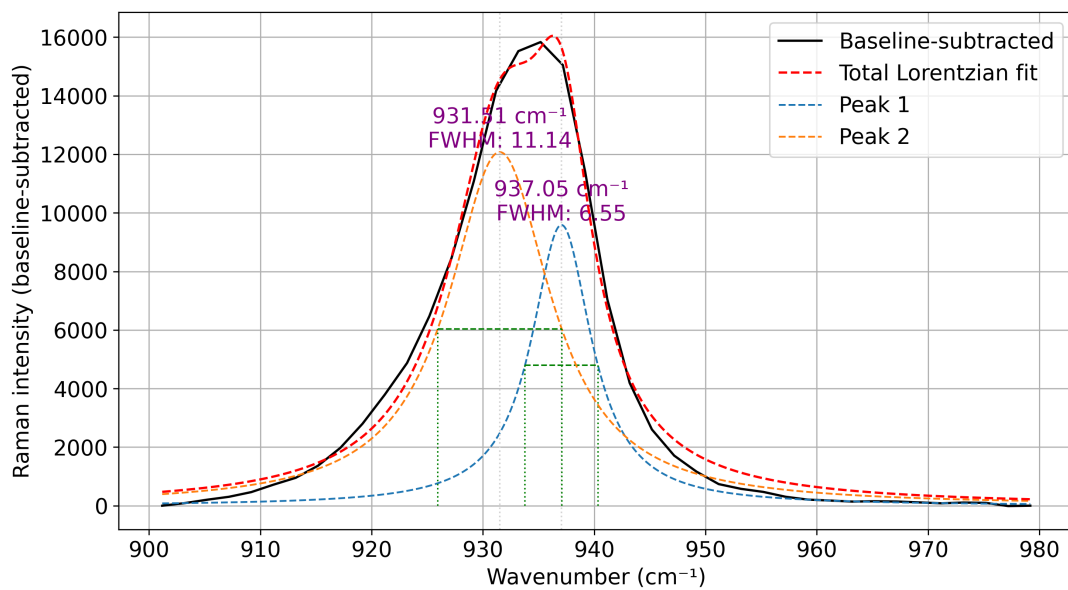
Lorentzian fit ν_1 region (PortableCal) -3°C | Components n=2

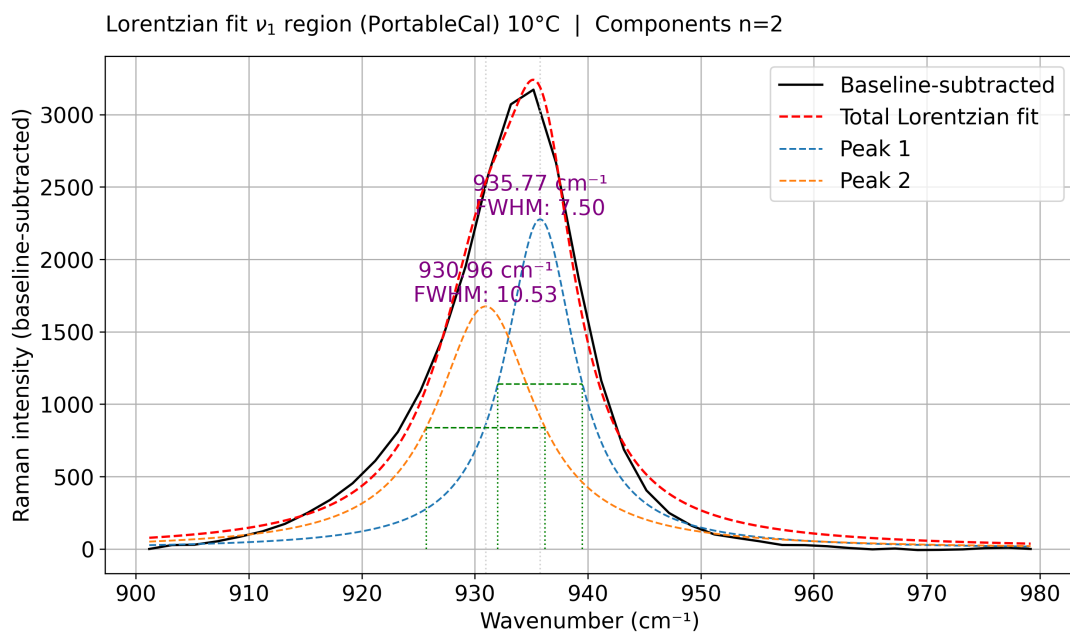
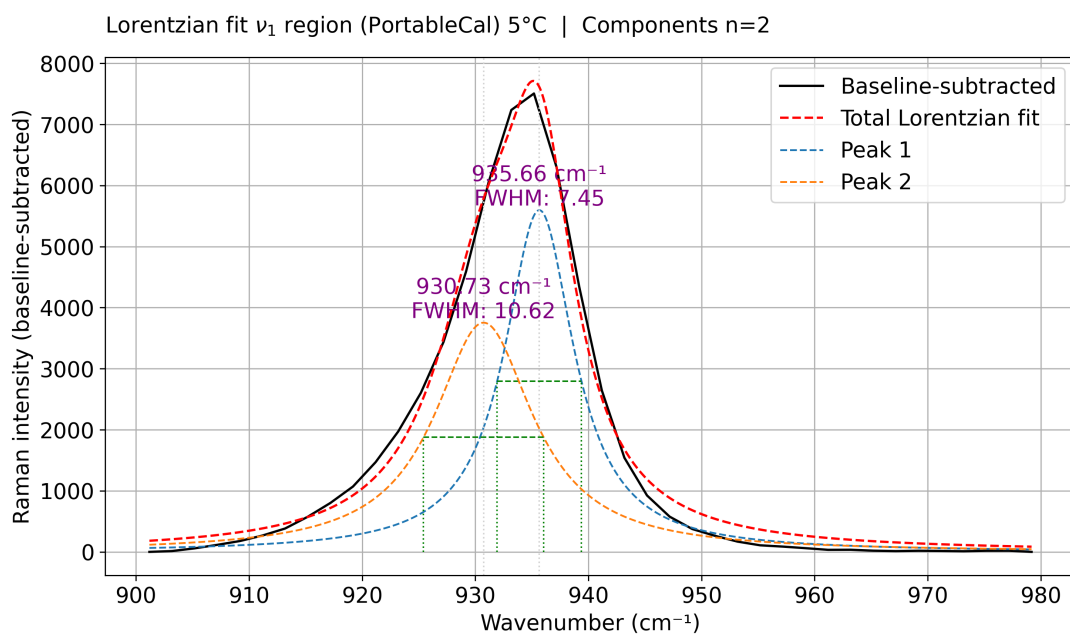


Lorentzian fit ν_1 region (PortableCal) -1°C | Components n=2

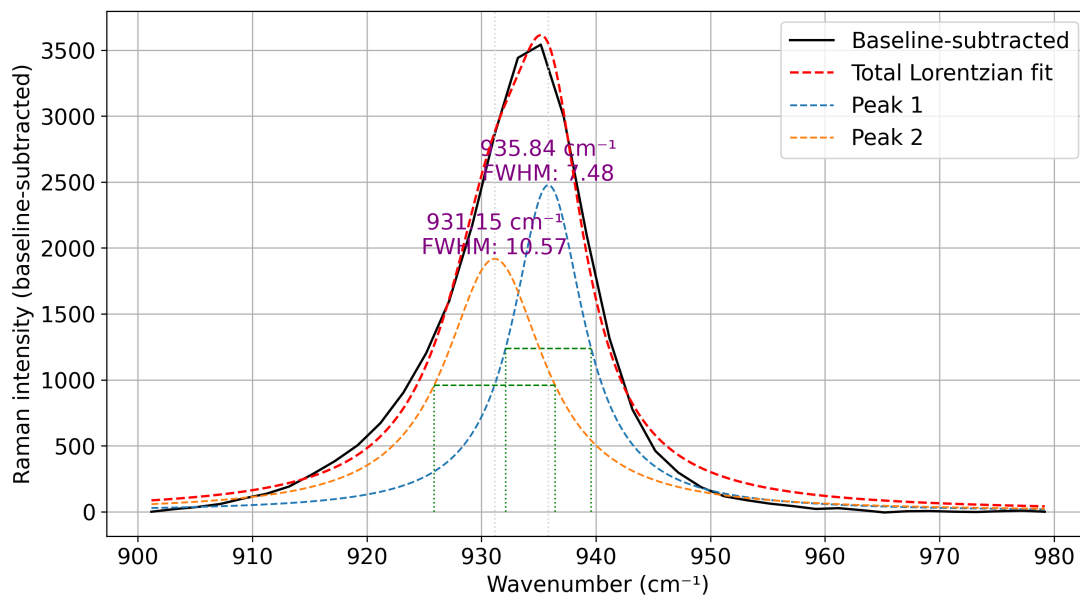


Lorentzian fit ν_1 region (PortableCal) 0°C | Components n=2

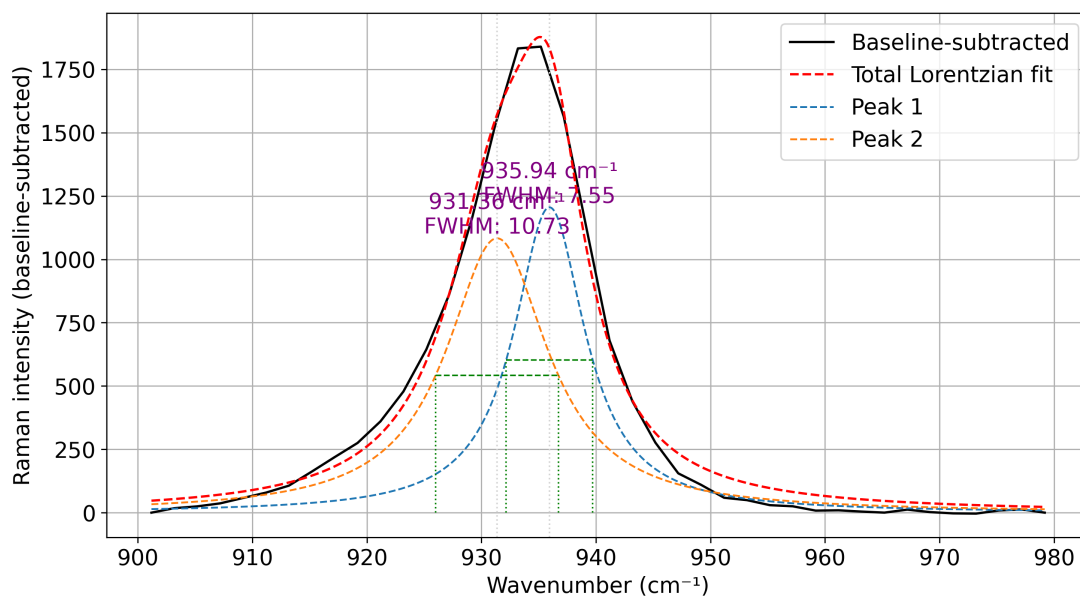




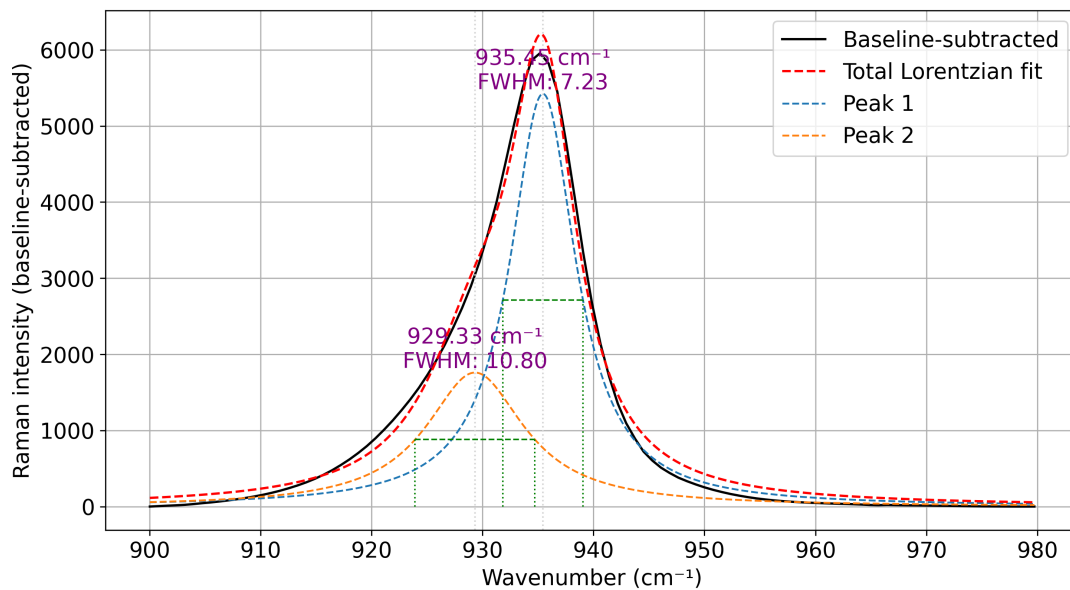
Lorentzian fit ν_1 region (PortableCal) 12°C | Components n=2



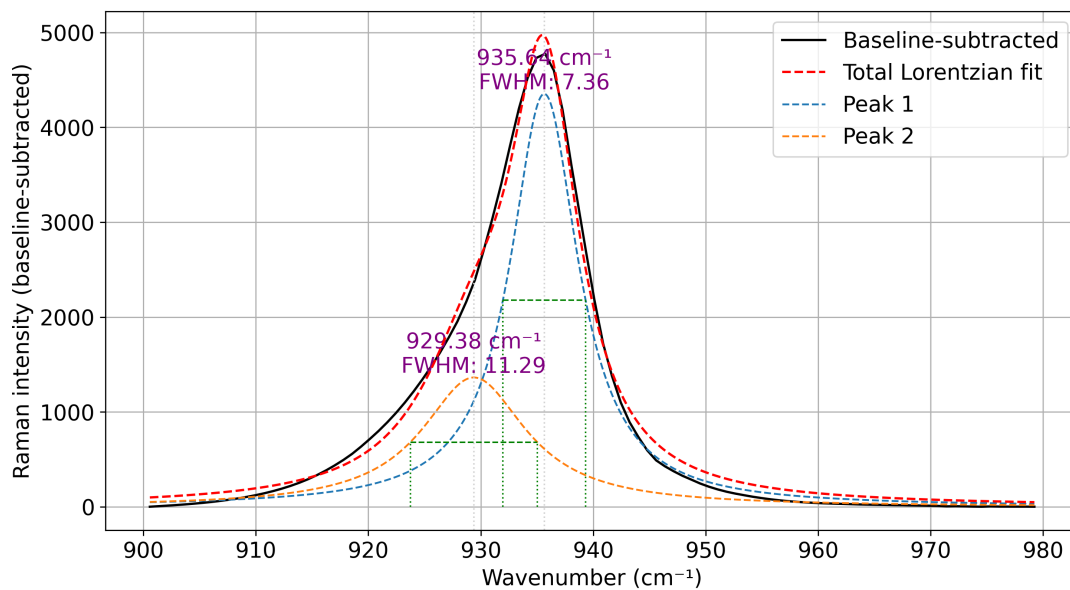
Lorentzian fit ν_1 region (PortableCal) 15°C | Components n=2



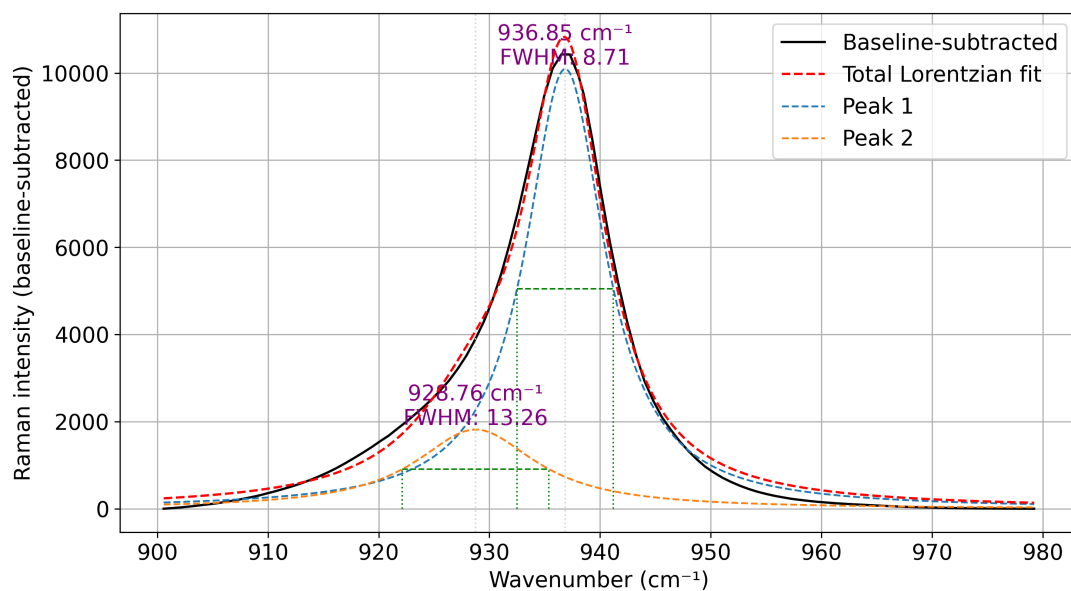
Lorentzian fit ν_1 region (Horiba) 20°C | Components n=2



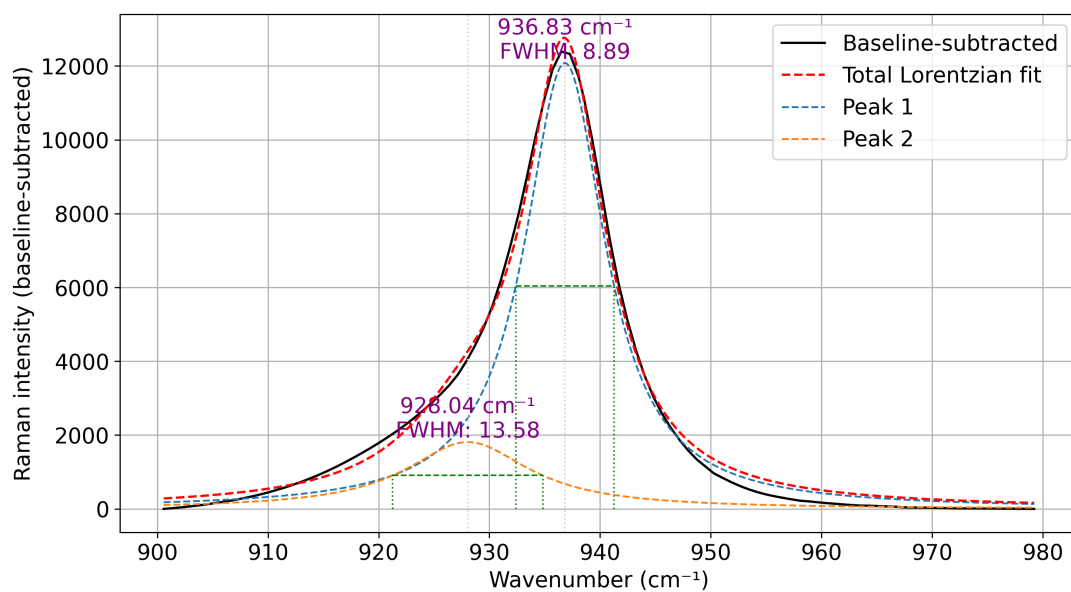
Lorentzian fit ν_1 region (Horiba) 35°C | Components n=2



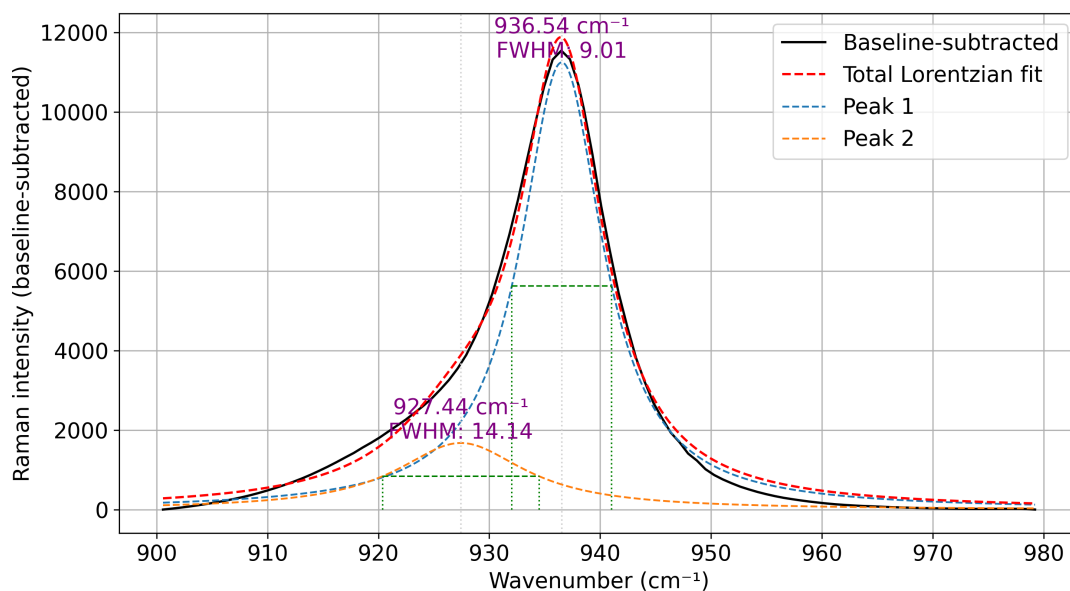
Lorentzian fit ν_1 region (Horiba) 75°C | Components n=2



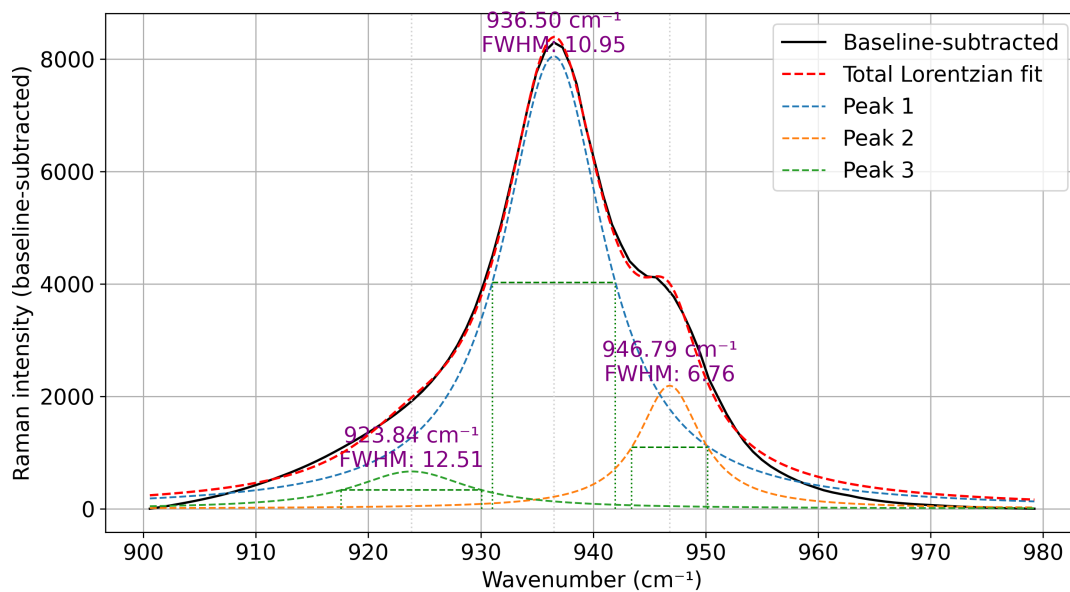
Lorentzian fit ν_1 region (Horiba) 100°C | Components n=2

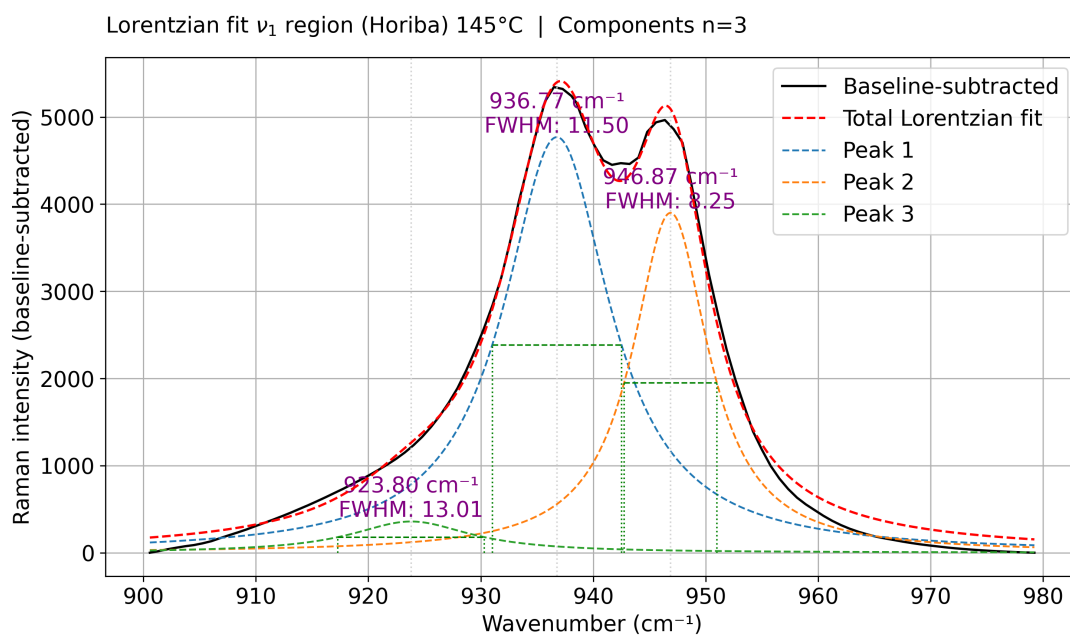
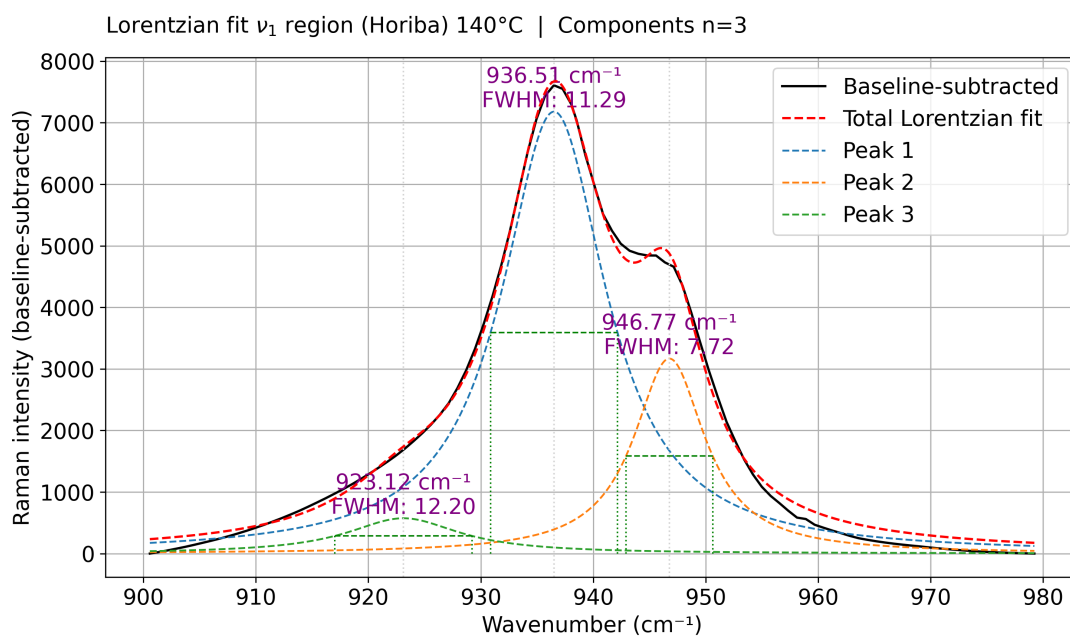


Lorentzian fit ν_1 region (Horiba) 125°C | Components n=2

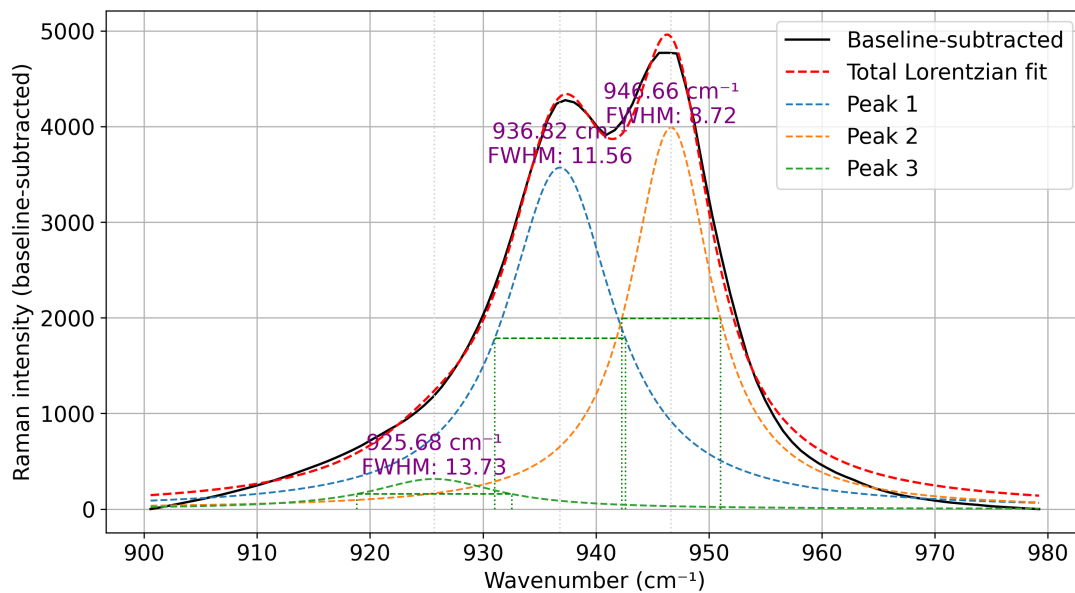


Lorentzian fit ν_1 region (Horiba) 135°C | Components n=3

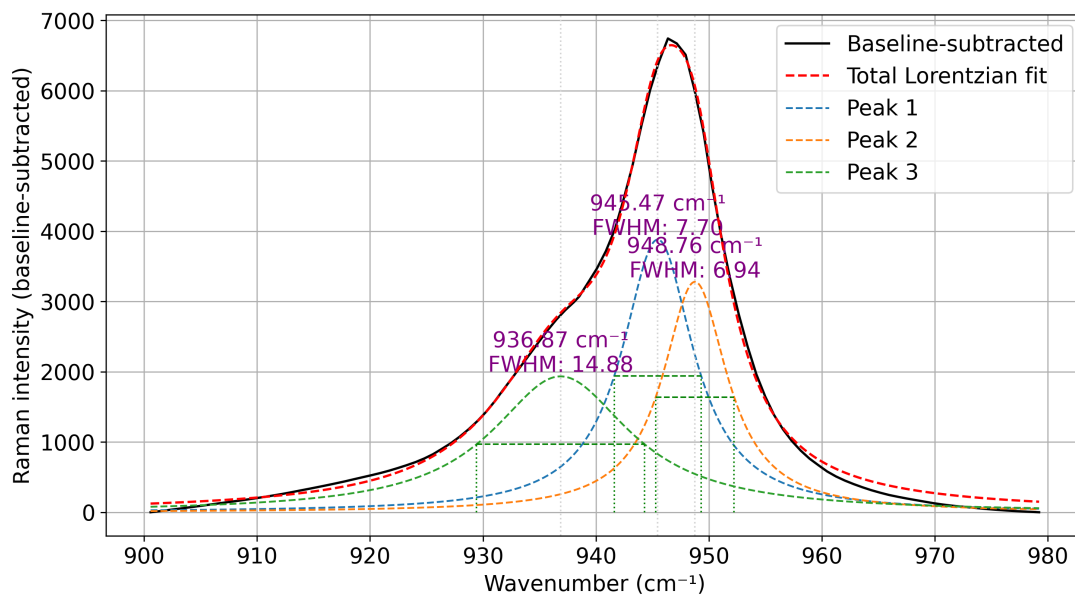




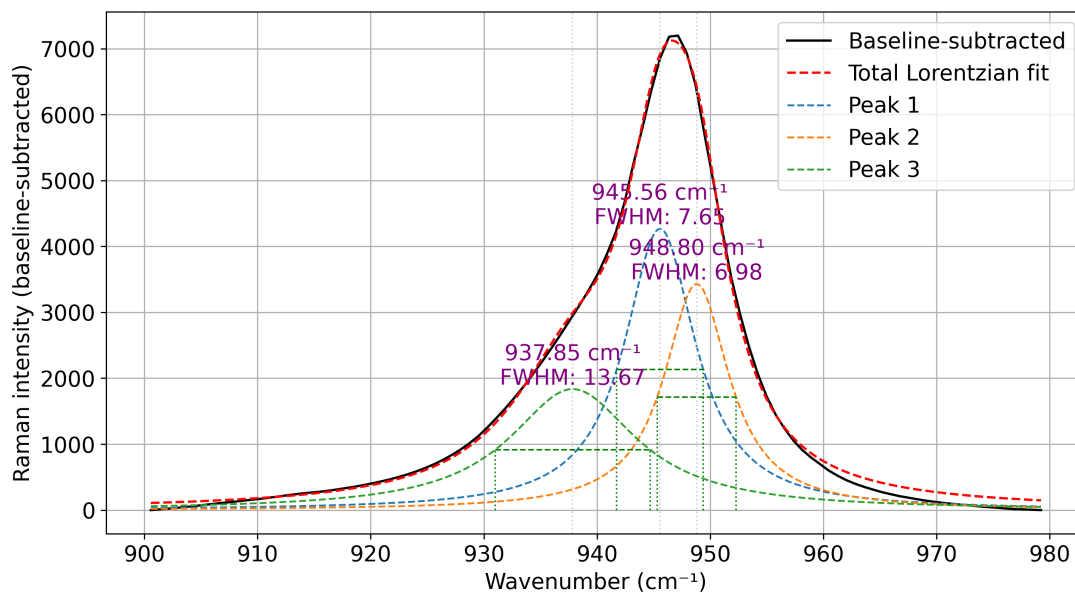
Lorentzian fit ν_1 region (Horiba) 147°C | Components n=3



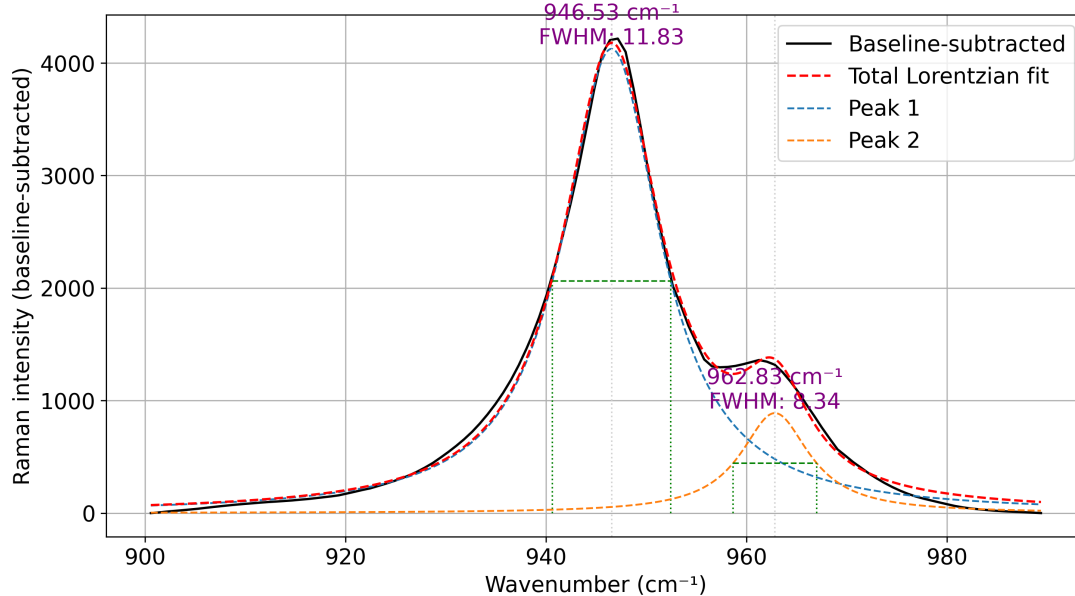
Lorentzian fit ν_1 region (Horiba) 150°C | Components n=3



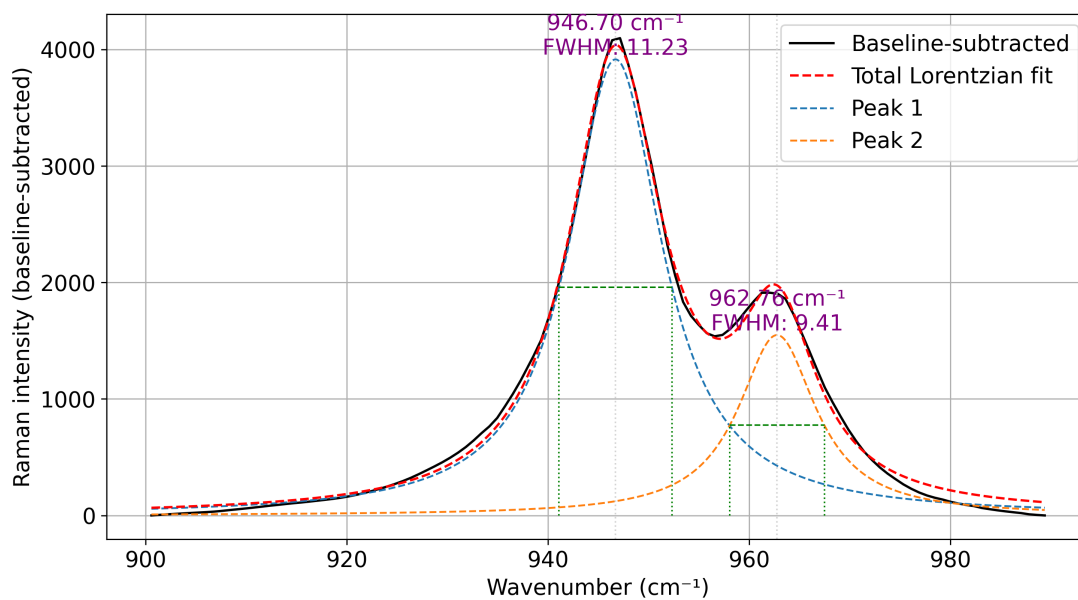
Lorentzian fit ν_1 region (Horiba) 155°C | Components n=3



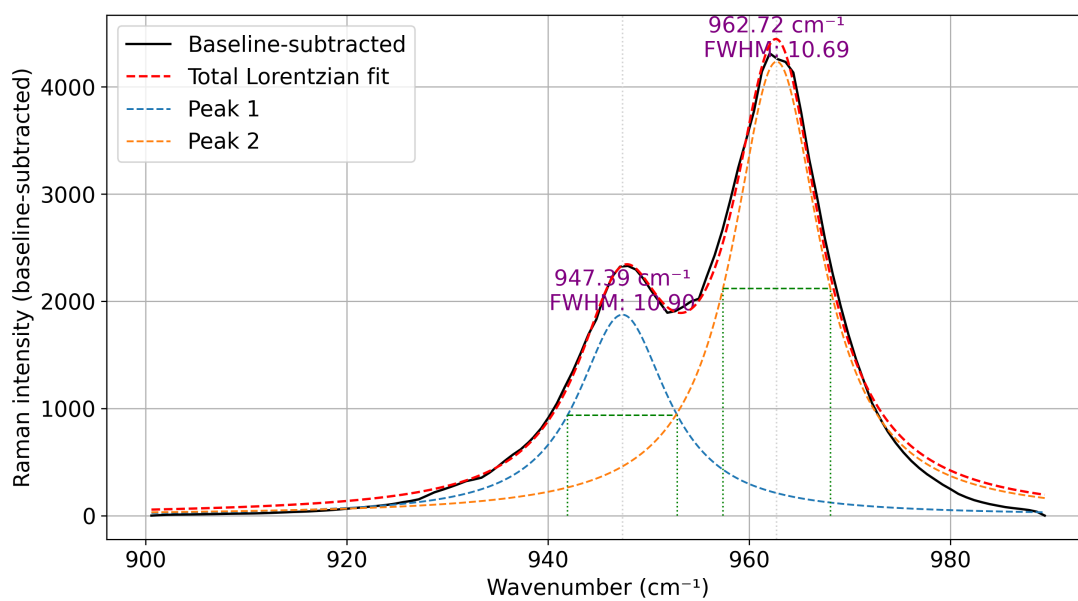
Lorentzian fit ν_1 region (Horiba) 160°C | Components n=2



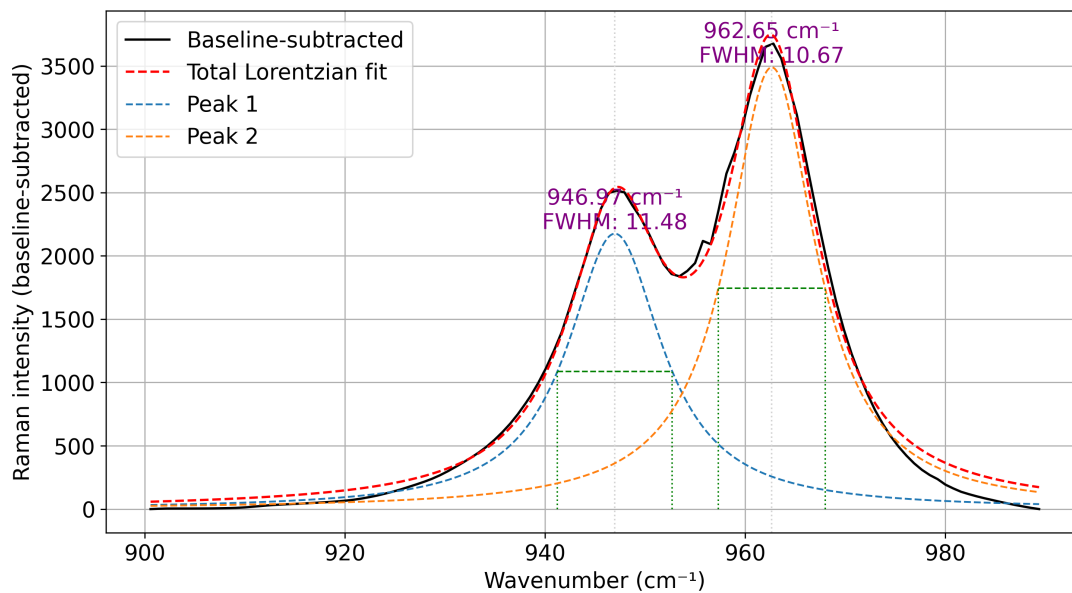
Lorentzian fit ν_1 region (Horiba) 161°C | Components n=2



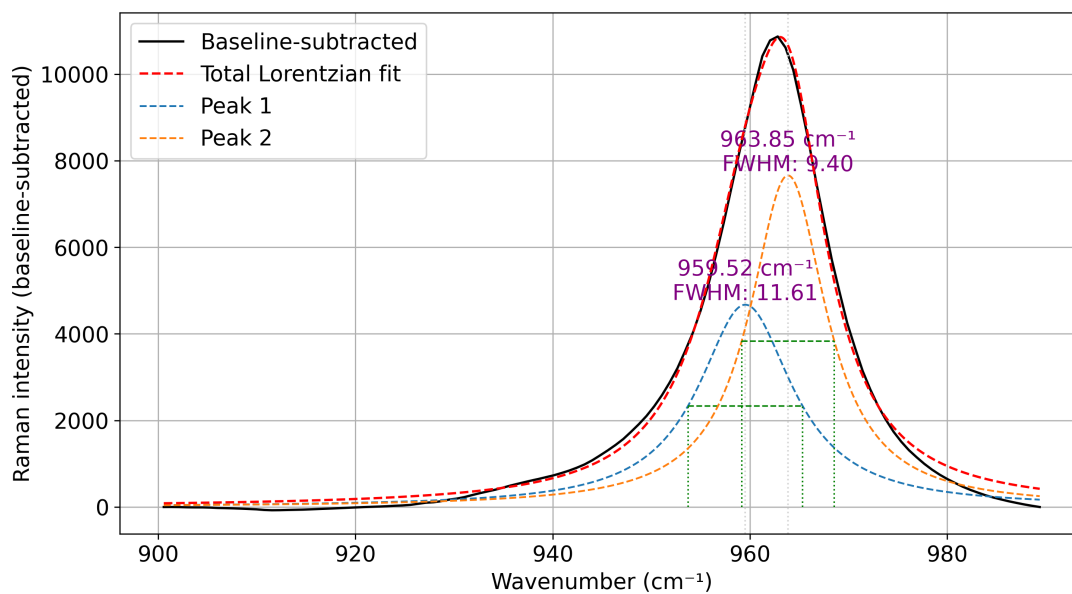
Lorentzian fit ν_1 region (Horiba) 162°C | Components n=2



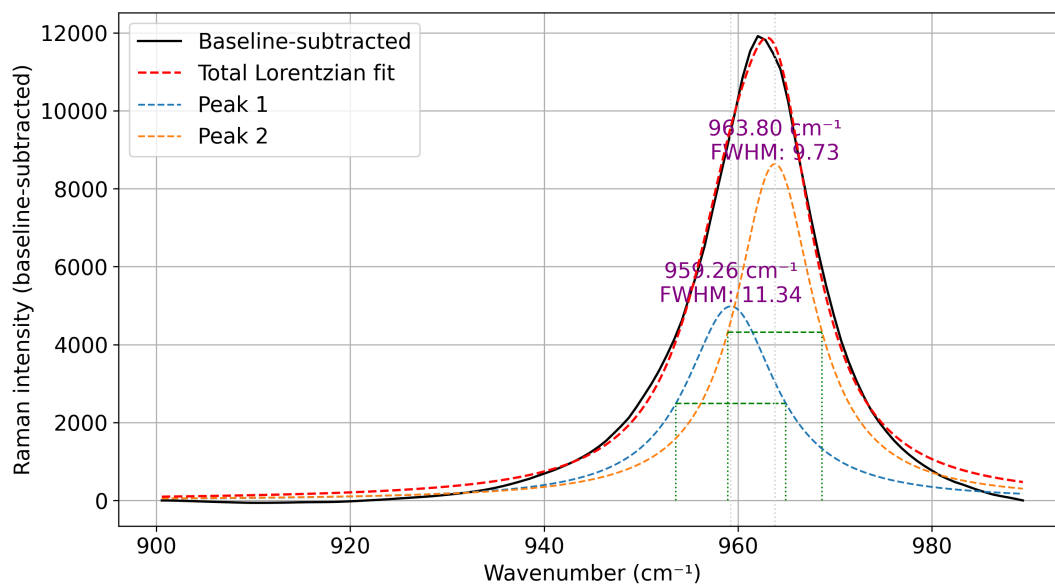
Lorentzian fit ν_1 region (Horiba) 163°C | Components n=2



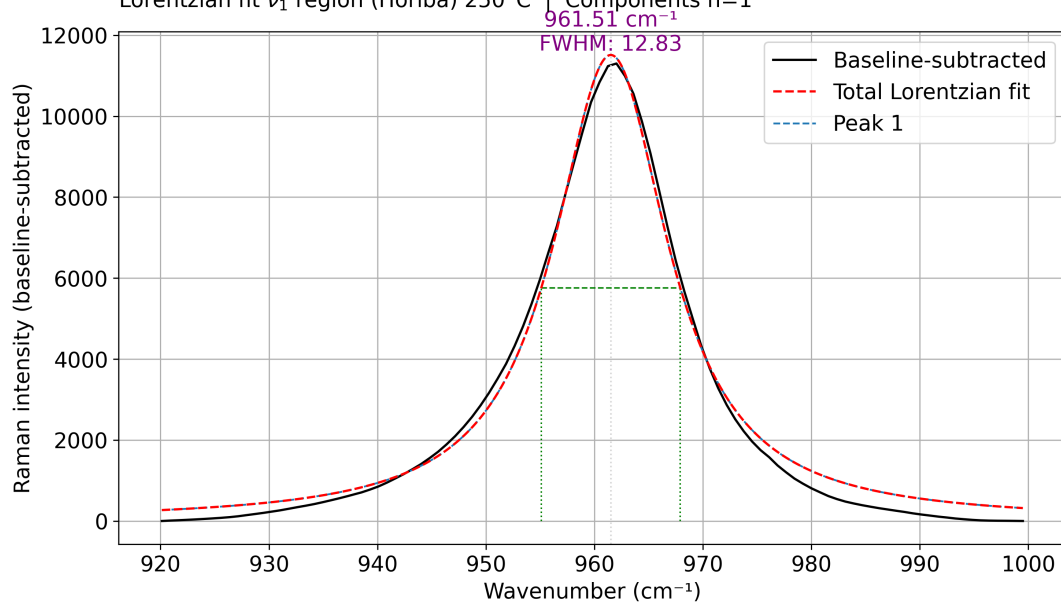
Lorentzian fit ν_1 region (Horiba) 180°C | Components n=2

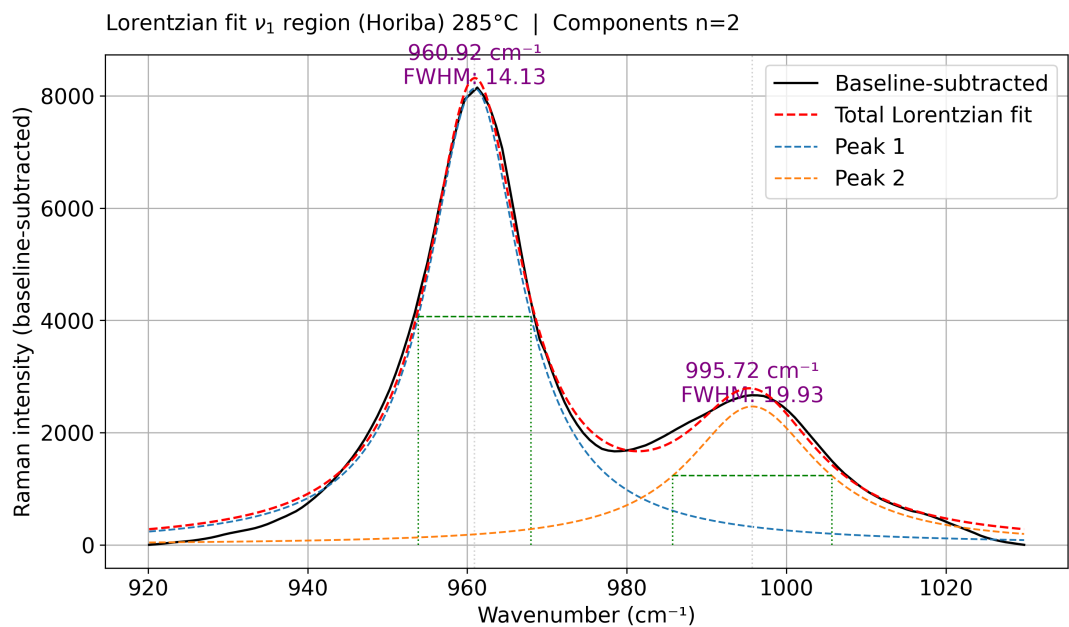
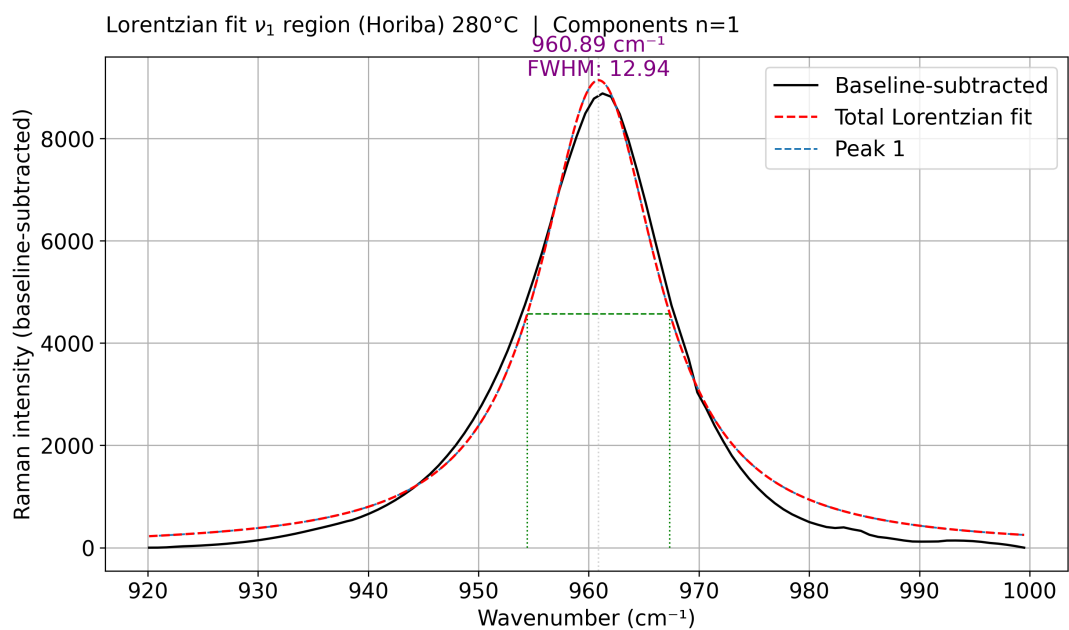


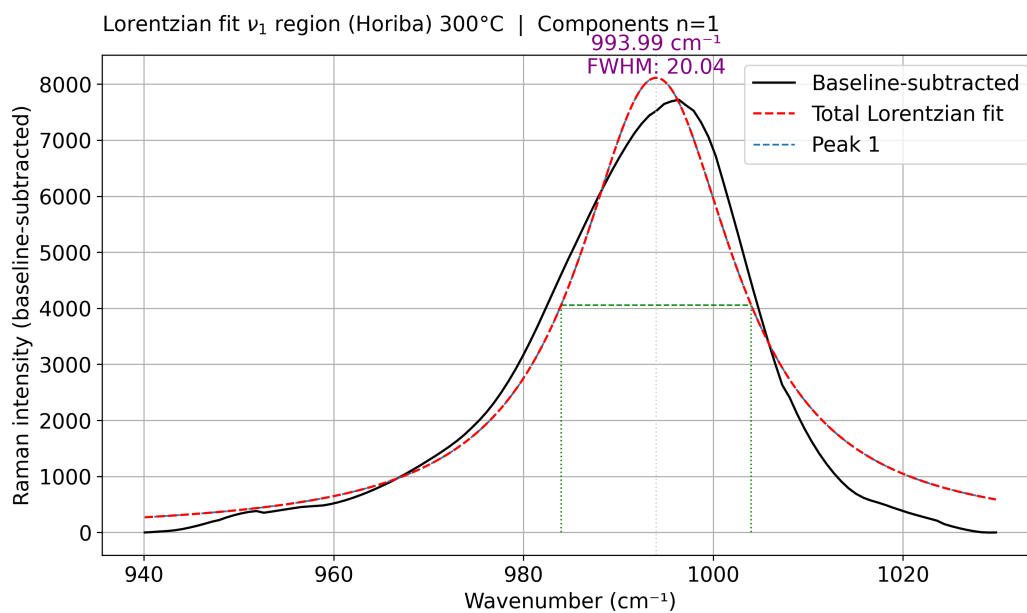
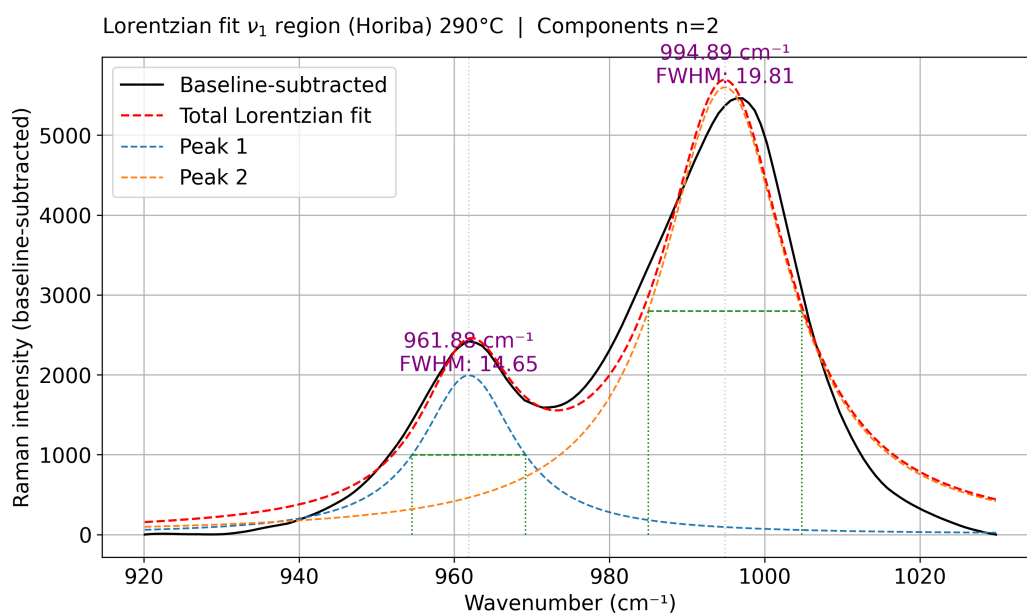
Lorentzian fit ν_1 region (Horiba) 200°C | Components n=2

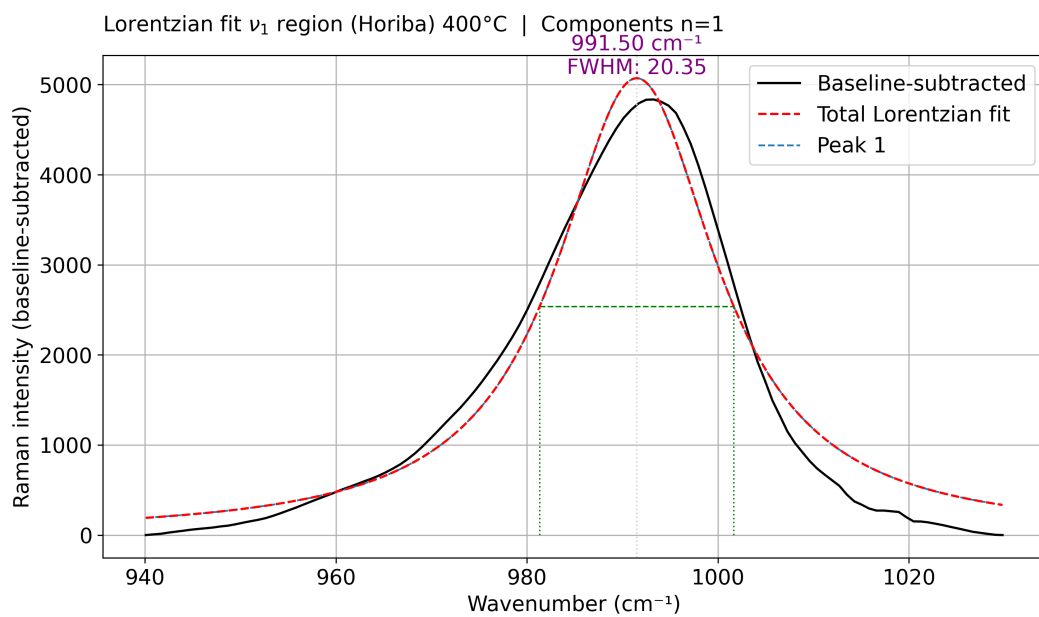
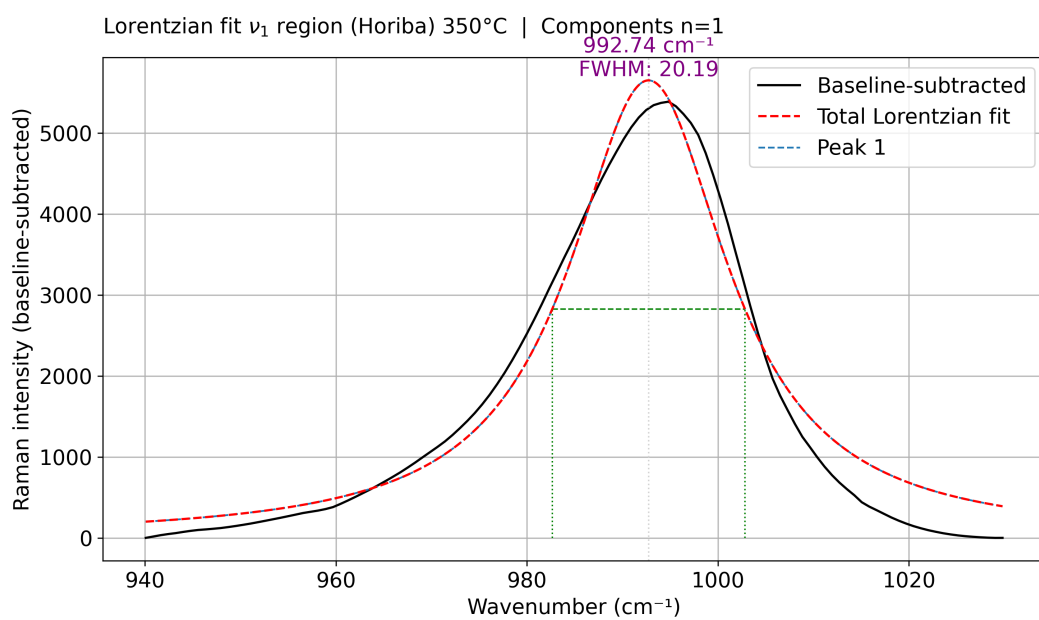


Lorentzian fit ν_1 region (Horiba) 250°C | Components n=1



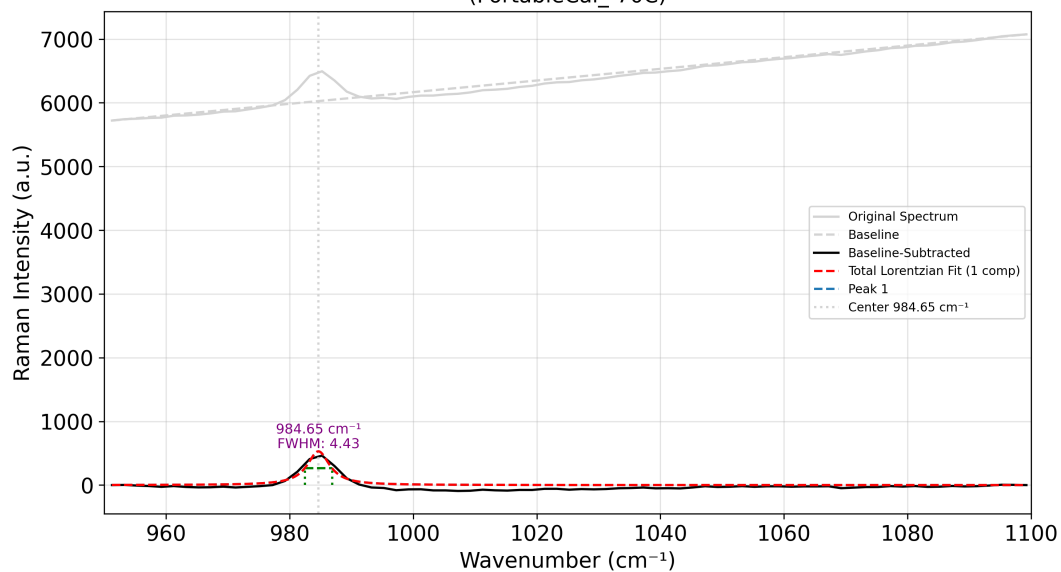




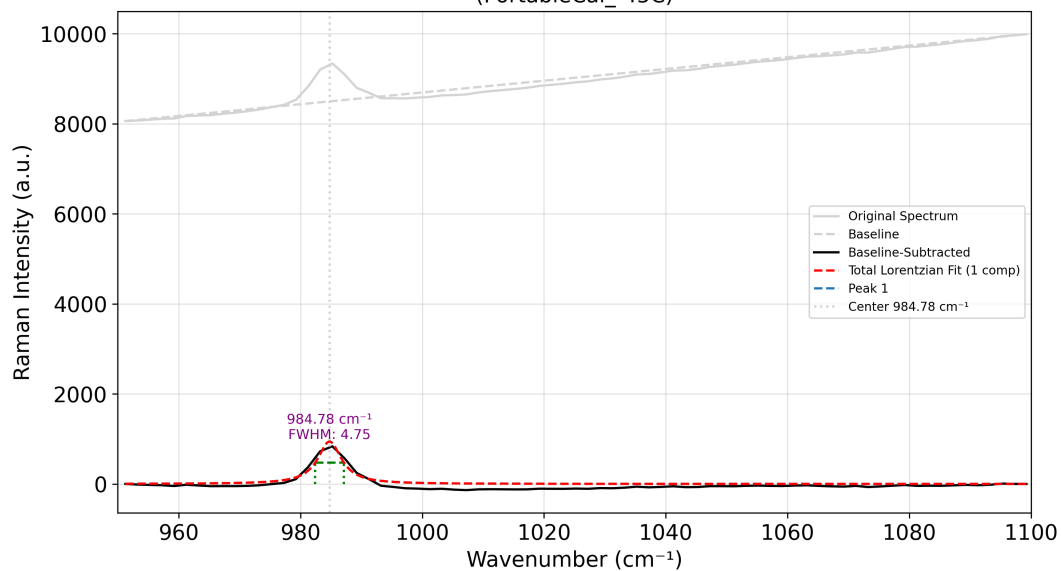


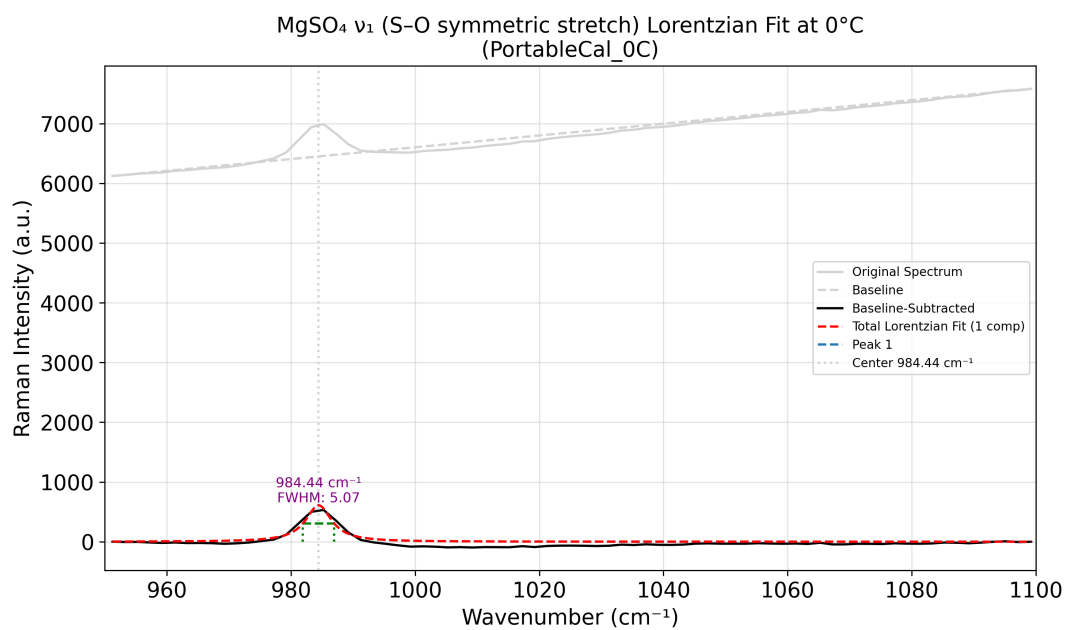
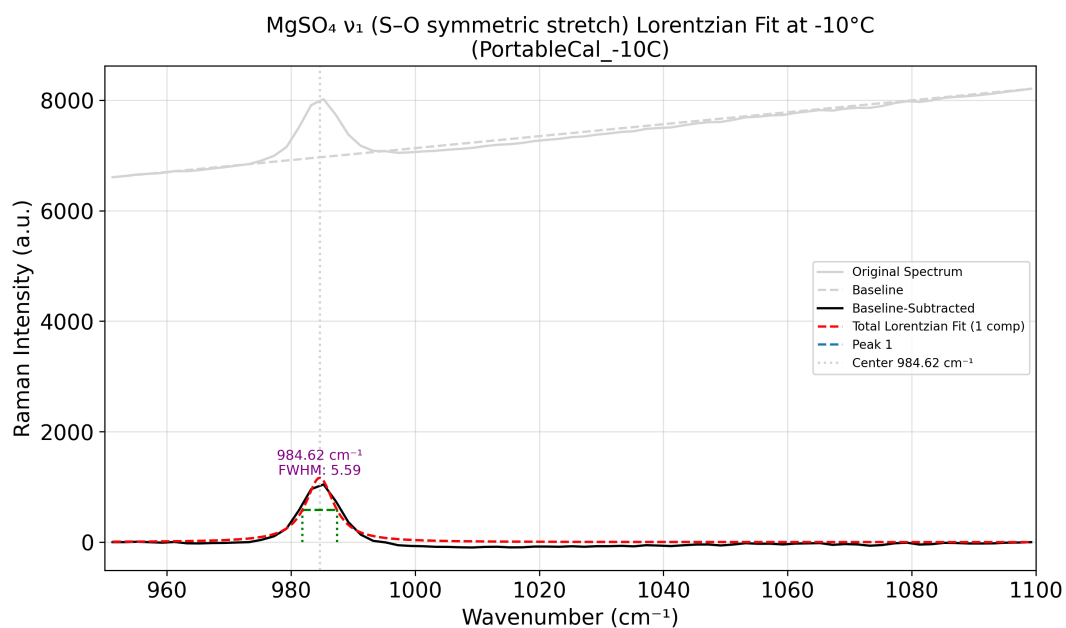
S1.2 $\text{MgSO}_4 \cdot \text{XH}_2\text{O}$ Plots -70 to 300 °C

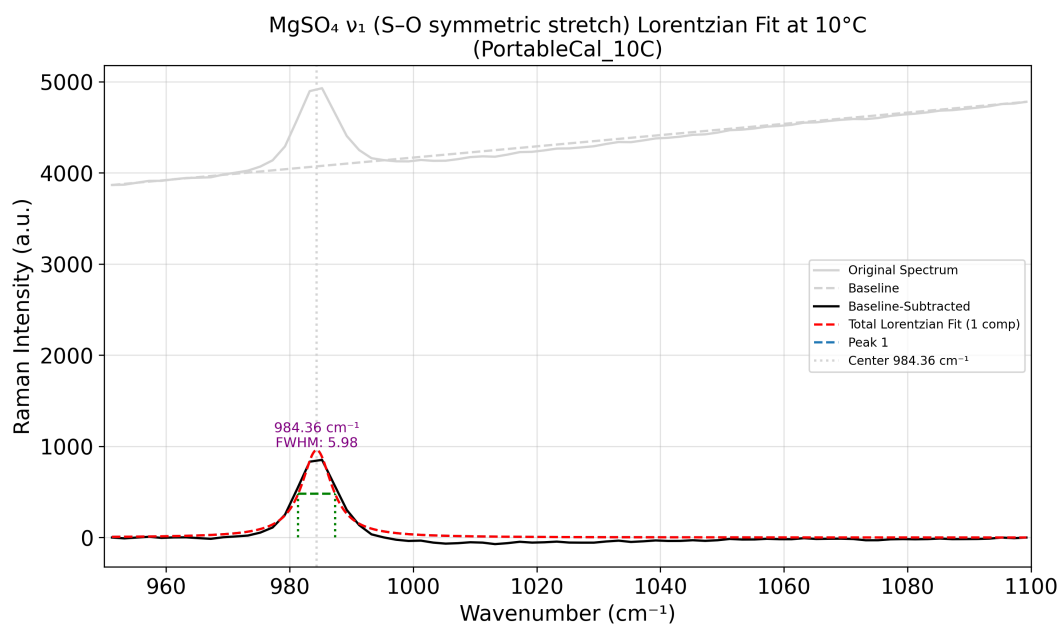
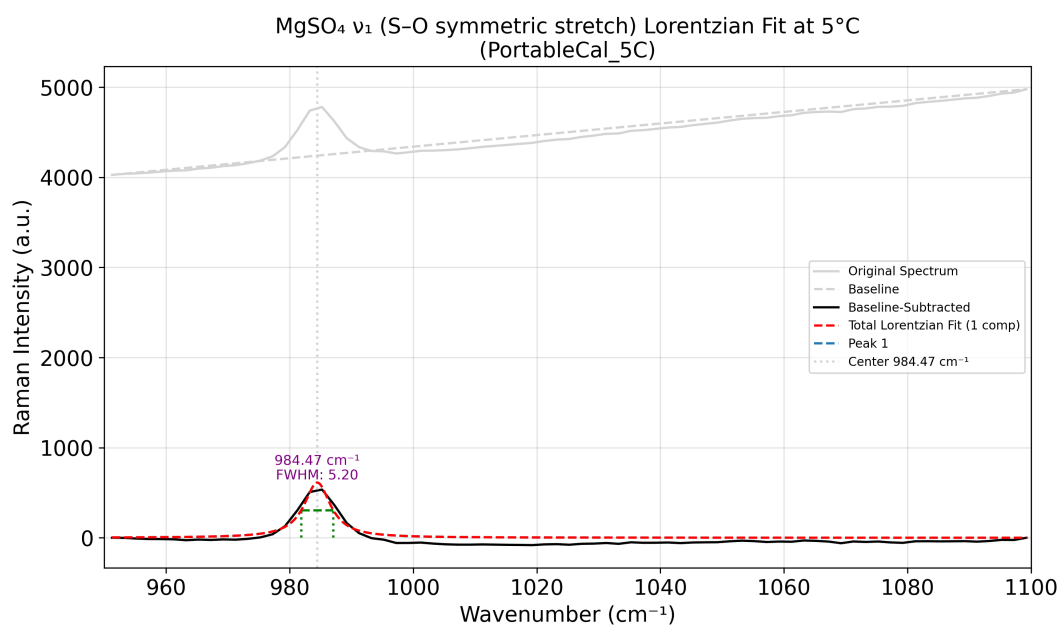
$\text{MgSO}_4 \nu_1$ (S-O symmetric stretch) Lorentzian Fit at -70°C
(PortableCal_-70C)

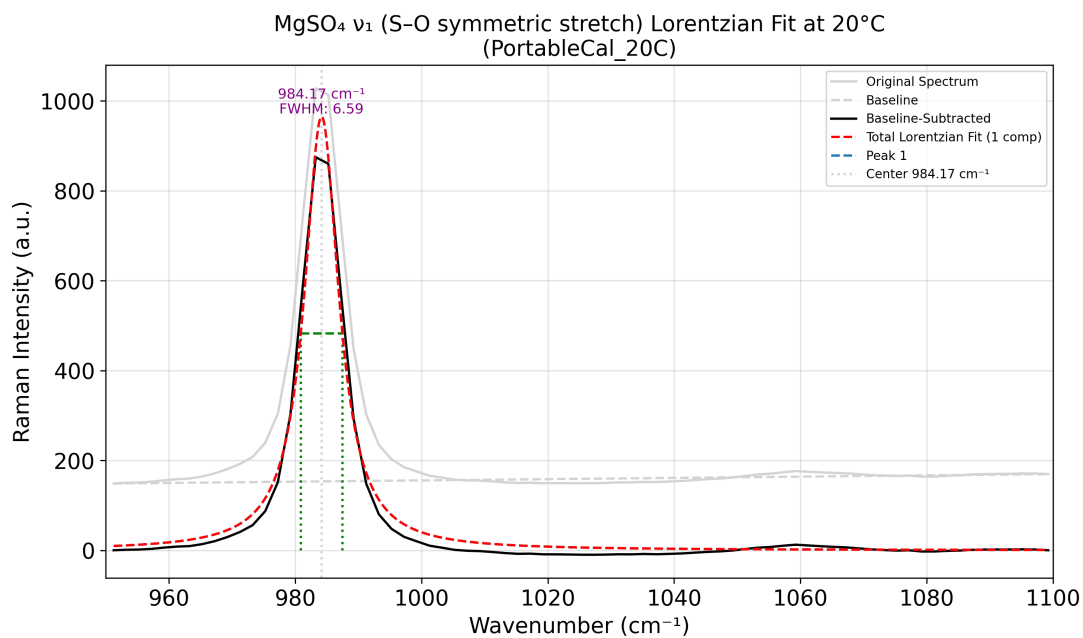
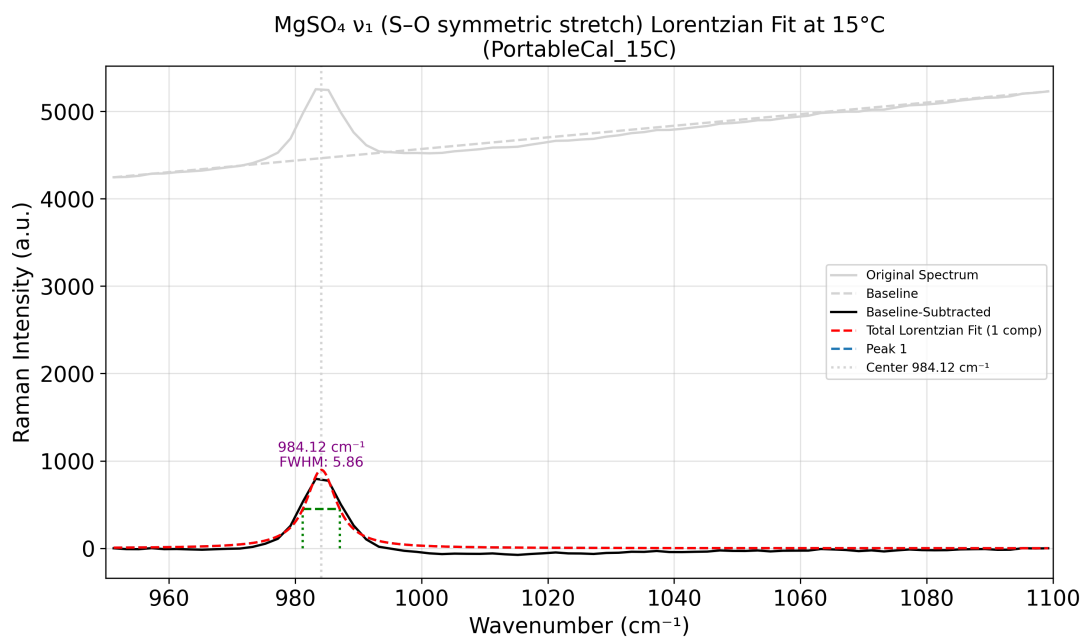


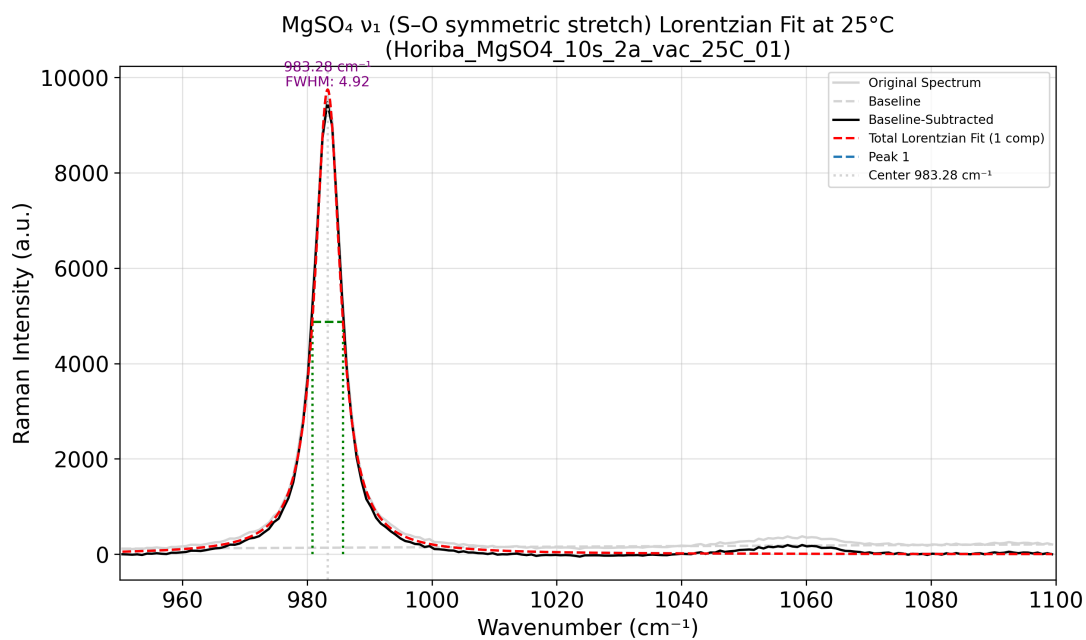
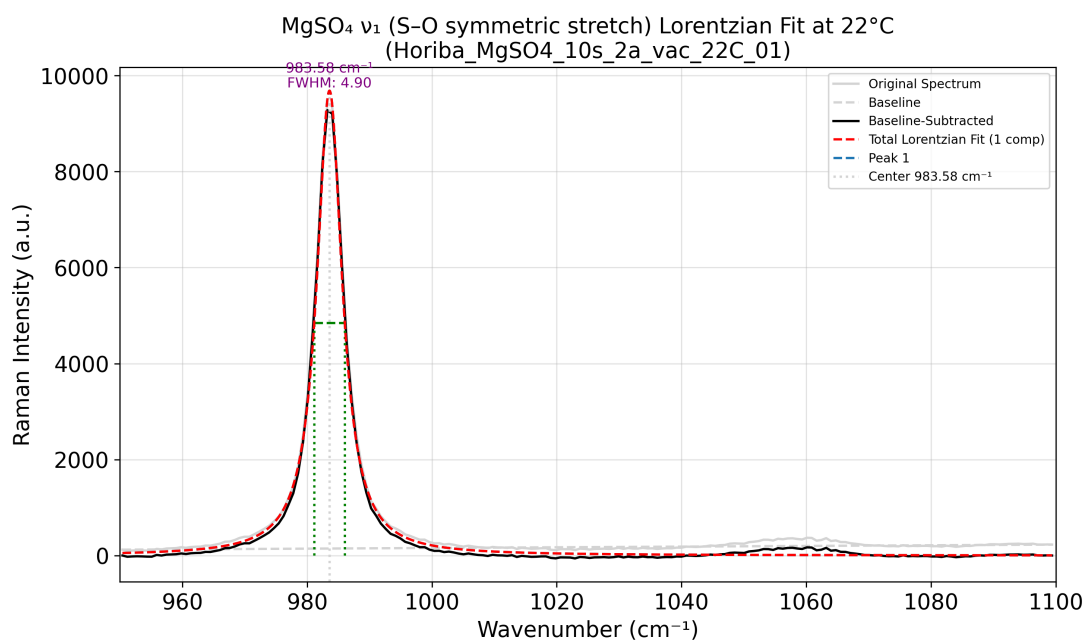
$\text{MgSO}_4 \nu_1$ (S-O symmetric stretch) Lorentzian Fit at -45°C
(PortableCal_-45C)

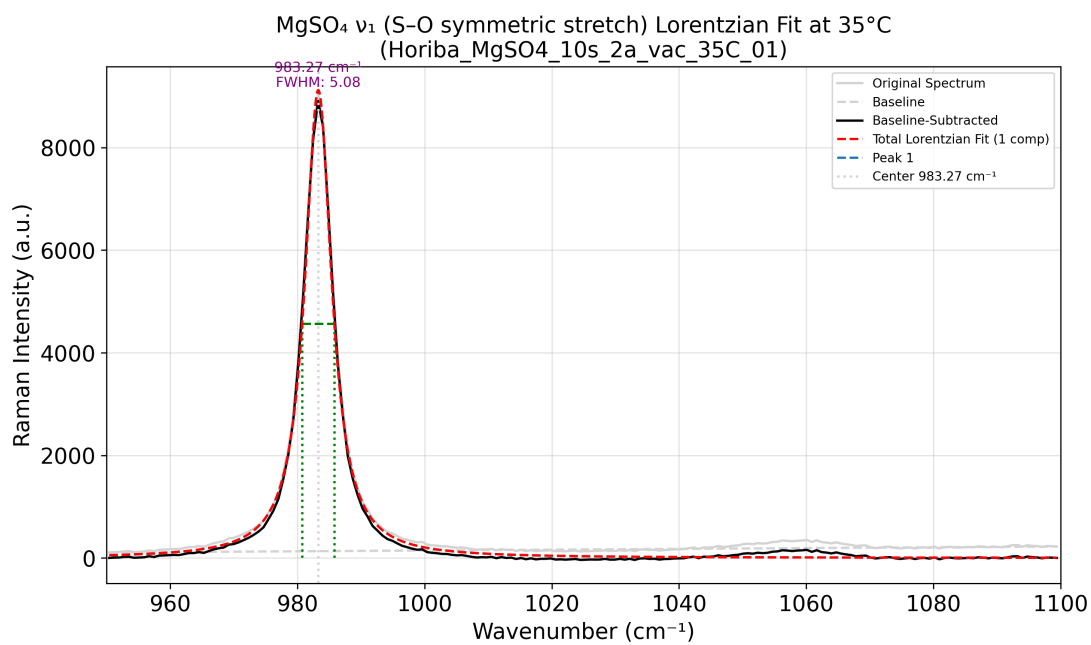
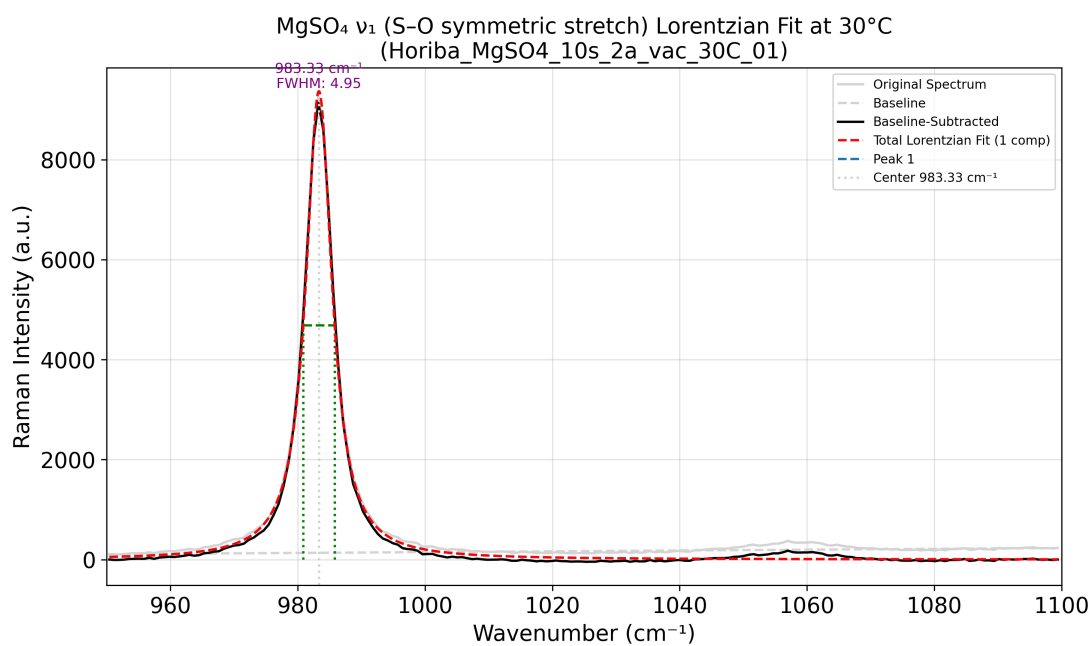


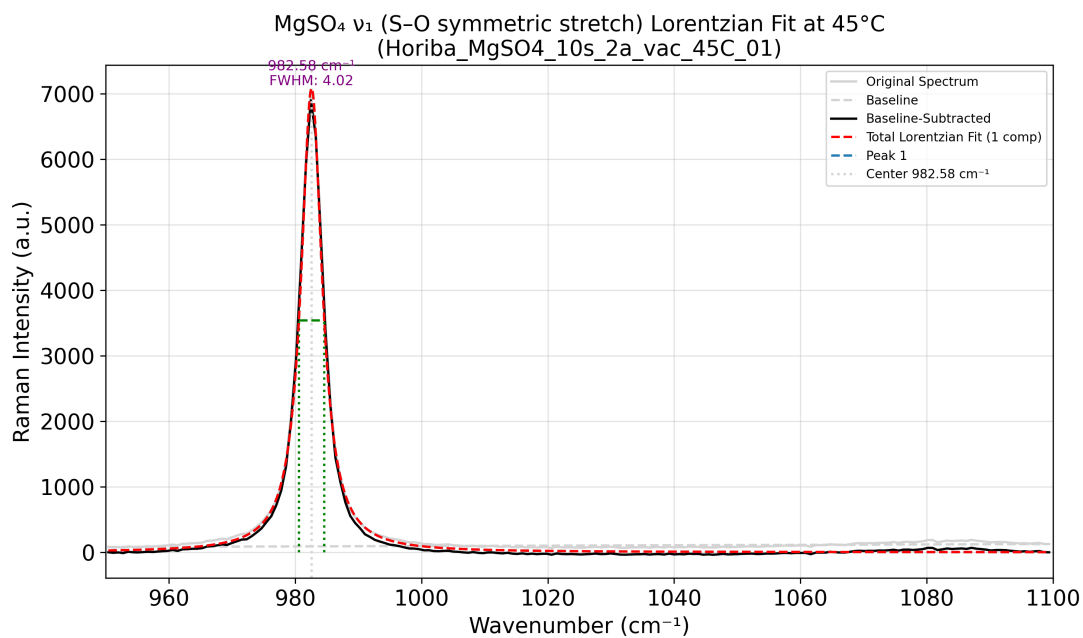
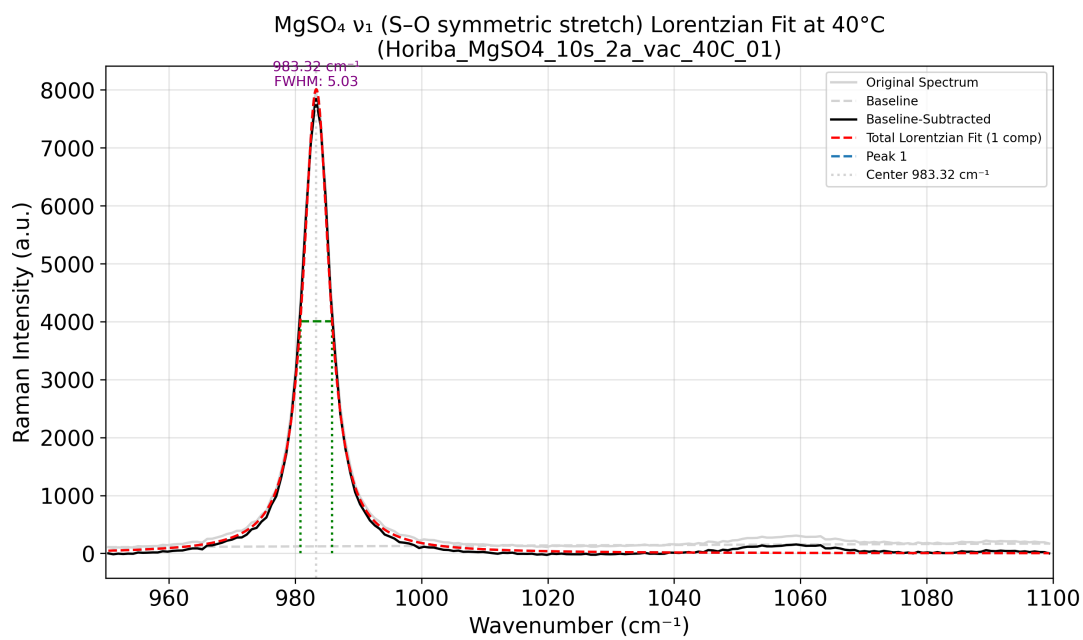


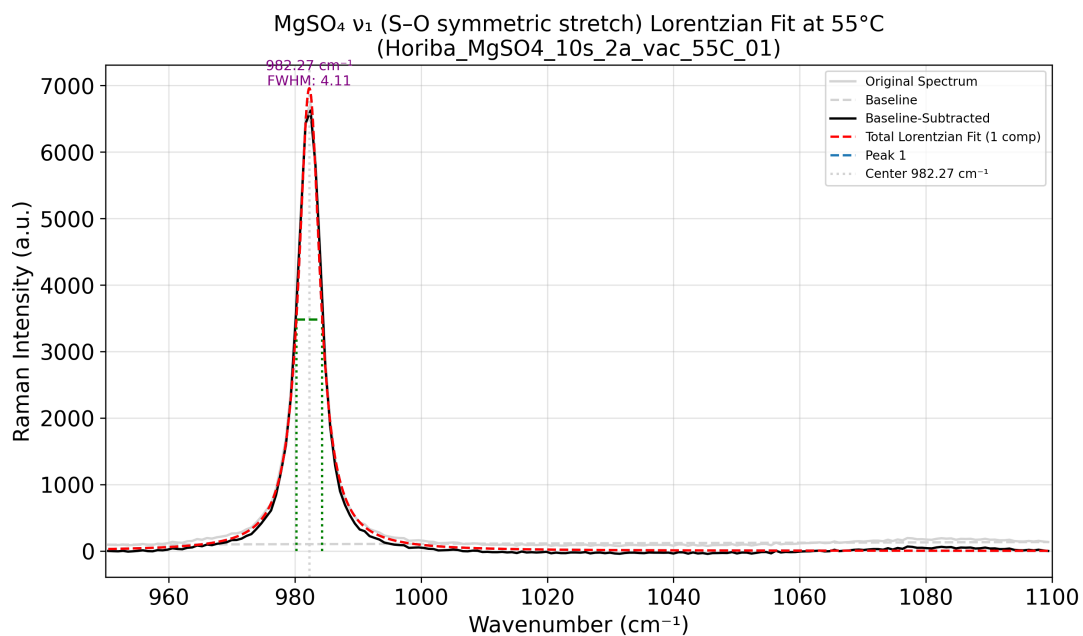
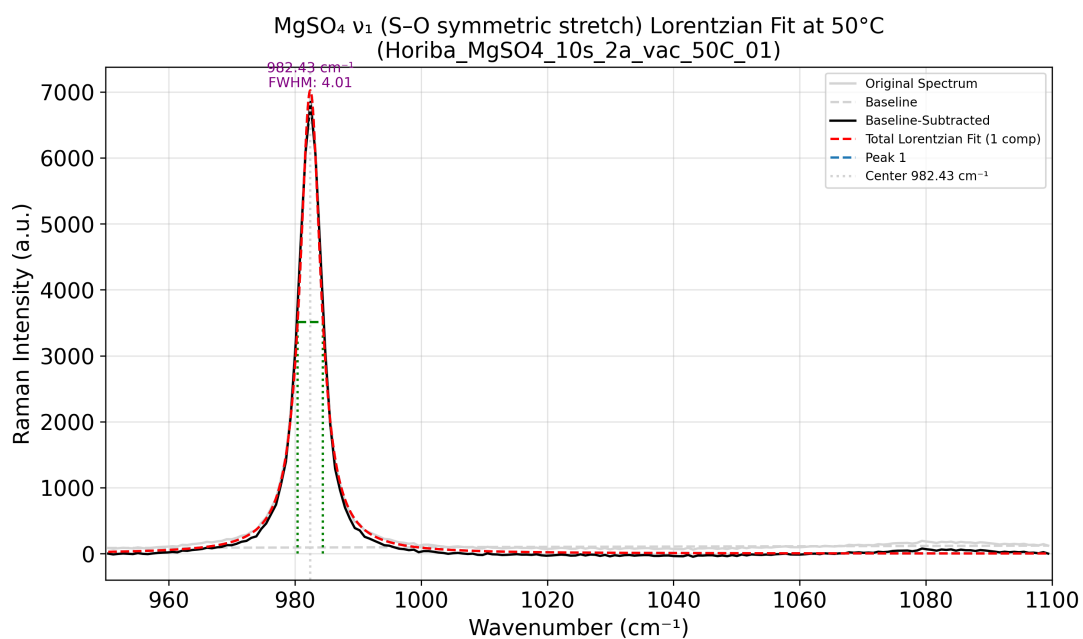


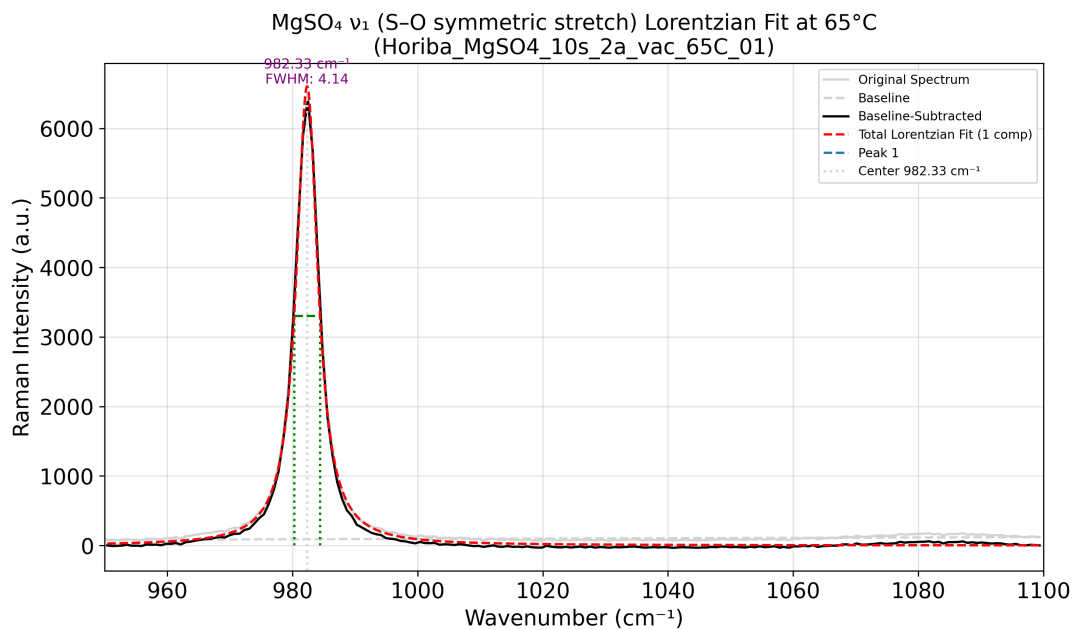
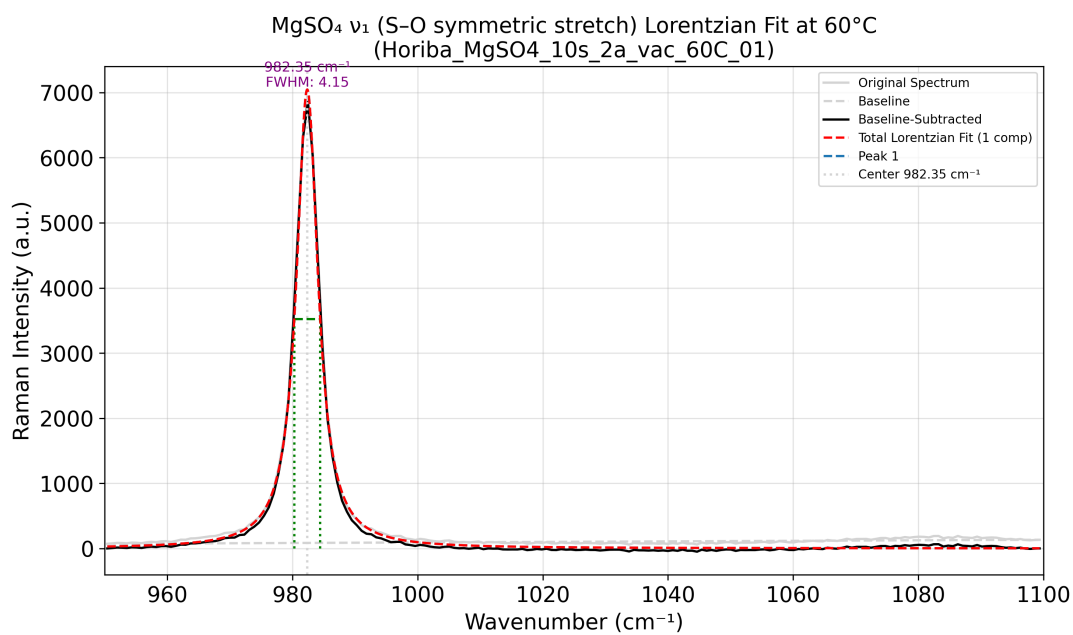


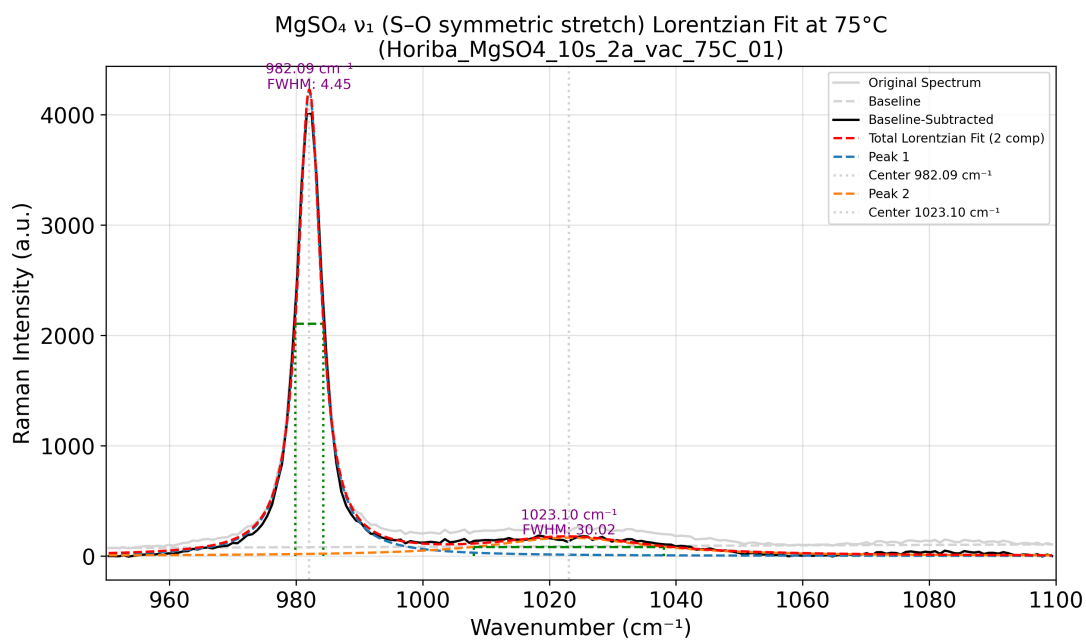
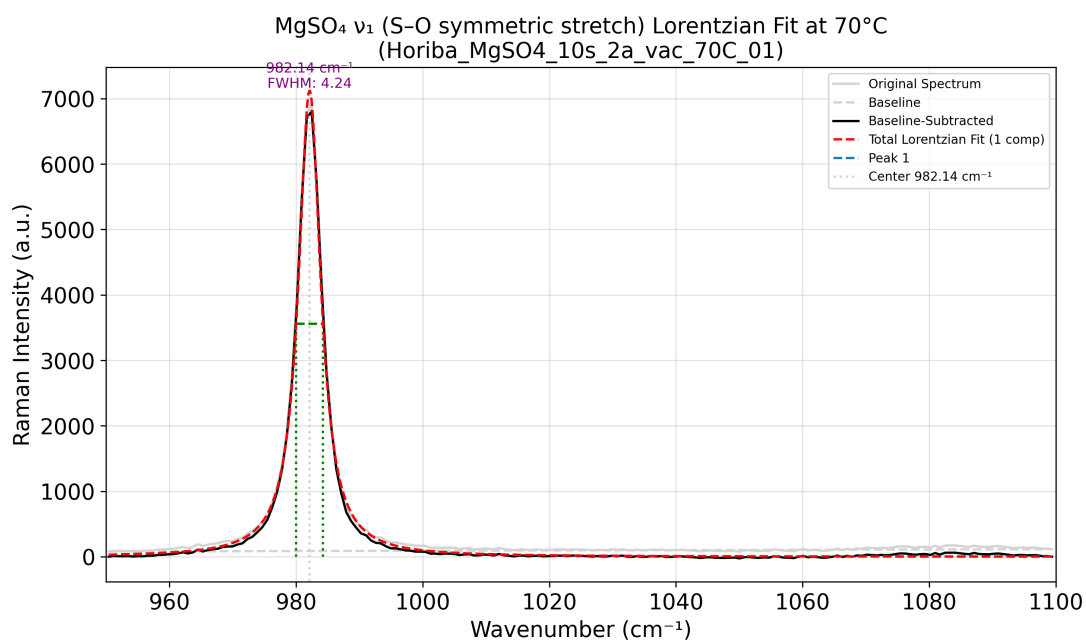


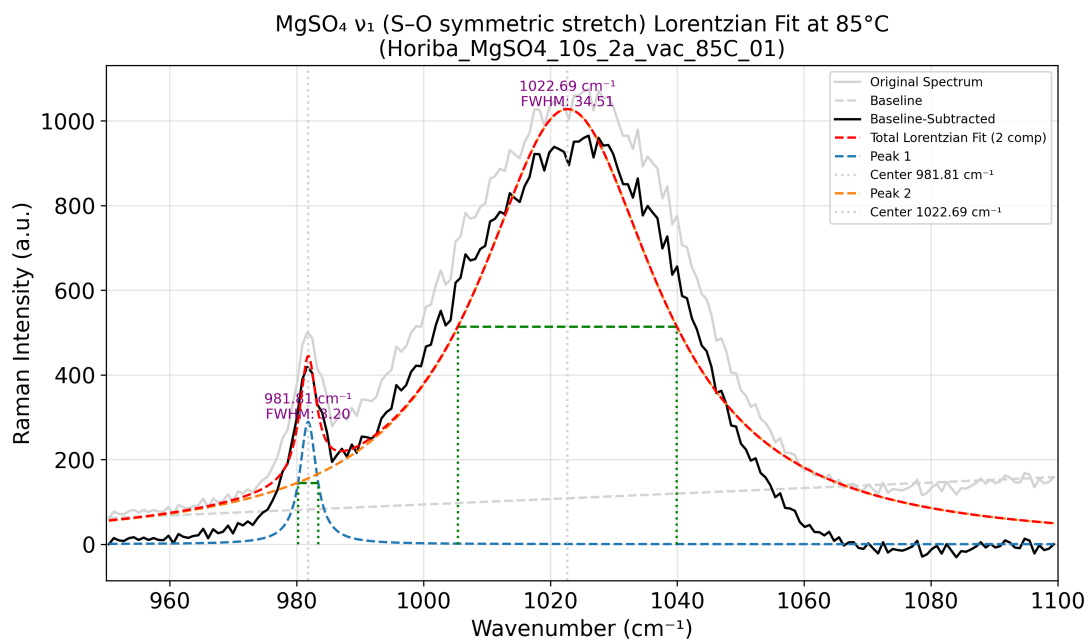
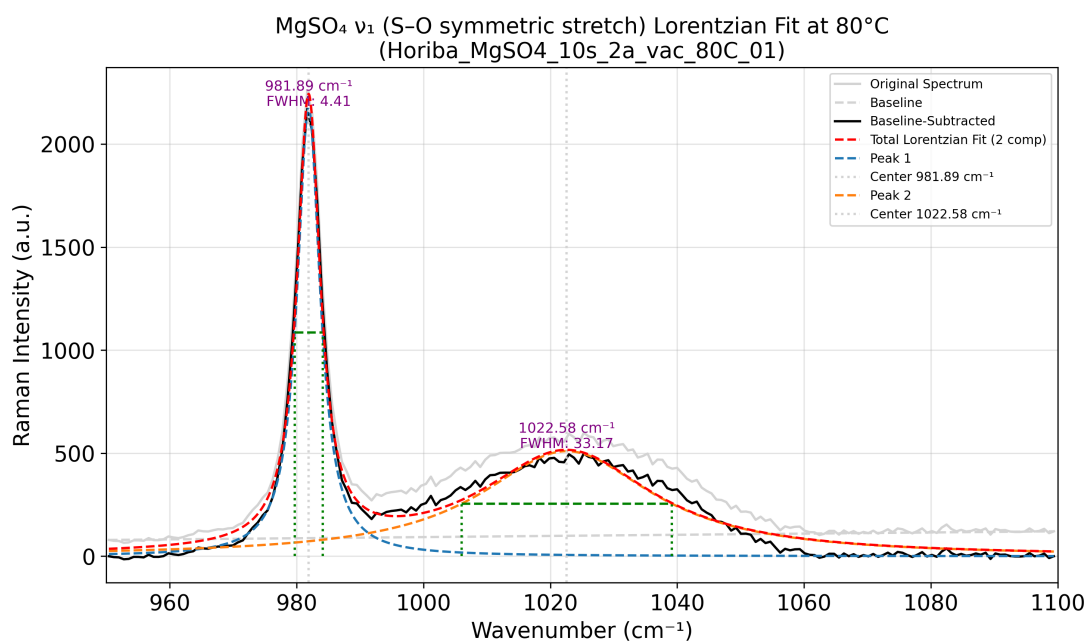


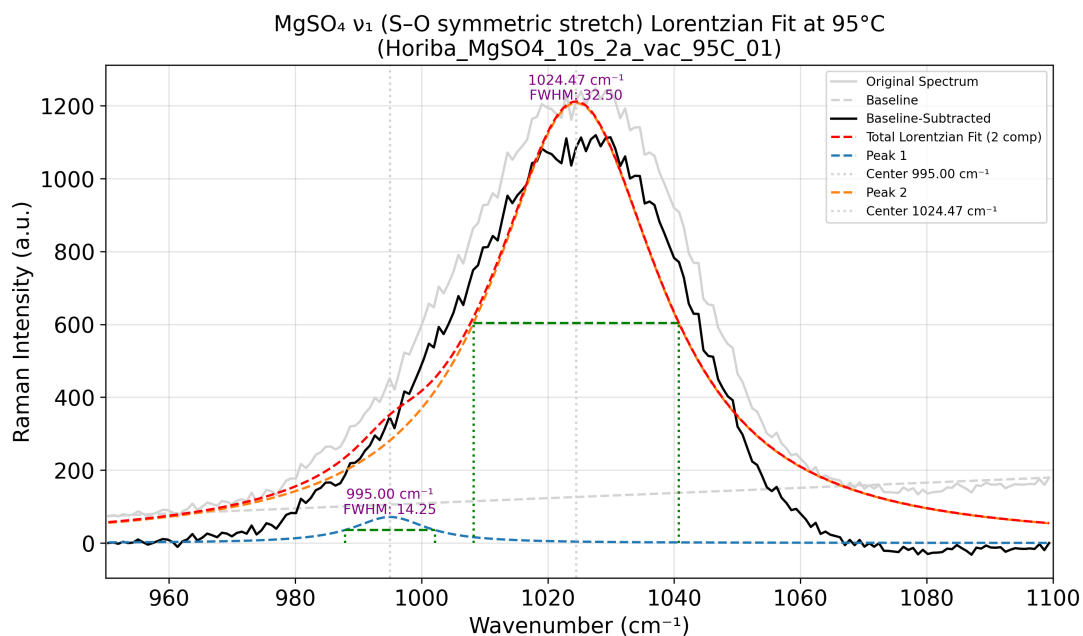
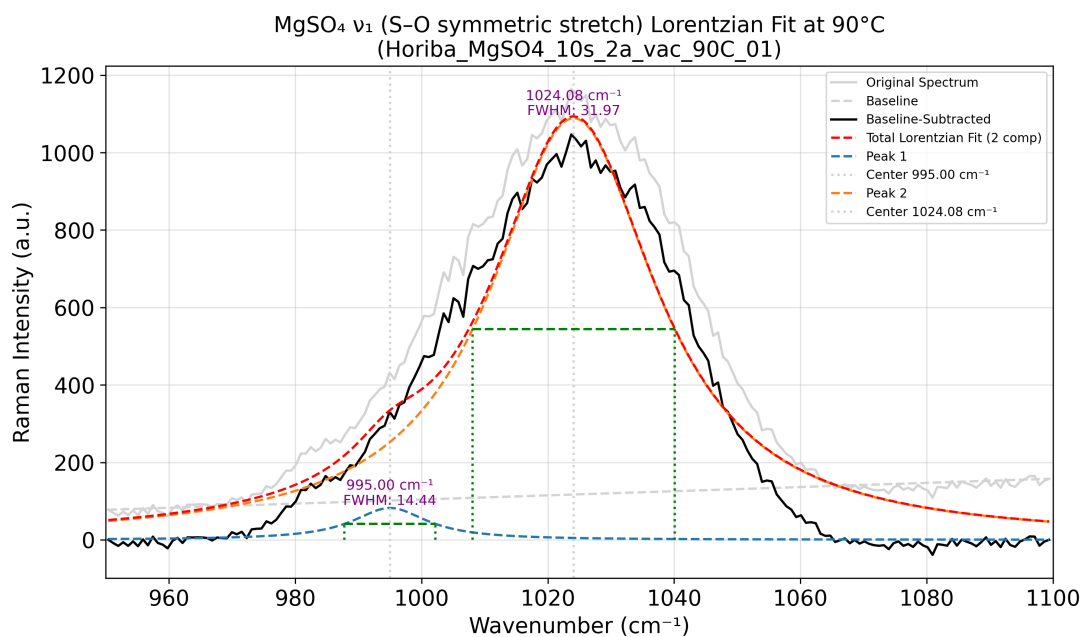




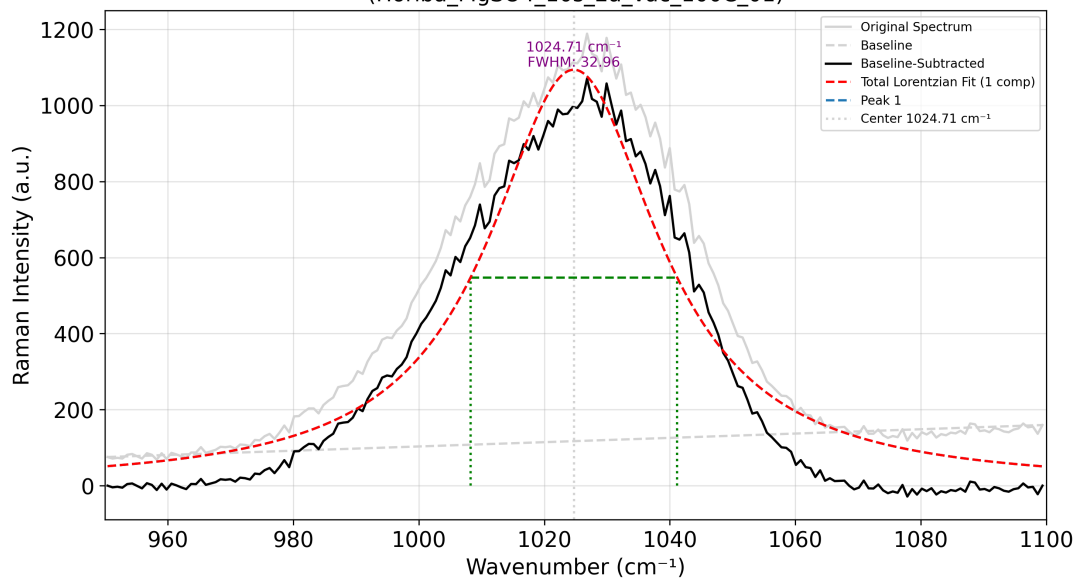




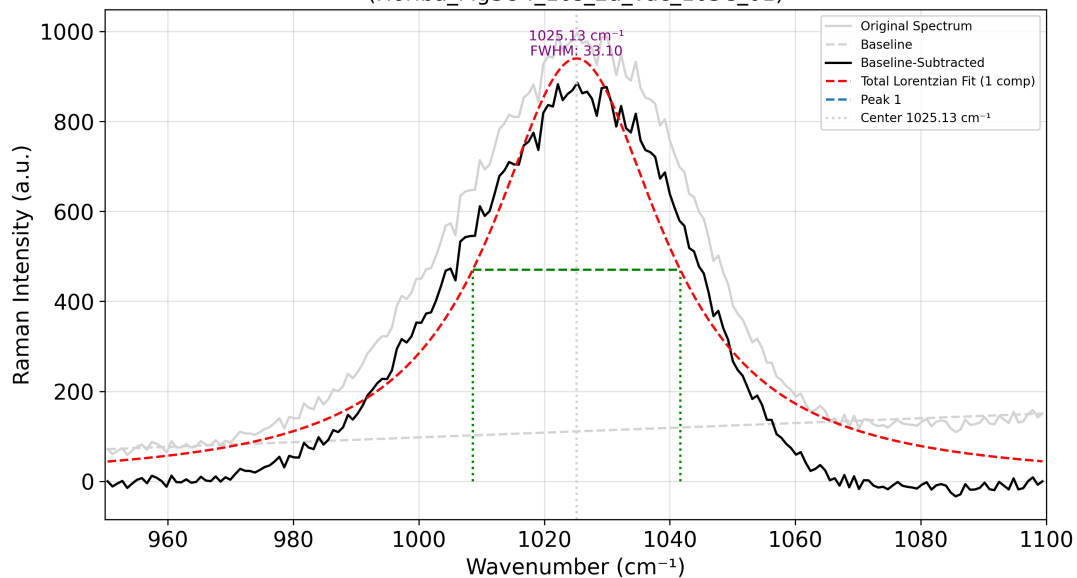




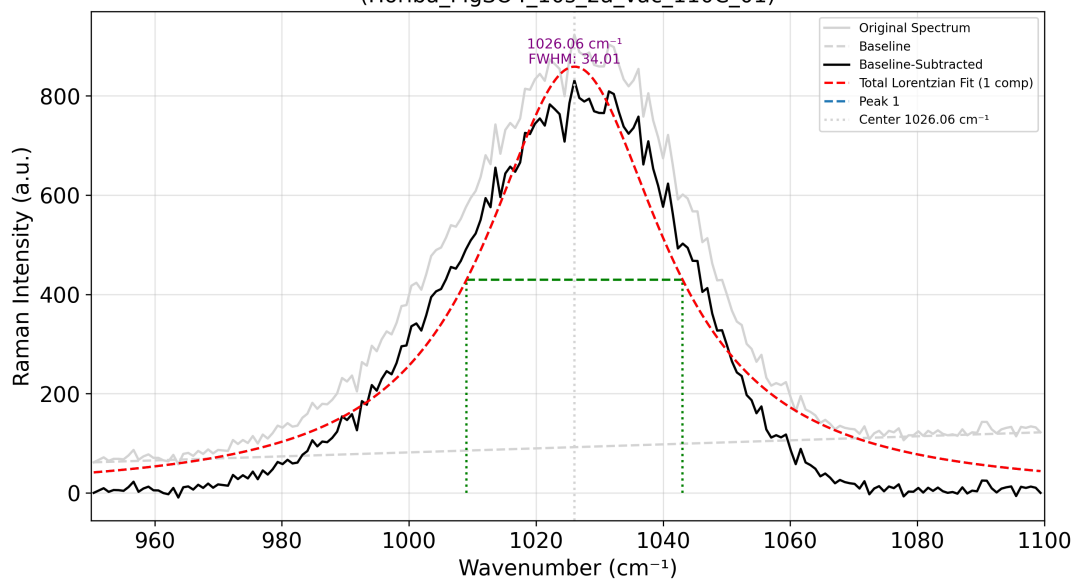
MgSO₄ ν_1 (S-O symmetric stretch) Lorentzian Fit at 100°C
(Horiba_MgSO4_10s_2a_vac_100C_01)



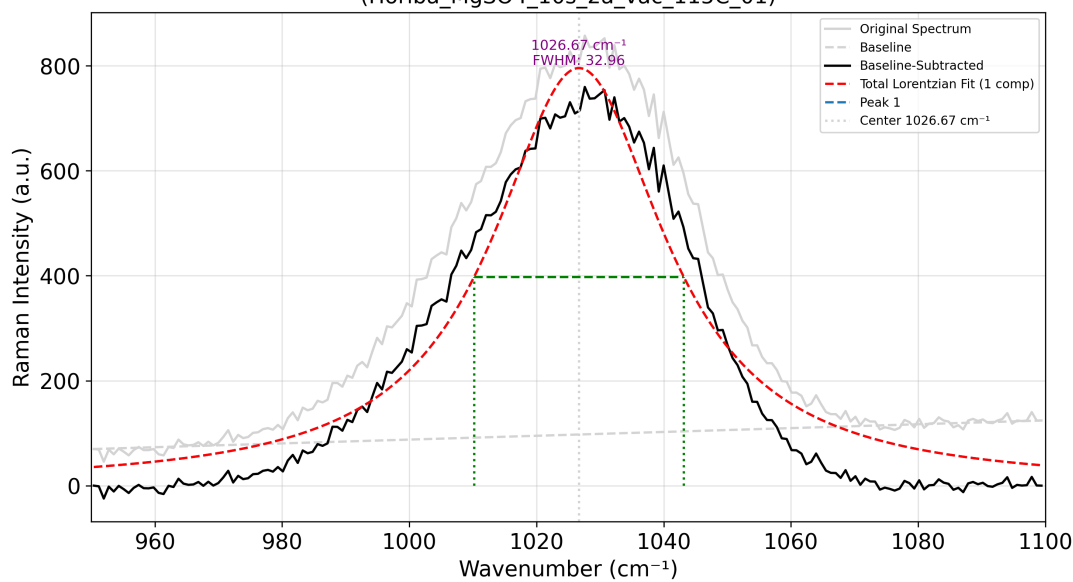
MgSO₄ ν_1 (S-O symmetric stretch) Lorentzian Fit at 105°C
(Horiba_MgSO4_10s_2a_vac_105C_01)

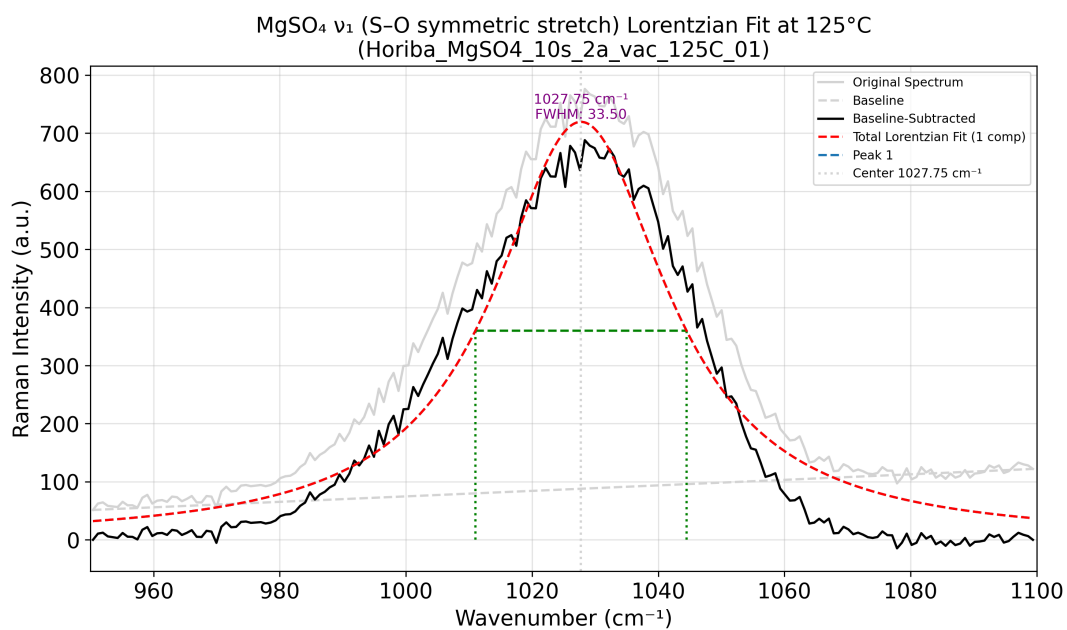
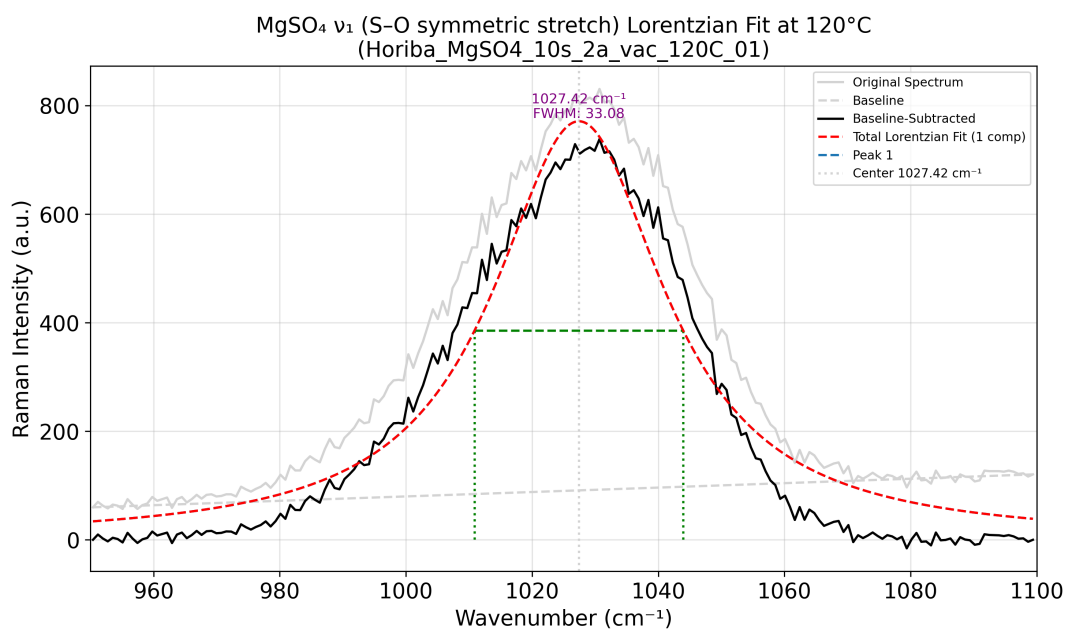


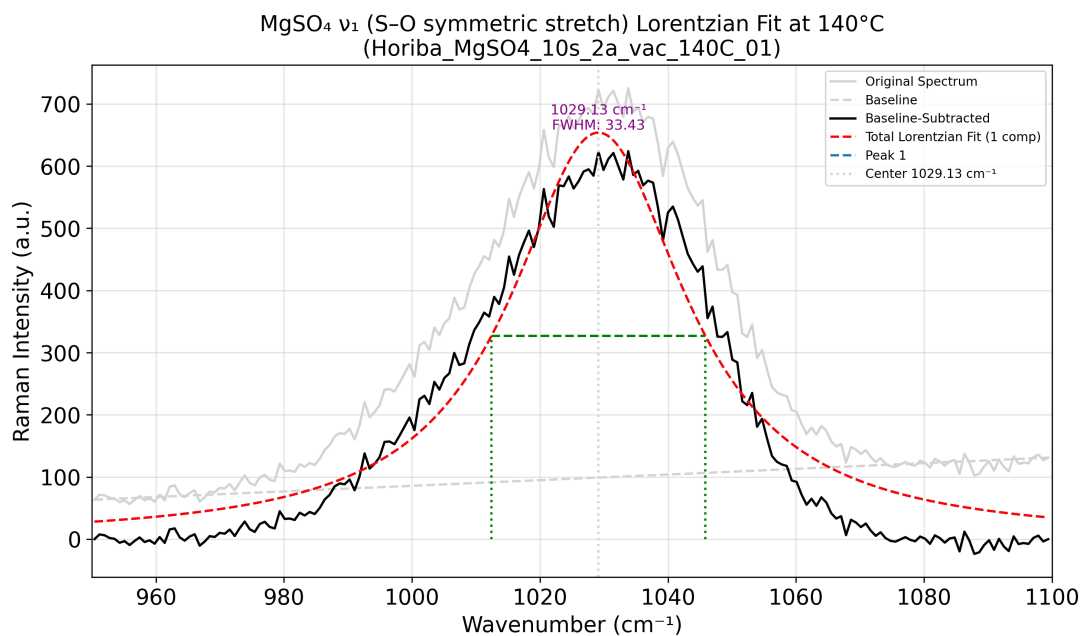
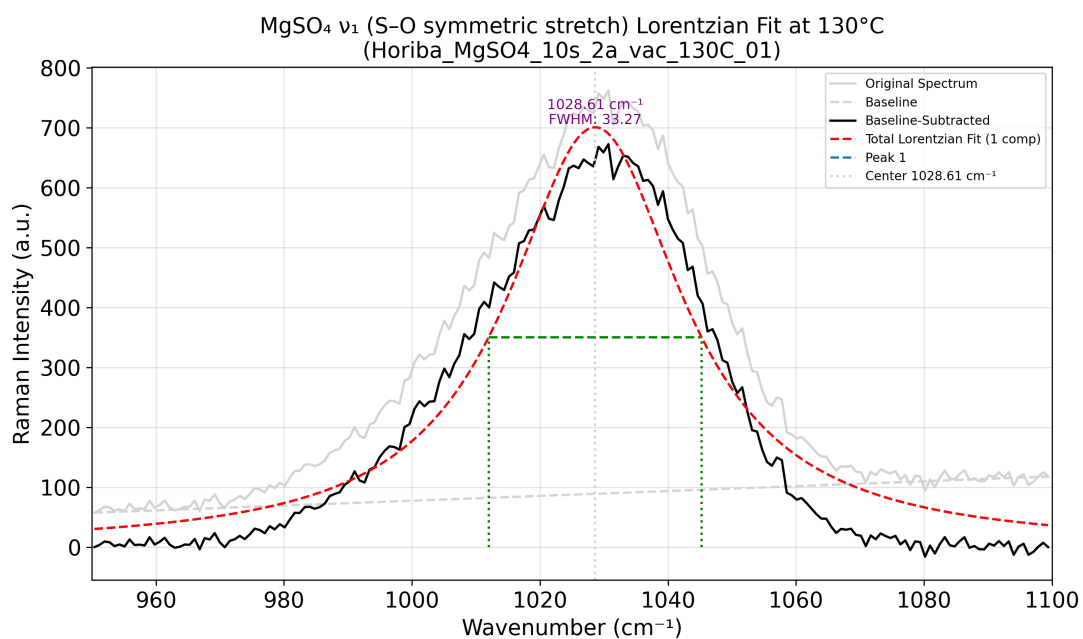
MgSO₄ ν_1 (S-O symmetric stretch) Lorentzian Fit at 110°C
(Horiba_MgSO4_10s_2a_vac_110C_01)

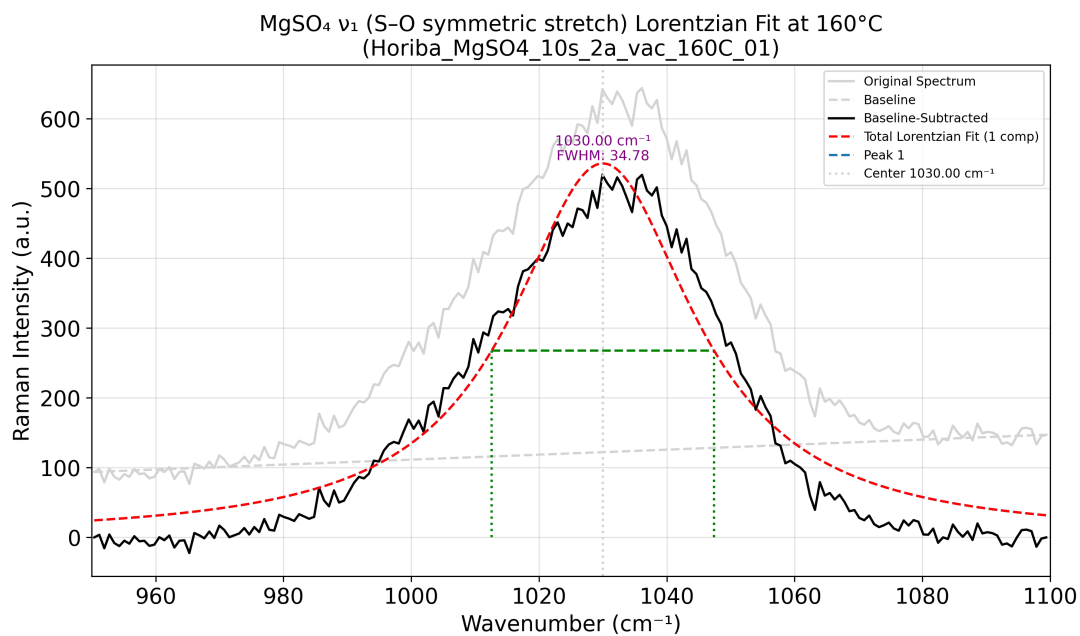
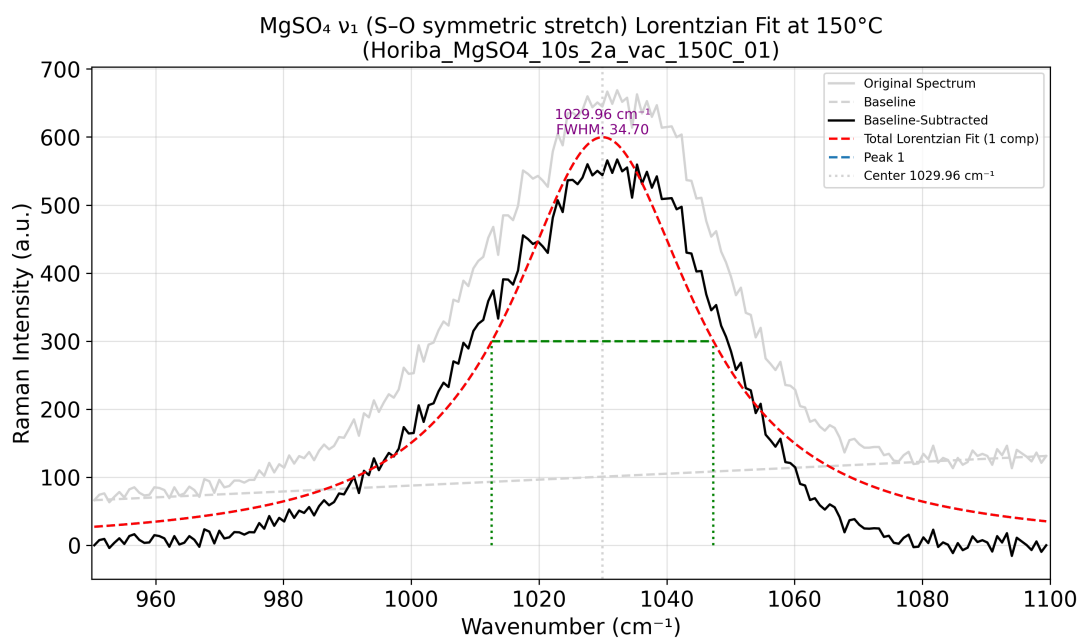


MgSO₄ ν_1 (S-O symmetric stretch) Lorentzian Fit at 115°C
(Horiba_MgSO4_10s_2a_vac_115C_01)

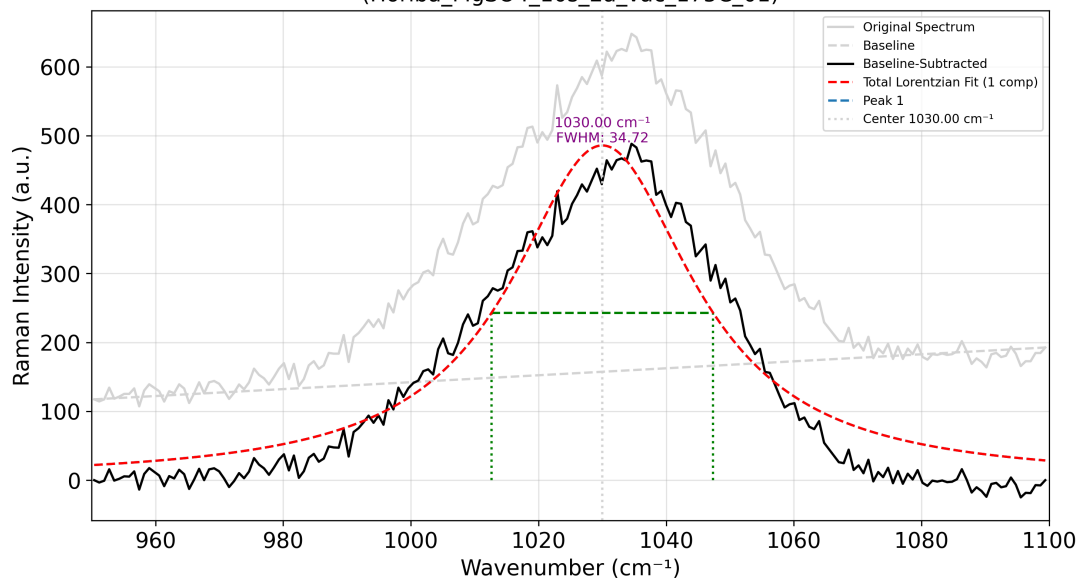




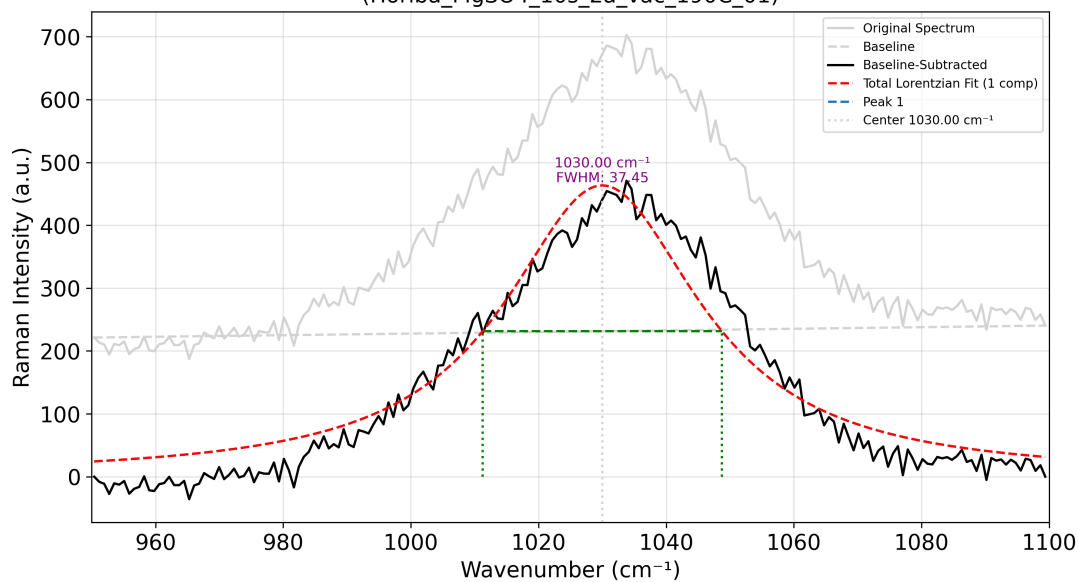


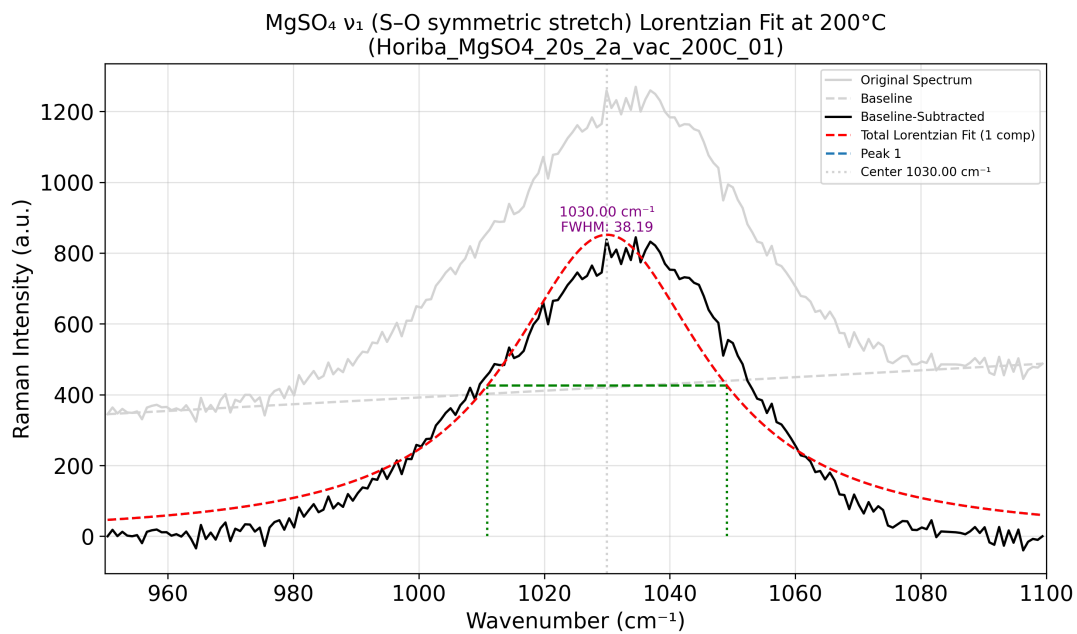
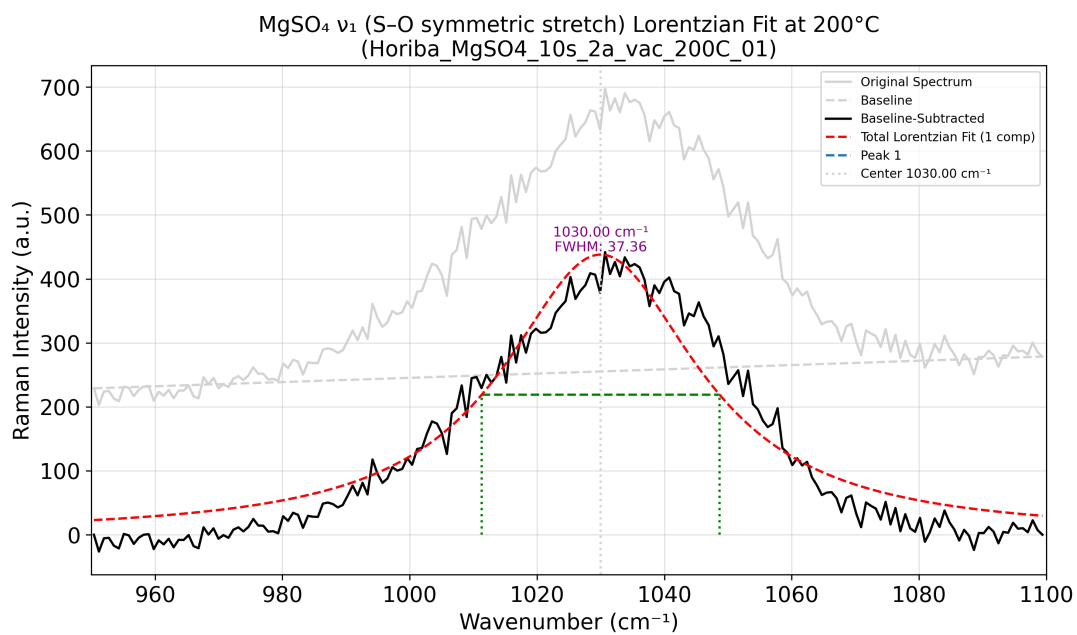


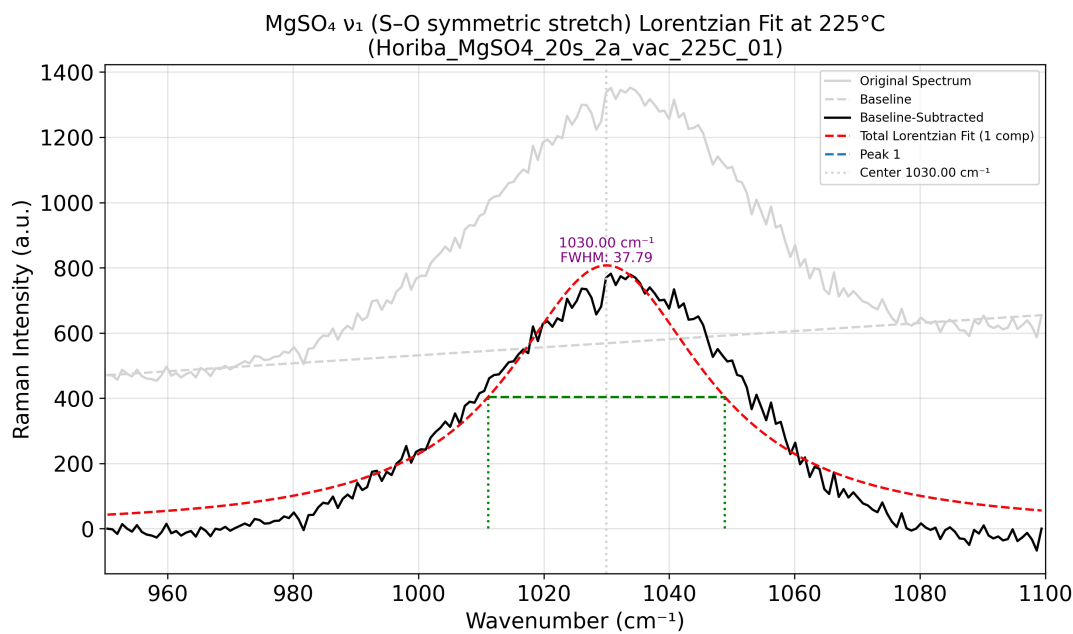
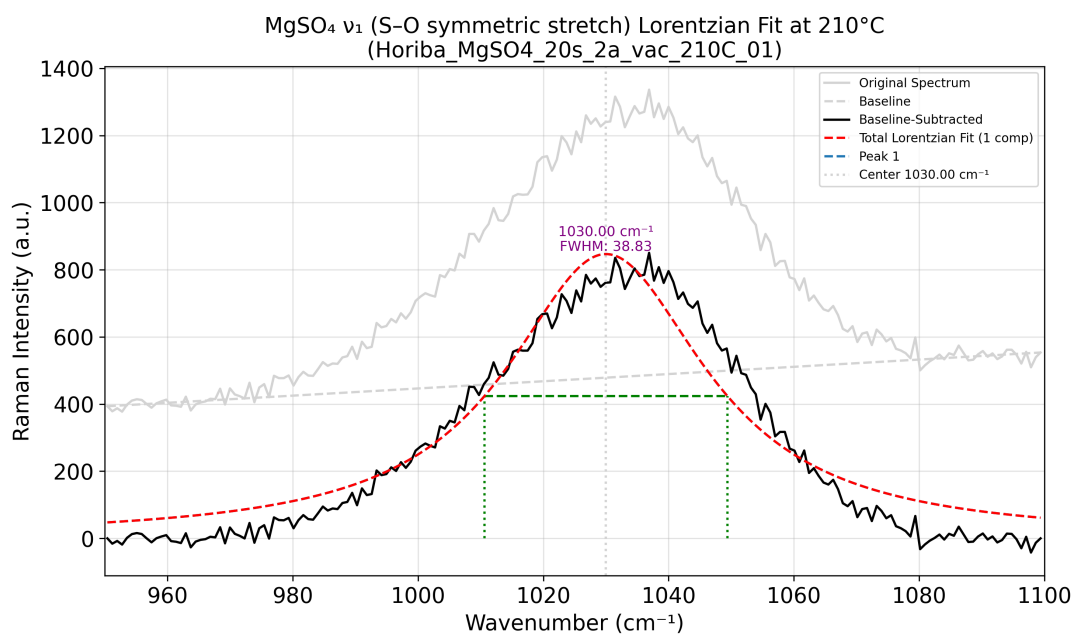
MgSO₄ ν_1 (S-O symmetric stretch) Lorentzian Fit at 175°C
(Horiba_MgSO4_10s_2a_vac_175C_01)

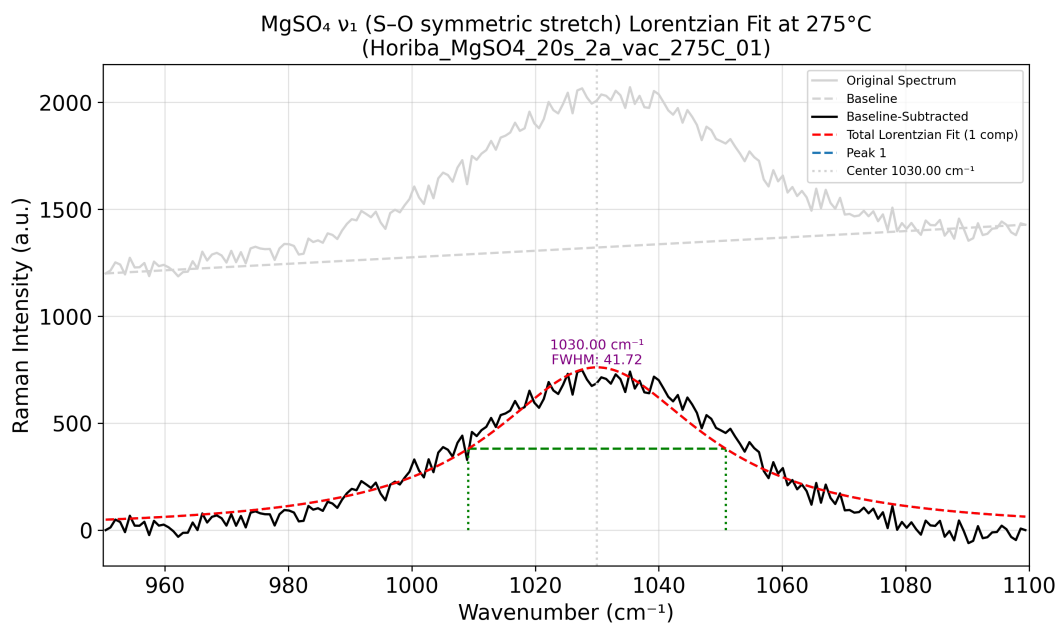
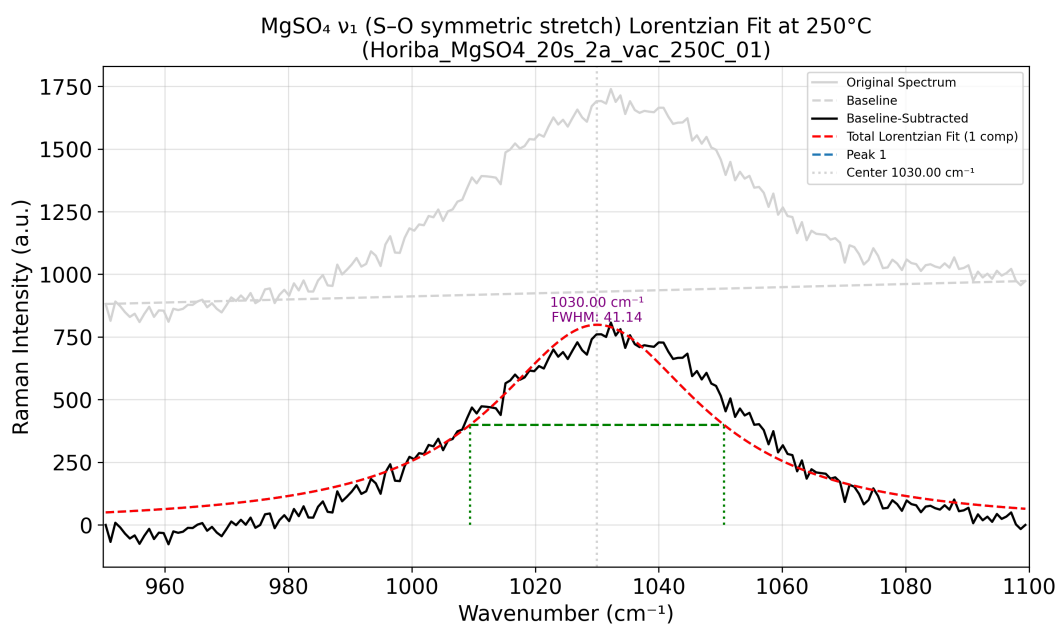


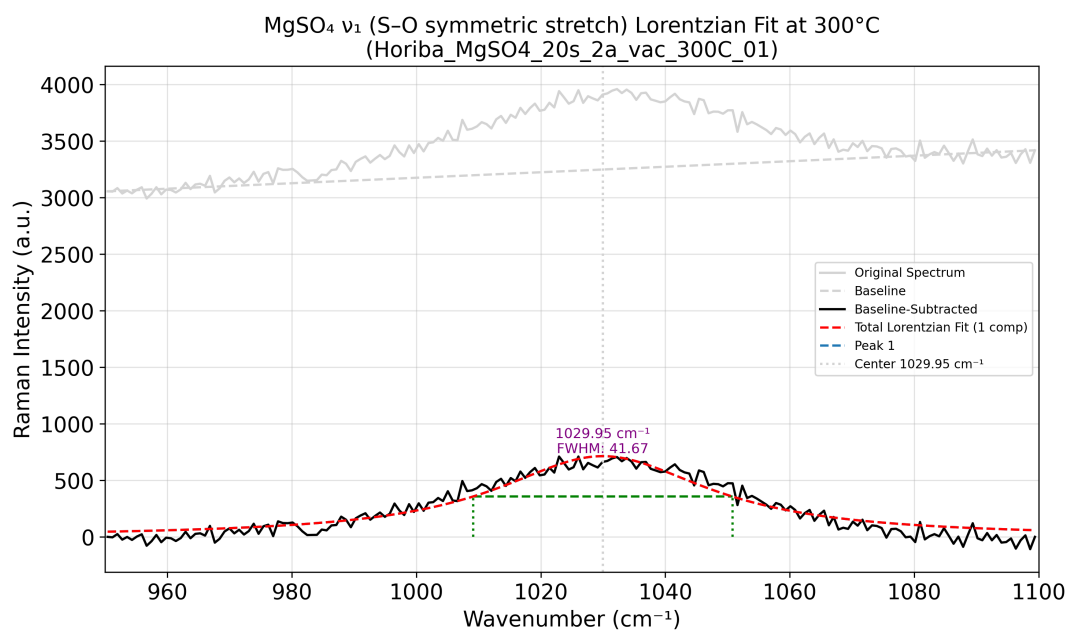
MgSO₄ ν_1 (S-O symmetric stretch) Lorentzian Fit at 190°C
(Horiba_MgSO4_10s_2a_vac_190C_01)





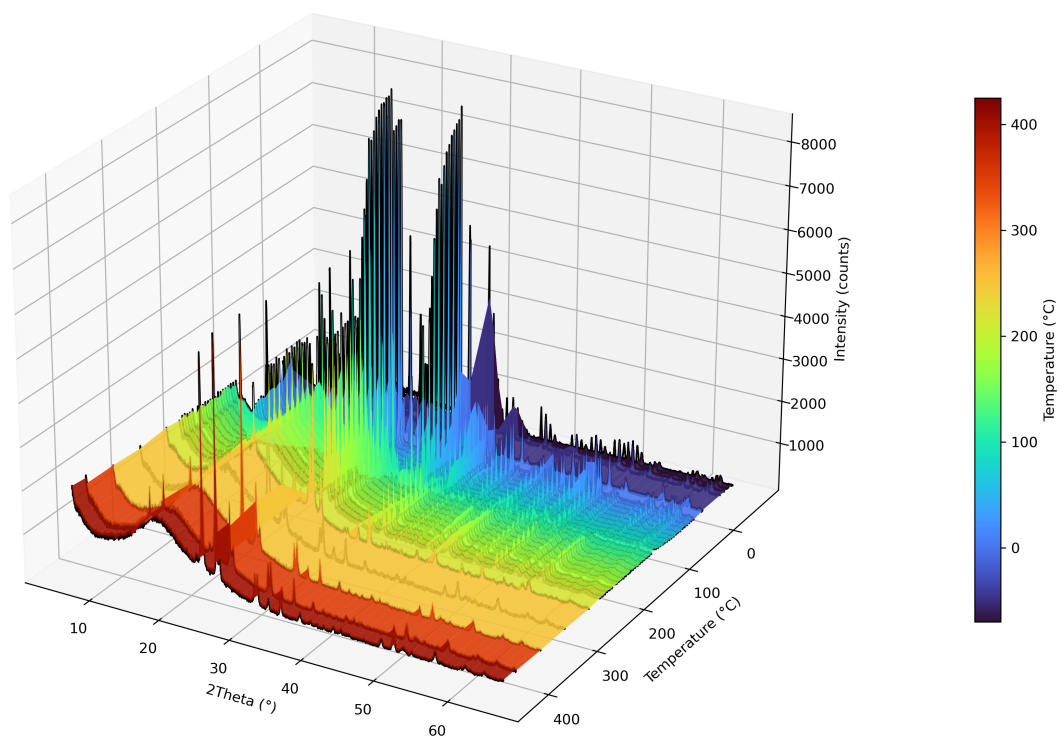






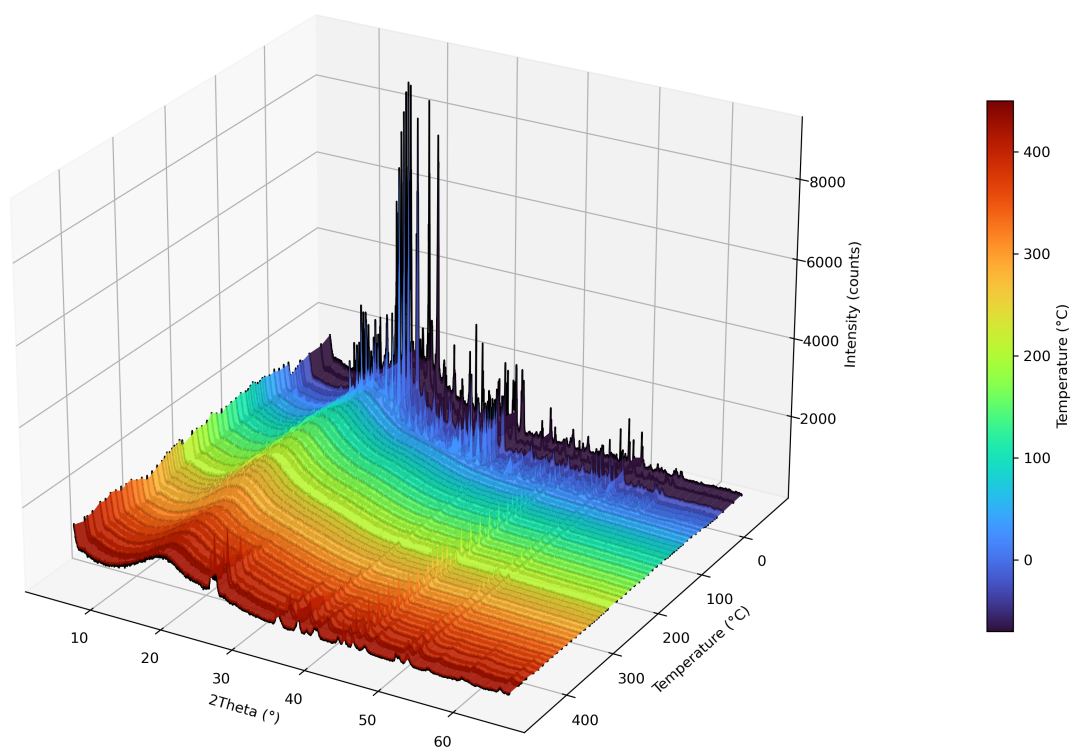
S2.0 XRD Patterns for Magnesium Perchlorate and Magnesium Sulfate

$\text{Mg}(\text{ClO}_4)_2$ XRD Patterns across Temperature (3D)



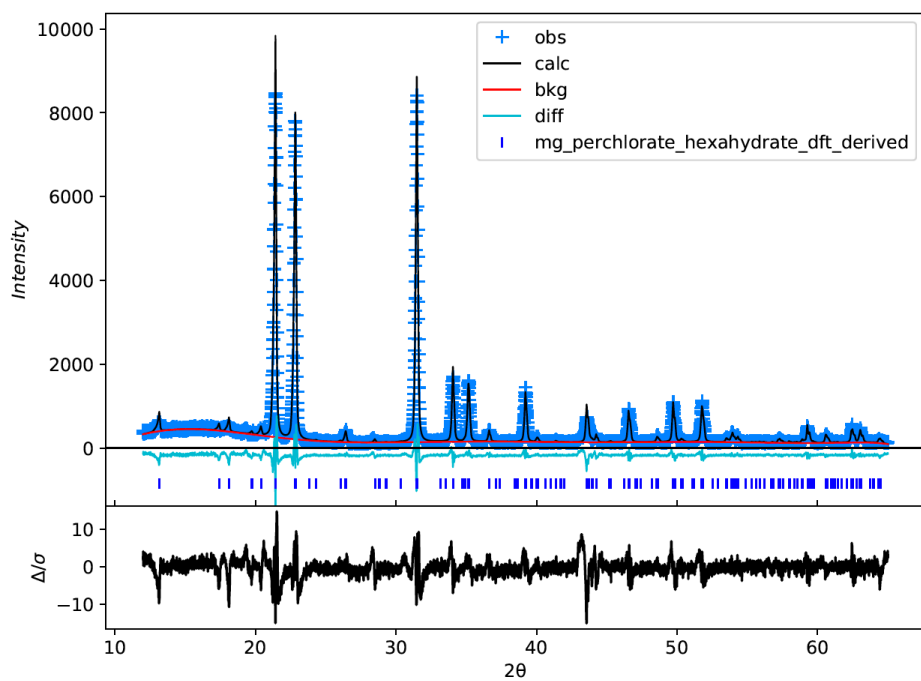
-70 to 400 °C

MgSO₄ XRD Patterns across Temperature (3D)

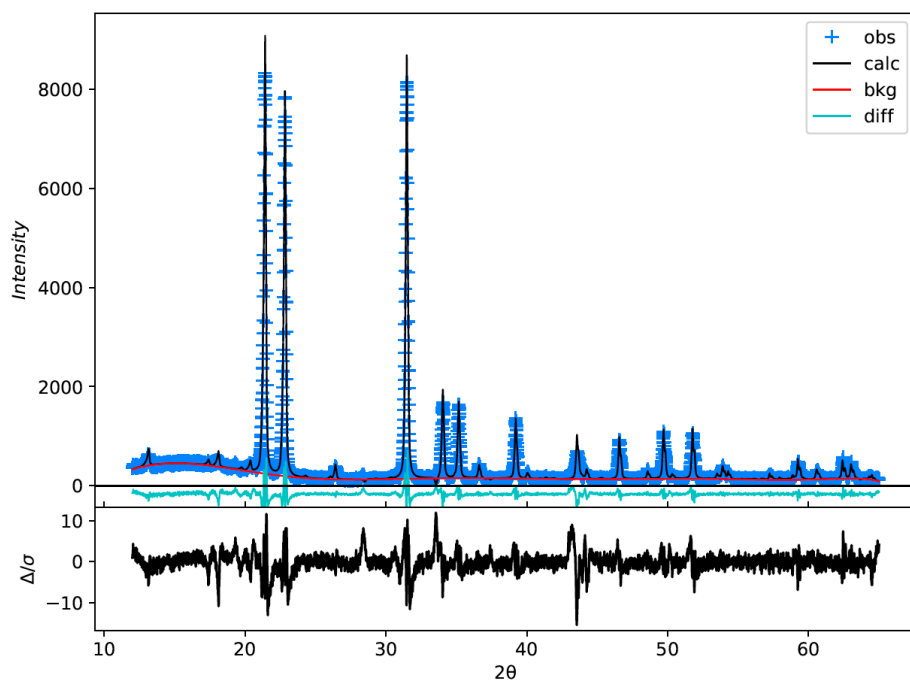


-70 to 425 °C

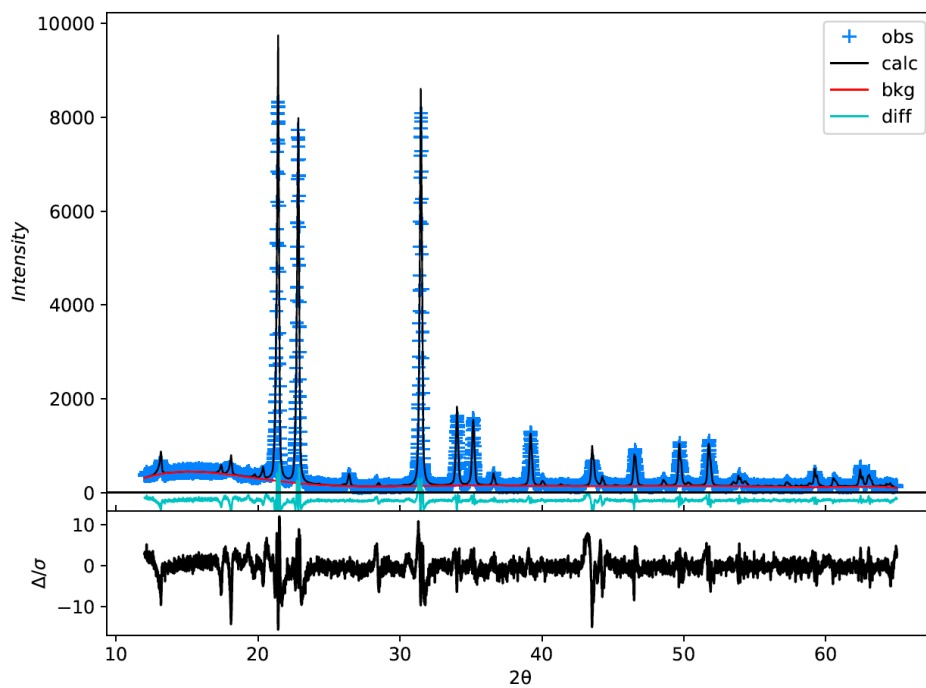
S2.1 $\text{Mg}(\text{ClO}_4)_2 \cdot \text{XH}_2\text{O}$ Refined XRD Plots 20 to 425 °C



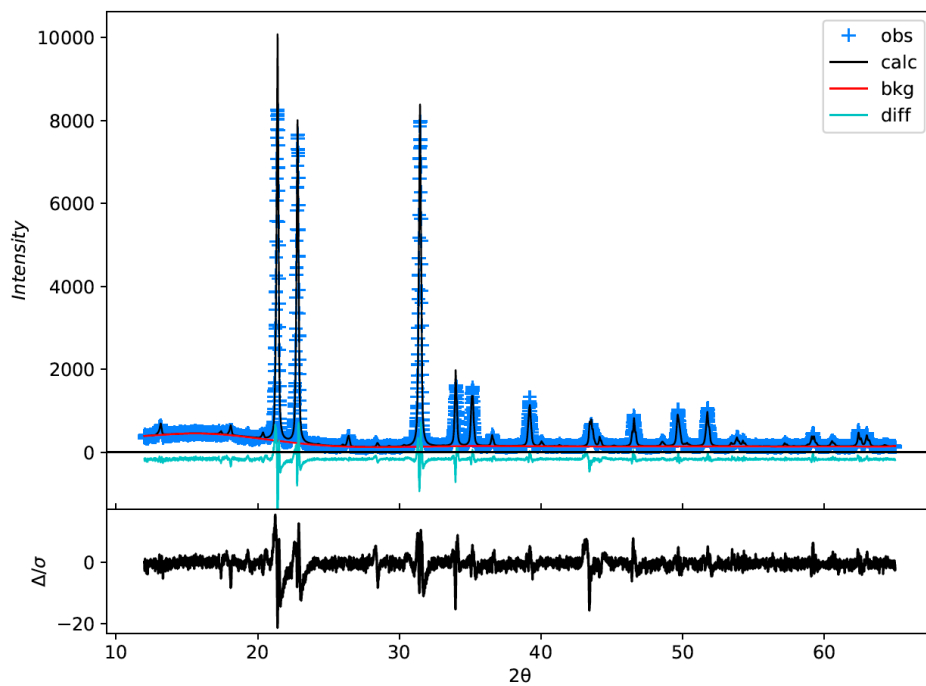
20 °C



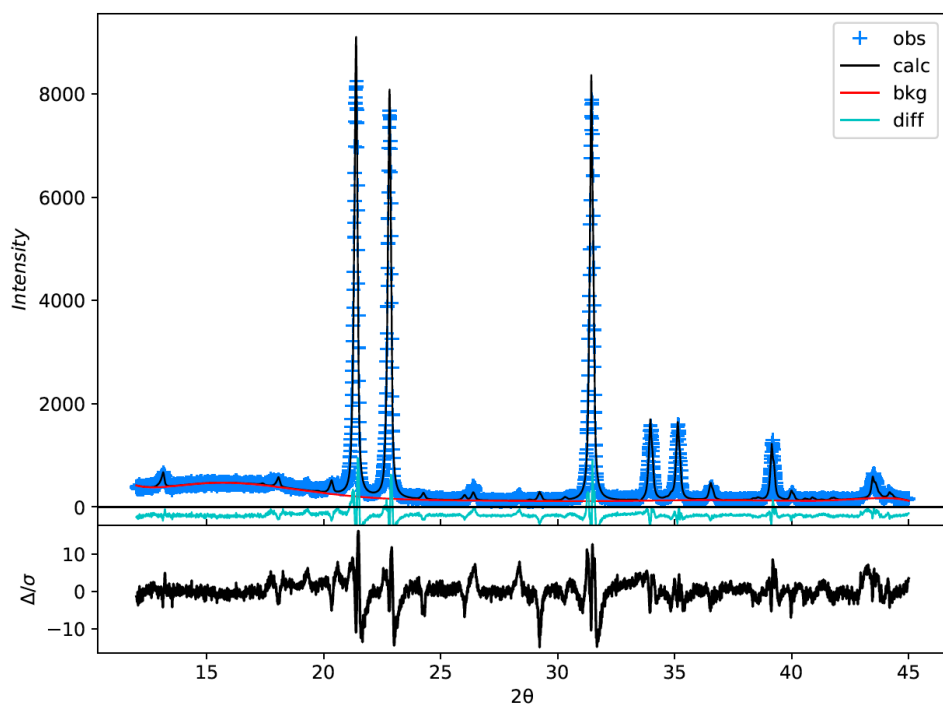
25 °C



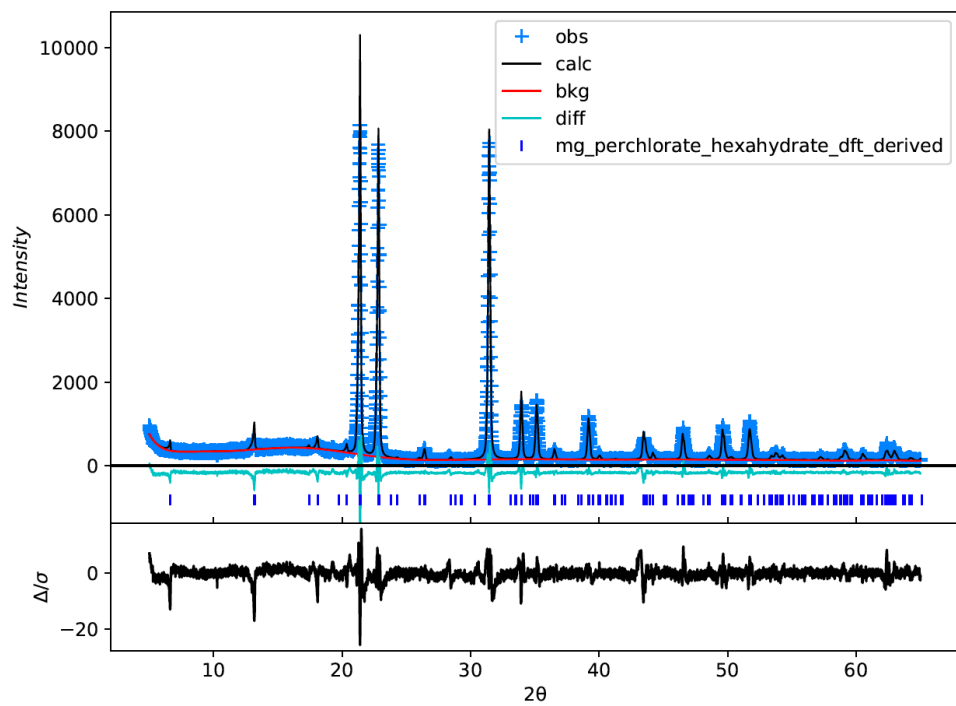
30 °C



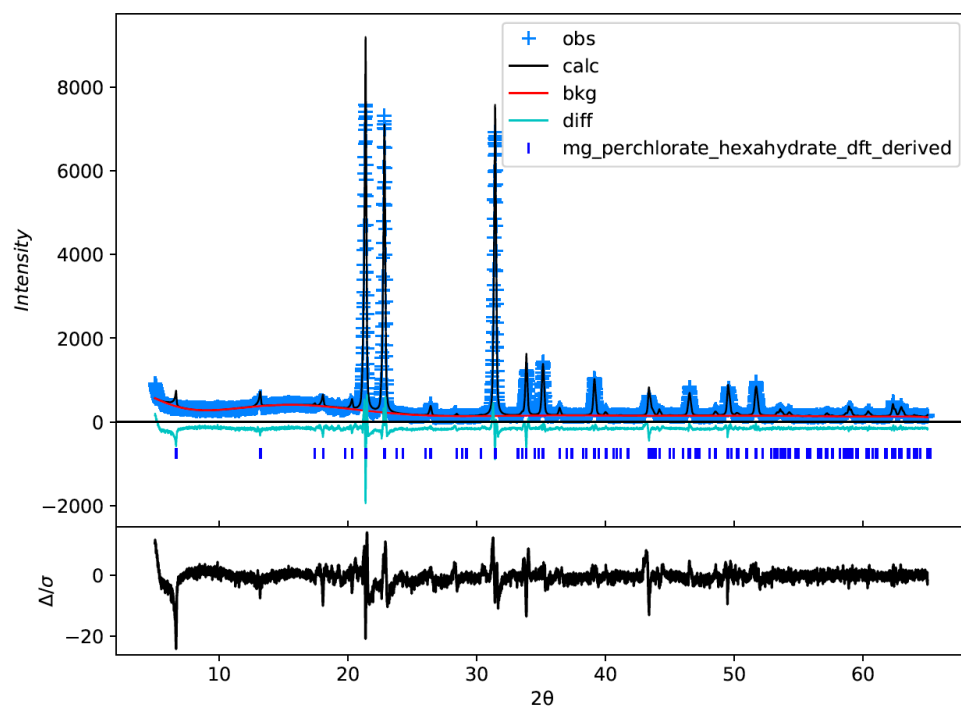
35 °C



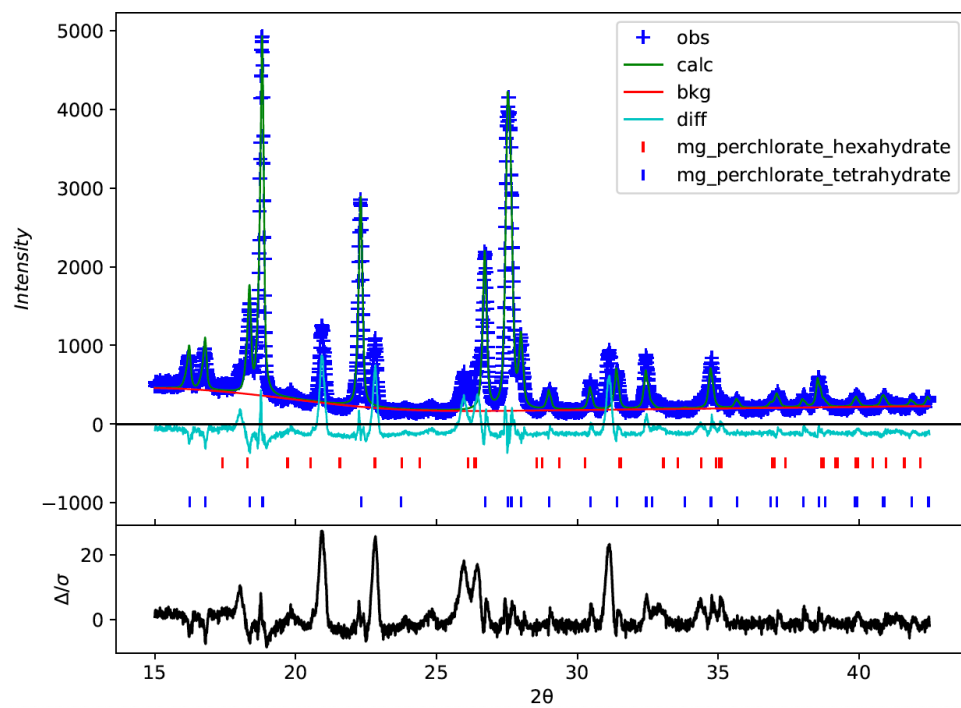
40 °C



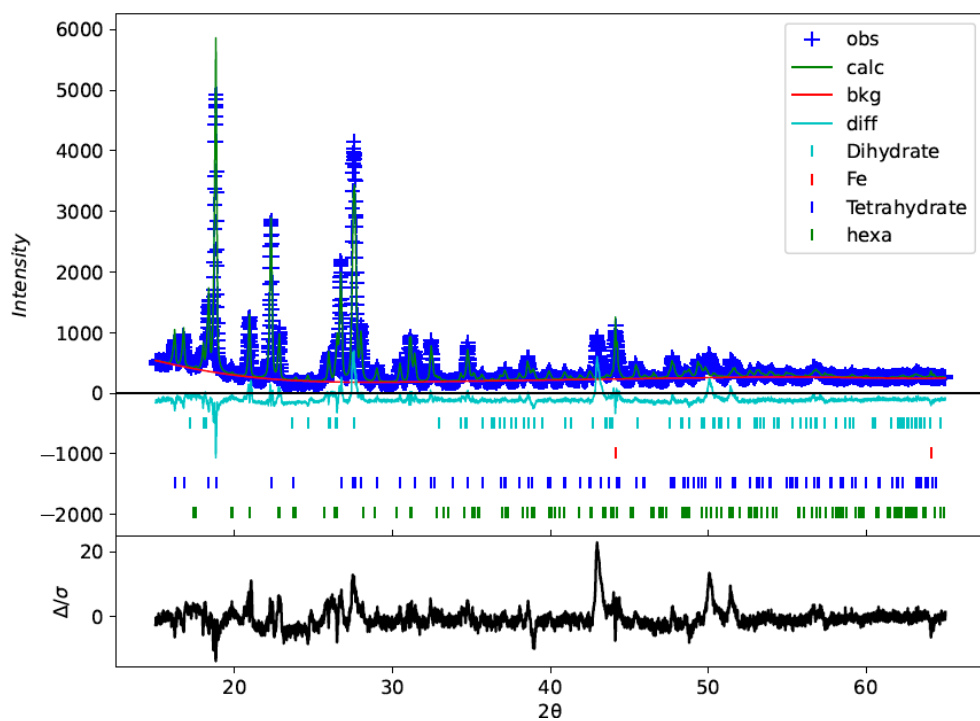
45 °C



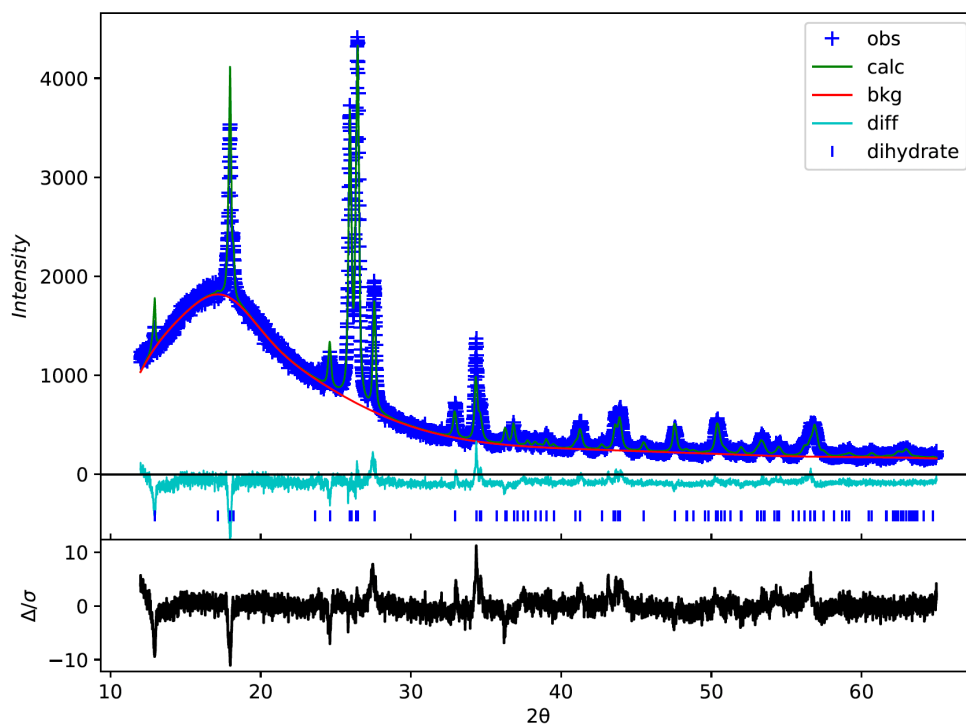
60 °C



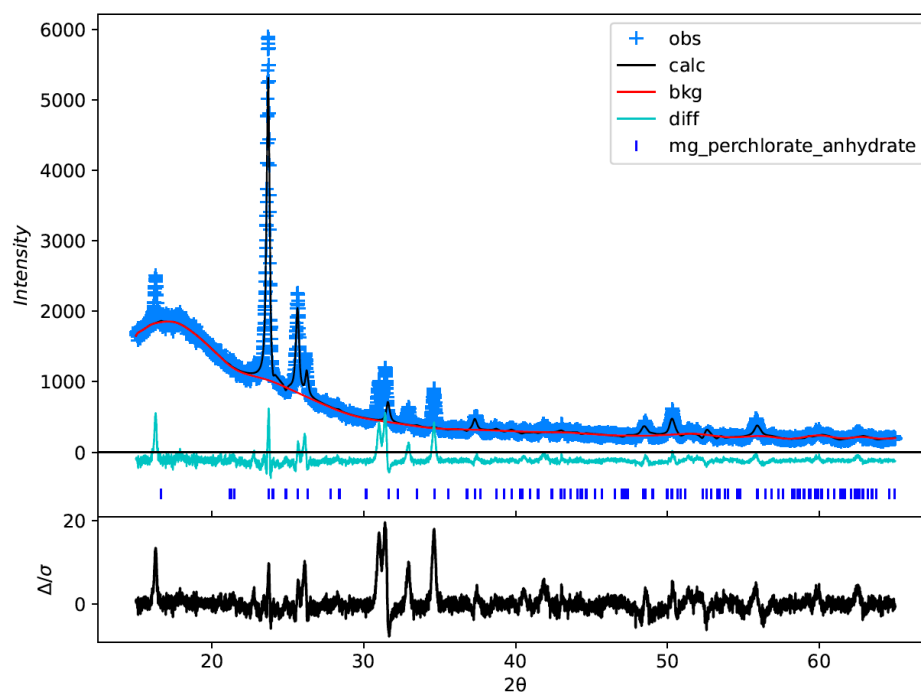
110 °C



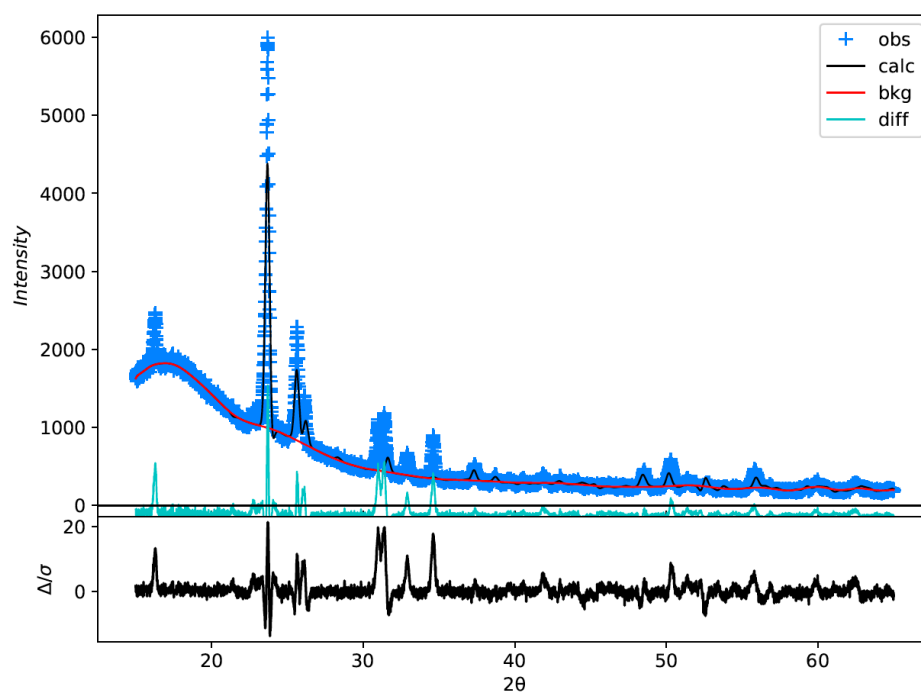
110 °C (includes Fe phase CIF to account for sample holder peaks in the 44 and 50 2-theta range)



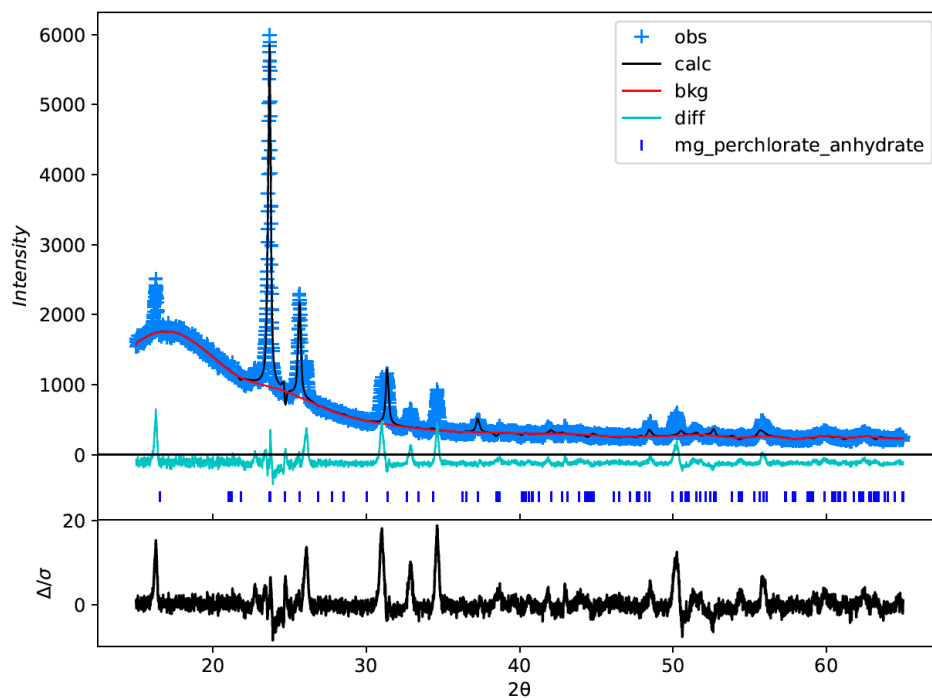
170 °C



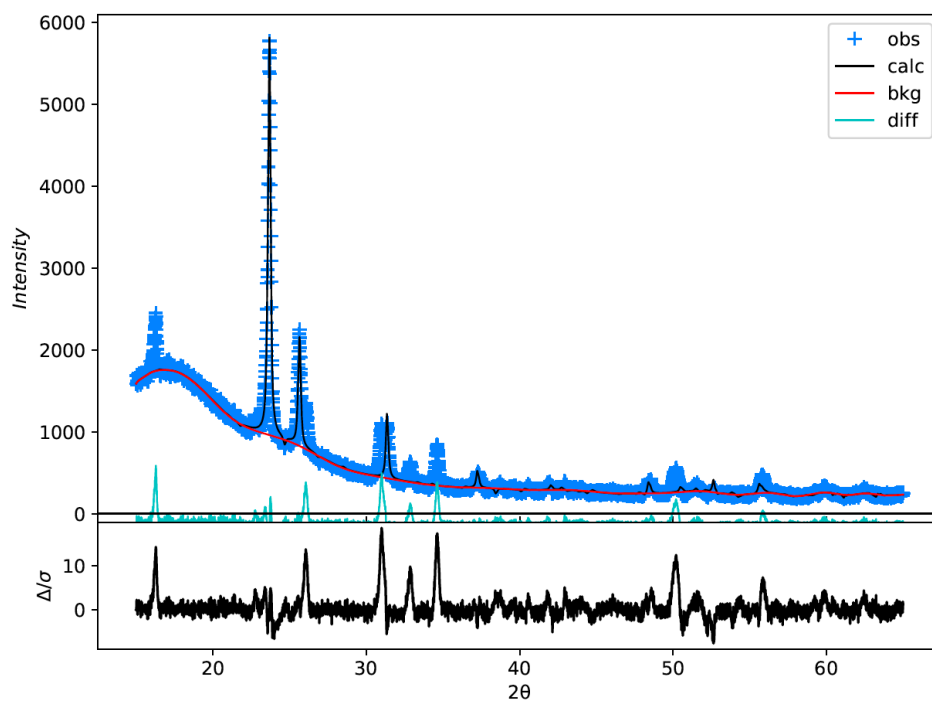
300 °C



350 °C

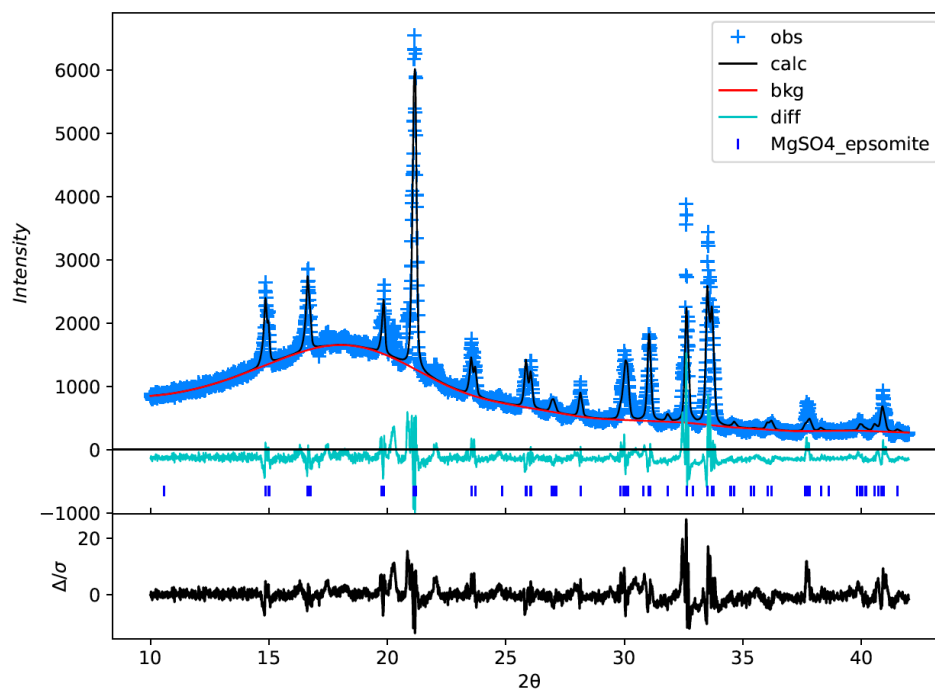


400 °C

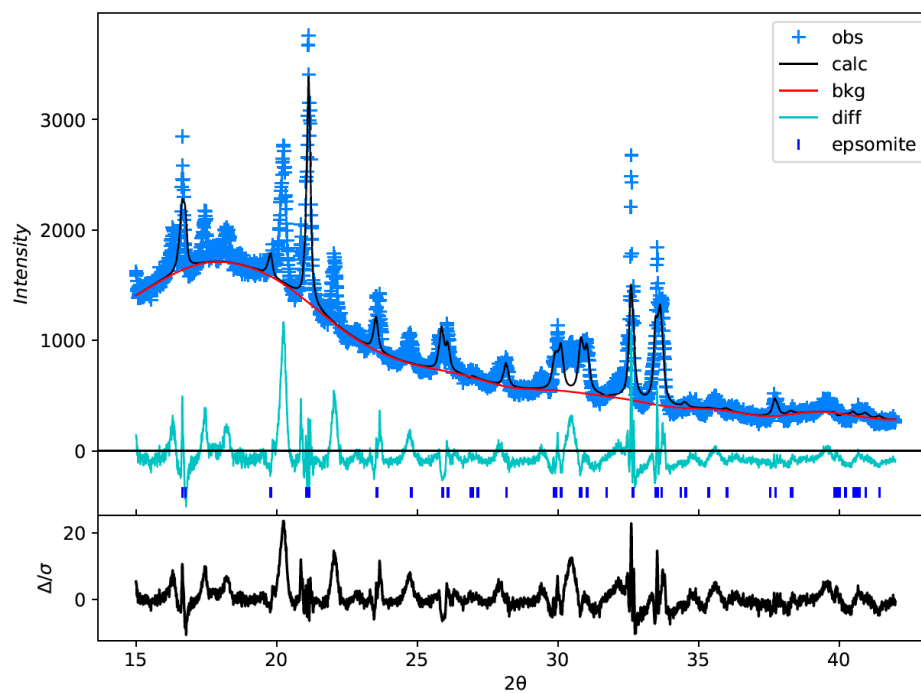


425 °C

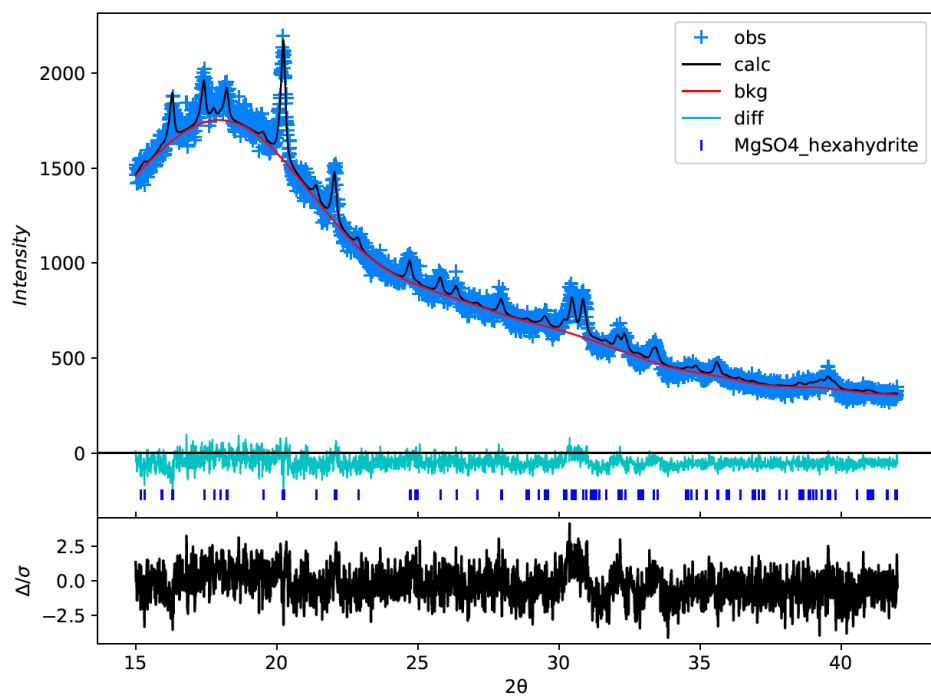
S2.2 $\text{MgSO}_4 \cdot \text{XH}_2\text{O}$ Refined XRD Plots 22, 29, and 40 °C



22 °C



29 °C



40 °C

S3.0 Wilson GF 4-Mode Force Constants Calculations and Derivation

There are clear systematic shifts in frequency of the tetrahedral vibrations across the dehydration transitions (particularly of n_1) for both magnesium perchlorate and magnesium sulfate and their respective hydrates. To gain insight into the bonding changes taking place between the different hydration states, we quantified changes in the internal bonding of the perchlorate and sulfate tetrahedra across hydration states by calculating a valence force field for the ClO_4^- and SO_4 tetrahedra using Wilson GF matrix methods (Wilson et al., 1955). This provides insight into the local bonding environment, bond stiffness or structural rigidity, and chemical interactions within a molecule or mineral. The perchlorate and sulfate anions were each approximated as an ideal tetrahedral XO_4 group, and the internal vibrational problem was expressed in terms of symmetry-adapted stretching and bending coordinates. A 4-parameter force constant model was used that involved a Cl-O bond stretch constant (f_r), an O-Cl-O stretch-bend constant ($f_{r\theta}$), an O-Cl-O bend constant (f_θ), and a bend-bend interaction constant ($f_{\theta\theta}$) for magnesium perchlorate at each temperature and hydration state. Similarly, a 4-parameter force constant model was calculated for the SO_4^{2-} tetrahedron in magnesium sulfate, including S-O stretching and O-S-O bending interactions. The internal force constants were determined from the experimentally observed n_1 (A_1 symmetric stretch), n_2 (E symmetric bend), n_3 (F_2 asymmetric stretch), and n_4 (F_2 asymmetric bend) frequencies using the Wilson GF formalism (Caracas & Bobocioiu, 2011; G. Herzberg, 1945; Hahn et al., 2017; Wilson et al., 1955).

Assumptions associated with the idealized XO_4 valence force analysis include treating the perchlorate tetrahedra as dynamically independent (their distances from one another in the unit cells suggests that this is likely a good assumption), neglecting explicit coupling to Mg^{2+} bonds or treatment of lattice modes since the n_1 , n_2 , n_3 , and n_4 internal modes of the ClO_4^- unit dominate the analysis, and assuming that bonding perturbations caused by dehydration, hydrogen bonding, or Mg-O interactions are absorbed into the 4 force constants. Since the perchlorate and sulfate sites within every single phase are equivalent to one another, a single effective force field should reflect the local tetrahedral environment in each phase.

Starting from a 4-parameter valence force-field for an ideal tetrahedral XO_4 group ($X = \text{Cl}$ or S), we constructed the Wilson F and G matrices in internal coordinates and transformed them into symmetry coordinates appropriate for T_d symmetry (A_1 , E, F_2). In this representation, the A_1 symmetric stretching, E symmetric bending, F_2 asymmetric stretching, and F_2 asymmetric bending modes are each described by symmetry-adapted force and kinetic matrix elements. The resulting Wilson FG normal-mode equations relate the observed vibrational frequencies to four internal force constants: the X-O stretching constant f_r , the O-X-O bending constant f_θ , the stretch-bend interaction constant $f_{r\theta}$, and the bend-bend interaction constant $f_{\theta\theta}$. After transformation of the internal-coordinate F and G matrices into tetrahedral symmetry coordinates, the normal-mode equations reduce to **Equations 1-4**. These

were solved simultaneously to obtain a set of internal force constants (**Equations 5-8**) across temperature and hydration states. A detailed derivation of the Wilson GF force constants can be found in the Supplement.

$$\mu_r(2\pi c\nu_1)^2 = f_r + 4f_{r\theta} + 6f_{\theta\theta} \quad (1)$$

$$\mu_\theta(2\pi c\nu_2)^2 = f_\theta + 2f_{\theta\theta} \quad (2)$$

$$\mu_r(2\pi c\nu_3)^2 = f_r - 2f_{r\theta} \quad (3)$$

$$\mu_\theta(2\pi c\nu_4)^2 = f_\theta - f_{\theta\theta} \quad (4)$$

Where ν_i are the vibrational mode frequencies in cm^{-1} , c is the speed of light in cm s^{-1} , μ_r is the reduced mass for the X-O stretching coordinate, and μ_θ is the effective reduced mass for the O-X-O bending coordinate. For magnesium perchlorate, X = Cl, and for magnesium sulfate, X = S.

Solving the four normal-mode equations gives:

$$f_{\theta\theta} = \frac{1}{3}(2\pi c)^2 \mu_\theta(\nu_2^2 - \nu_4^2) \quad (5)$$

$$f_\theta = (2\pi c)^2 \mu_\theta \nu_4^2 + f_{\theta\theta} \quad (6)$$

$$f_{r\theta} = \frac{1}{6} [(2\pi c)^2 \mu_r(\nu_1^2 - \nu_3^2) - 6f_{\theta\theta}] \quad (7)$$

$$f_r = (2\pi c)^2 \mu_r \nu_3^2 + 2f_{r\theta} \quad (8)$$

Equivalently, defining $K_r = \mu_r(2\pi c)^2$ and $K_\theta = \mu_\theta(2\pi c)^2$, these can be written in fully expanded form as:

$$f_{\theta\theta} = \frac{K_\theta}{3}(\nu_2^2 - \nu_4^2) \quad (9)$$

$$f_\theta = \frac{K_\theta}{3}(\nu_2^2 + 2\nu_4^2) \quad (10)$$

$$f_{r\theta} = \frac{K_r}{6}(\nu_1^2 - \nu_3^2) - \frac{K_\theta}{3}(\nu_2^2 - \nu_4^2) \quad (11)$$

$$f_r = \frac{K_r}{3}(\nu_1^2 + 2\nu_3^2) - \frac{2K_\theta}{3}(\nu_2^2 - \nu_4^2) \quad (12)$$

The force constants are reported in N m^{-1} .

The internal vibrational force constants for the ClO_4^- and SO_4^{2-} tetrahedra were calculated using the Wilson GF matrix method (Wilson, 1955). In this formalism, the molecular vibrational problem is expressed in terms of internal stretching and bending coordinates, from which the force matrix F and kinetic energy matrix G are constructed. The normal vibrational modes are obtained from the secular equation:

$$|F^\Gamma G^\Gamma - \lambda_k E| = 0 \quad (1)$$

where Γ denotes the irreducible representation of the tetrahedral T_d point group, E is the identity matrix, and λ_k is the eigenvalue associated with vibrational mode k . The eigenvalues are related to the experimentally observed vibrational wavenumbers through:

$$\lambda_k = (2\pi c \nu_k)^2 \quad (2)$$

where c is the speed of light and ν_k is the Raman vibrational frequency in cm^{-1} .

The valence coordinate system consists of four X -O stretching coordinates Δr_i and six O- X -O bending coordinates $\Delta \theta_{ij}$, where $X = \text{Cl}$ or S . These internal coordinates are transformed into symmetry coordinates appropriate for tetrahedral symmetry:

- A_1 : symmetric stretch (ν_1)
- E : symmetric bend (ν_2)
- F_2 : asymmetric stretch (ν_3)
- F_2 : asymmetric bend (ν_4)

The E representation is doubly degenerate, whereas the F_2 representations are triply degenerate. The transformation from internal coordinates s to symmetry coordinates S is:

$$S = Us \quad (3)$$

where U is the symmetry transformation matrix constructed from the irreducible representations of the T_d point group. The transformed force and kinetic matrices are:

$$F^\Gamma = U^\Gamma F (U^\Gamma)^T \quad (4)$$

$$G^\Gamma = U^\Gamma G (U^\Gamma)^T \quad (5)$$

After transformation into symmetry coordinates, the tetrahedral vibrational problem separates into independent symmetry blocks corresponding to the A_1 , E , and F_2 irreducible representations. Effectively, the A_1 , E , and degenerate F_2 symmetry species each reduce to independent secular relationships involving a single effective symmetry-coordinate force constant and corresponding G -matrix element. In the present four-parameter treatment, the F_2 representation is separated into effective stretching and bending subspaces corresponding to the ν_3 asymmetric stretch and ν_4 asymmetric bend, respectively. A four-parameter valence force field was adopted consisting of:

- f_r : X -O stretching force constant
- f_θ : O- X -O bending force constant
- $f_{r\theta}$: stretch-bend interaction constant
- $f_{\theta\theta}$: bend-bend interaction constant

The symmetry-coordinate Wilson GF secular equations reduce to:

$$\mu_r(2\pi c\nu_1)^2 = f_r + 4f_{r\theta} + 6f_{\theta\theta} \quad (6)$$

$$\mu_\theta(2\pi c\nu_2)^2 = f_\theta + 2f_{\theta\theta} \quad (7)$$

$$\mu_r(2\pi c\nu_3)^2 = f_r - 2f_{r\theta} \quad (8)$$

$$\mu_\theta(2\pi c\nu_4)^2 = f_\theta - f_{\theta\theta} \quad (9)$$

where μ_r is the reduced mass associated with the X -O stretching coordinates and μ_θ is the effective reduced mass associated with O- X -O bending motions. The stretching reduced mass is:

$$\mu_r = \frac{m_X m_O}{m_X + m_O} \quad (10)$$

and the effective bending reduced mass is approximated as:

$$\mu_\theta = \frac{2m_X m_O}{m_X + m_O} \quad (11)$$

where m_X and m_O are the atomic masses of the central atom and oxygen, respectively.

The resulting symmetry-coordinate equations relate experimentally observed Raman frequencies directly to the underlying tetrahedral valence force field. The four symmetry-coordinate secular equations were solved simultaneously to obtain the internal valence force constants. Solving first for the bend-bend coupling term gives:

$$f_{\theta\theta} = \frac{1}{3}(2\pi c)^2 \mu_{\theta}(\nu_2^2 - \nu_4^2) \quad (12)$$

Substituting into the bending equation gives:

$$f_{\theta} = (2\pi c)^2 \mu_{\theta} \nu_4^2 + f_{\theta\theta} \quad (13)$$

The stretch-bend coupling term is then:

$$f_{r\theta} = \frac{1}{6} [(2\pi c)^2 \mu_r(\nu_1^2 - \nu_3^2) - 6f_{\theta\theta}] \quad (14)$$

Finally, the stretching force constant becomes:

$$f_r = (2\pi c)^2 \mu_r \nu_3^2 + 2f_{r\theta} \quad (15)$$

Defining:

$$K_r = (2\pi c)^2 \mu_r \quad (16)$$

$$K_{\theta} = (2\pi c)^2 \mu_{\theta} \quad (17)$$

the fully expanded equations become:

$$f_{\theta\theta} = \frac{K_{\theta}}{3}(\nu_2^2 - \nu_4^2) \quad (18)$$

$$f_{\theta} = \frac{K_{\theta}}{3}(\nu_2^2 + 2\nu_4^2) \quad (19)$$

$$f_{r\theta} = \frac{K_r}{6}(\nu_1^2 - \nu_3^2) - \frac{K_{\theta}}{3}(\nu_2^2 - \nu_4^2) \quad (20)$$

$$f_r = \frac{K_r}{3}(\nu_1^2 + 2\nu_3^2) - \frac{2K_{\theta}}{3}(\nu_2^2 - \nu_4^2) \quad (21)$$

The Wilson force constants describe internal-coordinate stretching, bending, and coupling interactions within the tetrahedral unit and therefore provide a more complete internal-coordinate description than Herzberg-style mode force constants, which are defined for individual normal modes as:

$$k(\nu) = \mu(2\pi c\nu)^2 \quad (22)$$

All force constants are reported in N m^{-1} .

The calculated Wilson force constants provide insight into distinct aspects of the internal tetrahedral bonding environment. The stretching force constant f_r primarily reflects the intrinsic X-O bond stiffness within the tetrahedron and is therefore sensitive to bond strengthening or weakening associated with dehydration and hydrogen-bond modification. The bending force constant f_{θ} describes the angular rigidity of the O-X-O framework and reflects resistance to tetrahedral angular distortion. The stretch-bend coupling term $f_{r\theta}$ quantifies the degree of coupling between bond stretching and angular deformation motions, while the bend-bend

coupling term $f_{\theta\theta}$ describes cooperative interactions between neighboring angular bending coordinates within the tetrahedral framework. In contrast, Herzberg force constants $k(\nu)$ represent effective stiffnesses associated with individual observed normal modes rather than the underlying internal-coordinate force field. Consequently, the Wilson GF formalism provides a more physically complete description of structural distortions, symmetry lowering, and coupled vibrational behavior within the perchlorate and sulfate tetrahedra. Because the Wilson GF formalism explicitly incorporates coupling between stretching and bending coordinates, the derived force constants are sensitive to symmetry lowering, hydrogen-bond perturbations, and structural distortions associated with dehydration and phase transitions.

S4.0 Herzberg 4-Mode Force Constants Calculations and Derivation

In addition to Wilson GF force constants, Herzberg-style mode force constants were also calculated for both magnesium perchlorate and magnesium sulfate across the full temperature and hydration profiles (equations below). The Herzberg constants treat each vibrational mode as an independent harmonic oscillator and were calculated directly from the observed Raman frequencies using:

$$k(\nu_i) = \mu_i(2\pi c\nu_i)^2 \quad (13)$$

where μ_i is the effective reduced mass associated with vibrational mode i . For the tetrahedral XO_4 groups, the stretching modes ν_1 and ν_3 use the X-O stretching reduced mass μ_r , while the bending modes ν_2 and ν_4 use the O-X-O bending reduced mass μ_θ :

$$k(\nu_1) = \mu_r(2\pi c\nu_1)^2 \quad (14)$$

$$k(\nu_3) = \mu_r(2\pi c\nu_3)^2 \quad (15)$$

$$k(\nu_2) = \mu_\theta(2\pi c\nu_2)^2 \quad (16)$$

$$k(\nu_4) = \mu_\theta(2\pi c\nu_4)^2 \quad (17)$$

The Wilson GF force constants differ fundamentally from the Herzberg mode force constants because the Wilson approach solves the coupled vibrational problem in internal coordinates and explicitly includes stretching, bending, bend-bend, and stretch-bend interaction terms within the tetrahedral force field. Consequently, the Wilson force constants describe the intrinsic internal-coordinate force field of the XO_4 tetrahedron, whereas the Herzberg constants represent effective stiffnesses associated with the individual observed normal modes (ν_1 - ν_4). The Wilson formalism, therefore, provides a more physically complete description of structural changes accompanying dehydration, hydrogen-bond modification, and symmetry lowering because it incorporates coupling between stretching and bending motions rather than treating each vibrational mode independently.

Herzberg force constants provide a concise, mode-resolved framework for evaluating how tetrahedral bonding evolves with dehydration and offer a direct comparison to the derived Wilson GF force constants. Plotted Herzberg force constants can be found below. Because the Herzberg constants are calculated independently for each vibrational mode ($k(n) = \mu(2\pi c\nu)^2$), they isolate the behavior of individual stretching and bending modes without explicitly incorporating coupling terms, making them complementary to the fully coupled Wilson GF treatment.

In $\text{Mg}(\text{ClO}_4)_2$, the Herzberg constants closely mirror the trends observed in the Wilson GF force field. The symmetric and asymmetric stretching constants, $k(n_1)$ and $k(n_3)$, increase stepwise across the hexahydrate to anhydrate phase transitions, directly reflecting progressive Cl-O bond stiffening as hydrogen bonding associated with structural water is removed. The asymmetric stretch $k(n_3)$ shows the strongest sensitivity to these transitions, with pronounced increases at phase boundaries that track symmetry lowering and structural reorganization of the tetrahedron. The

bending constants $k(n_2)$ and $k(n_4)$ exhibit smaller but distinct discontinuities and clear splitting beginning in the tetrahydrate phase, consistent with the divergence of n_2 and n_4 observed in the Raman spectra. This splitting propagates into the Herzberg constants and reflects the emergence of inequivalent angular environments, in agreement with the bifurcation observed in f_0 from the Wilson GF analysis. In the anhydrate phase, the bending constants begin to reconverge, reflecting the partial recovery of symmetry.

In contrast, MgSO_4 exhibits a more gradual evolution of Herzberg constants, consistent with the smoother trends observed in the Wilson GF force constants. The symmetric stretch $k(n_1)$ remains relatively stable across epsomite and hexahydrate, indicating that S-O bond strength is largely preserved in the hydrated phases. The asymmetric stretch $k(n_3)$ increases progressively with dehydration, with the largest increase occurring at higher temperatures ($\sim 200\text{--}300\text{ }^\circ\text{C}$), where the material is largely amorphous. This increase reflects strengthening of S-O bonds within a disordered framework rather than a discrete phase transition. The bending constants $k(n_2)$ and $k(n_4)$ evolve smoothly with no splitting, indicating that n_2 and n_4 remain comparatively coherent and that symmetry breaking is limited relative to $\text{Mg}(\text{ClO}_4)_2$. This behavior is consistent with gradual structural reorganization rather than abrupt hydrogen-bond-driven symmetry lowering.

The Herzberg and Wilson GF force constant approaches are highly consistent and reinforce a fundamental difference in dehydration behavior between the two systems. $\text{Mg}(\text{ClO}_4)_2$ is governed by hydration-driven bond stiffening, symmetry breaking, and dynamic redistribution of vibrational interactions, whereas MgSO_4 responds primarily through gradual bond strengthening and structural reorganization within a more robust and less hydration-sensitive sulfate framework.

Derivation:

Herzberg mode force constants were calculated independently using the harmonic oscillator approximation for each observed vibrational mode (Herzberg, 1945). In this approach, each vibrational band is treated as an effective normalmode oscillator with a mode-specific reduced mass. The force constant is obtained directly from the measured Raman frequency. In contrast to the Wilson GF formalism, the Herzberg treatment does not explicitly resolve stretch-bend or bend-bend coupling interactions within the tetrahedral force field.

For a harmonic oscillator, the vibrational angular frequency is related to the force constant by:

$$\omega_i^2 = \frac{k_i}{\mu_i} \quad (23)$$

where k_i is the effective force constant for vibrational mode i , μ_i is the effective reduced mass for that mode, and ω_i is the angular frequency in s^{-1} . The angular frequency is related to the observed Raman wavenumber ν_i , in cm^{-1} , by:

$$\omega_i = 2\pi c \nu_i \quad (24)$$

where c is the speed of light in cm s^{-1} . Substituting this expression into the harmonic oscillator relation gives:

$$(2\pi c\nu_i)^2 = \frac{k_i}{\mu_i} \quad (25)$$

Solving for the force constant gives the Herzberg mode force constant:

$$k_i = \mu_i(2\pi c\nu_i)^2 \quad (26)$$

or equivalently:

$$k_i = 4\pi^2 c^2 \mu_i \nu_i^2 \quad (27)$$

For the tetrahedral XO_4 groups considered here, where $X = \text{Cl}$ for perchlorate and $X = \text{S}$ for sulfate, the stretching modes ν_1 and ν_3 were assigned the $X\text{-O}$ stretching reduced mass:

$$\mu_r = \frac{m_X m_O}{m_X + m_O} \quad (28)$$

The bending modes ν_2 and ν_4 were assigned an effective O-X-O bending reduced mass:

$$\mu_\theta = \frac{2m_X m_O}{m_X + m_O} \quad (29)$$

Thus, the Herzberg force constants for the four tetrahedral modes are:

$$k(\nu_1) = \mu_r(2\pi c\nu_1)^2 \quad (30)$$

$$k(\nu_3) = \mu_r(2\pi c\nu_3)^2 \quad (31)$$

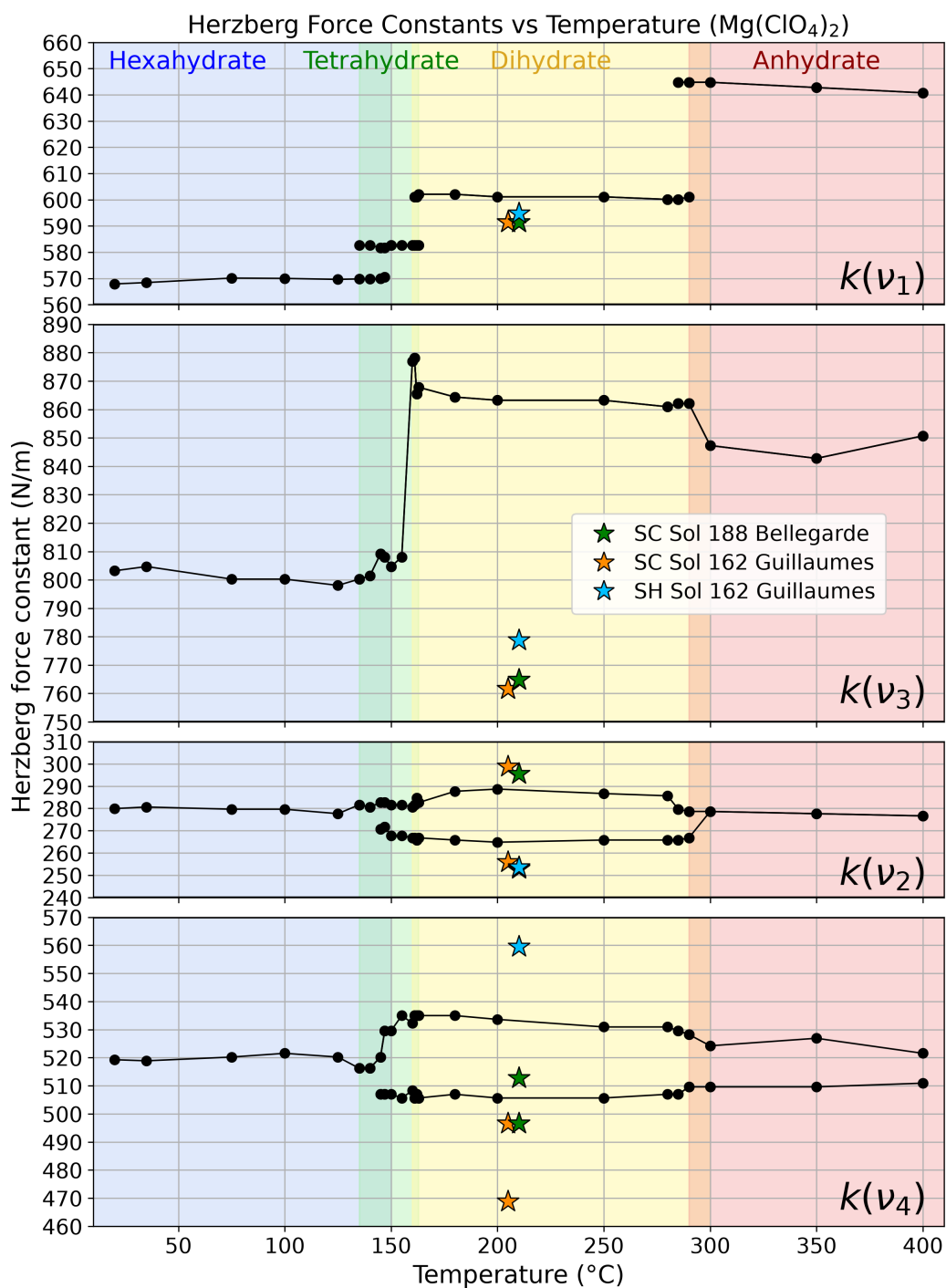
$$k(\nu_2) = \mu_\theta(2\pi c\nu_2)^2 \quad (32)$$

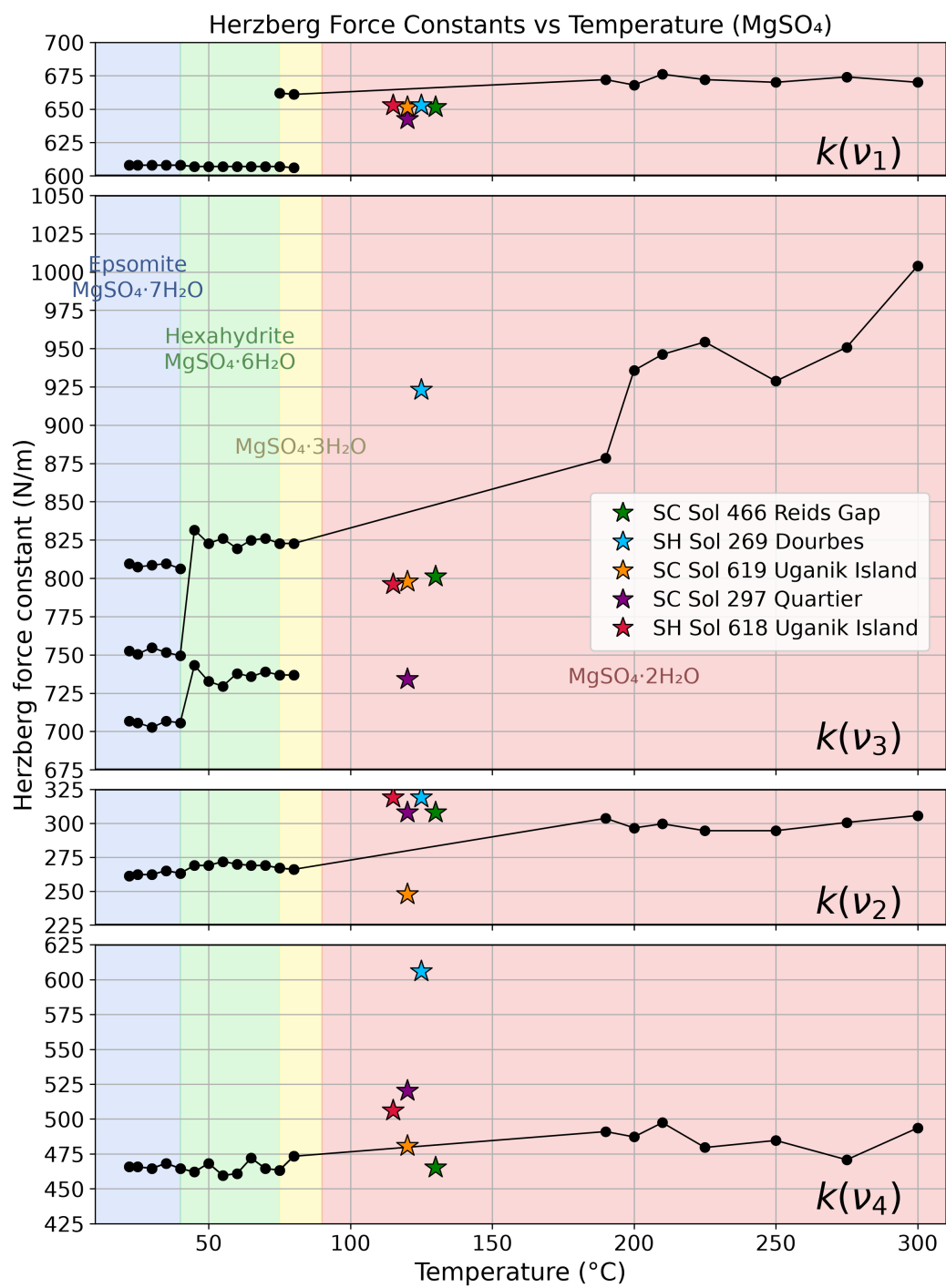
$$k(\nu_4) = \mu_\theta(2\pi c\nu_4)^2 \quad (33)$$

where ν_1 is the A_1 symmetric stretch, ν_3 is the F_2 asymmetric stretch, ν_2 is the E bending mode, and ν_4 is the F_2 bending mode. All Herzberg force constants are reported in N m^{-1} .

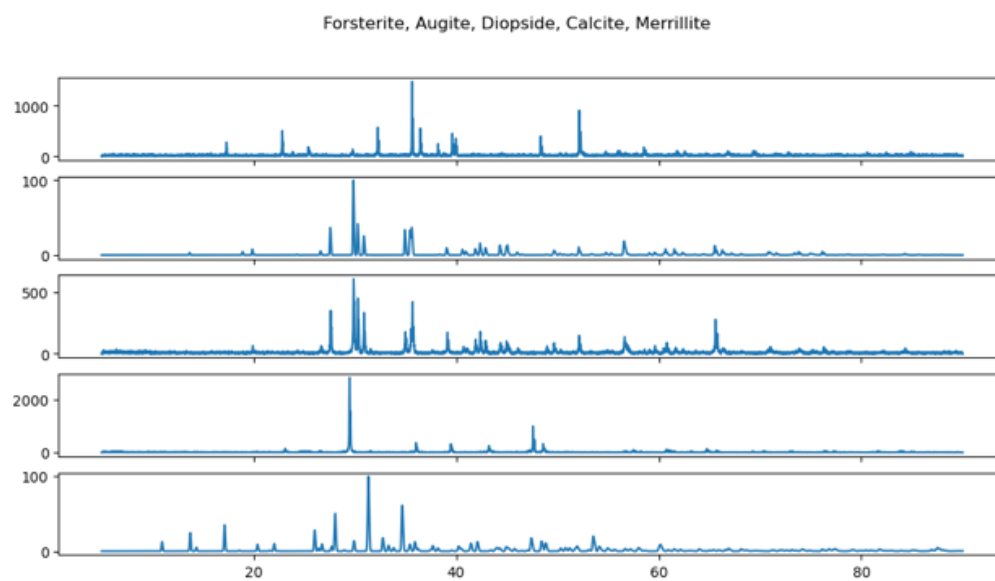
All force constants are reported in N m^{-1} .

S5.0 Herzberg Force Constants Plots and Comparison to Wilson GF Force Constants

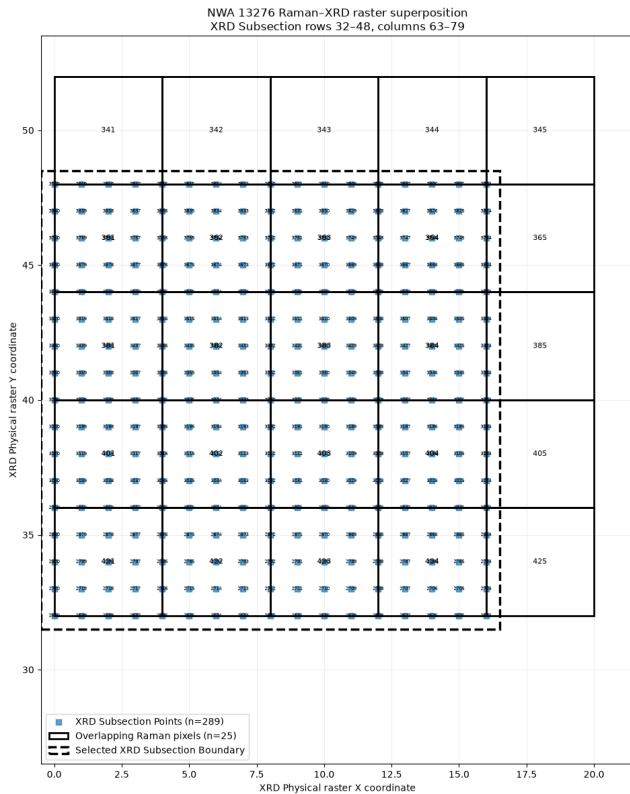
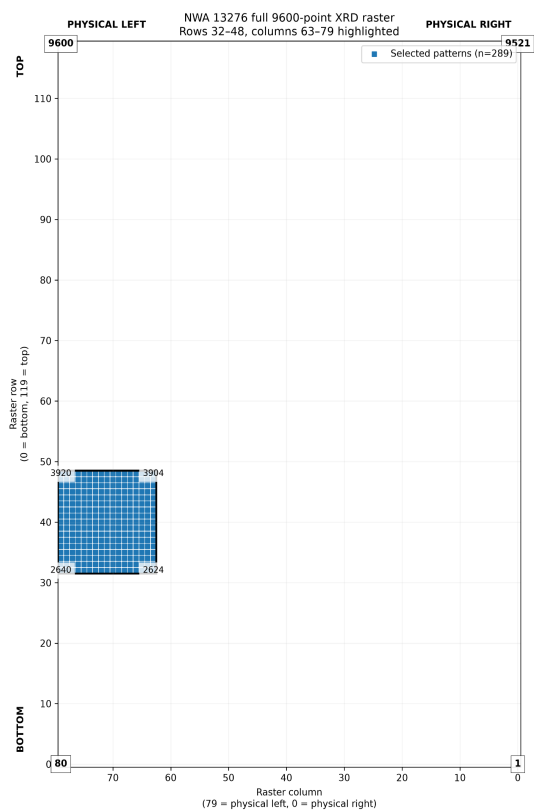




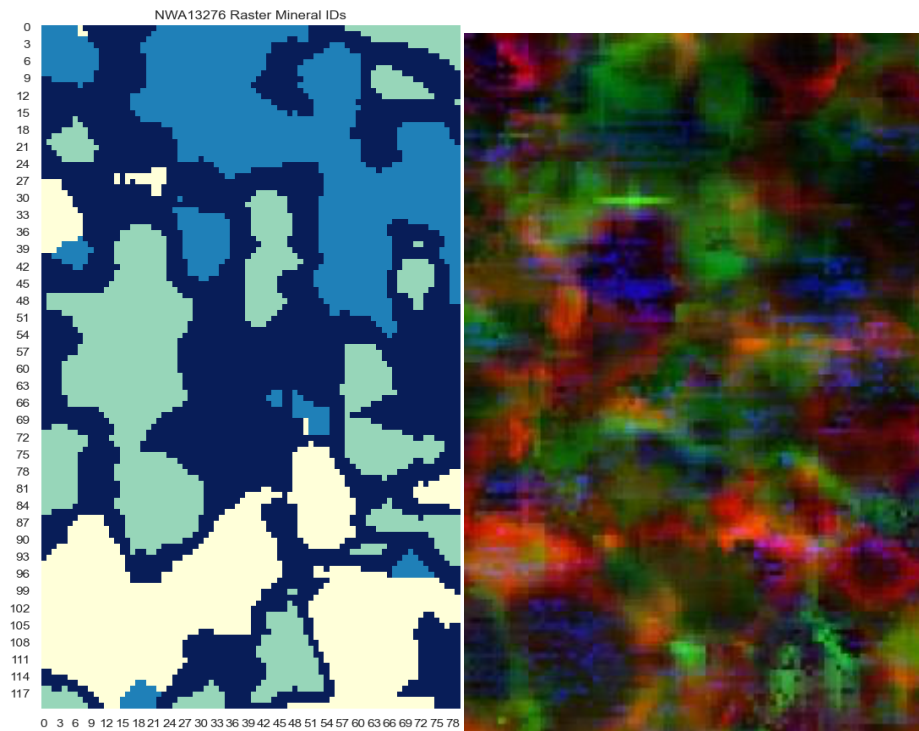
Chapter 3 Supplementary Information



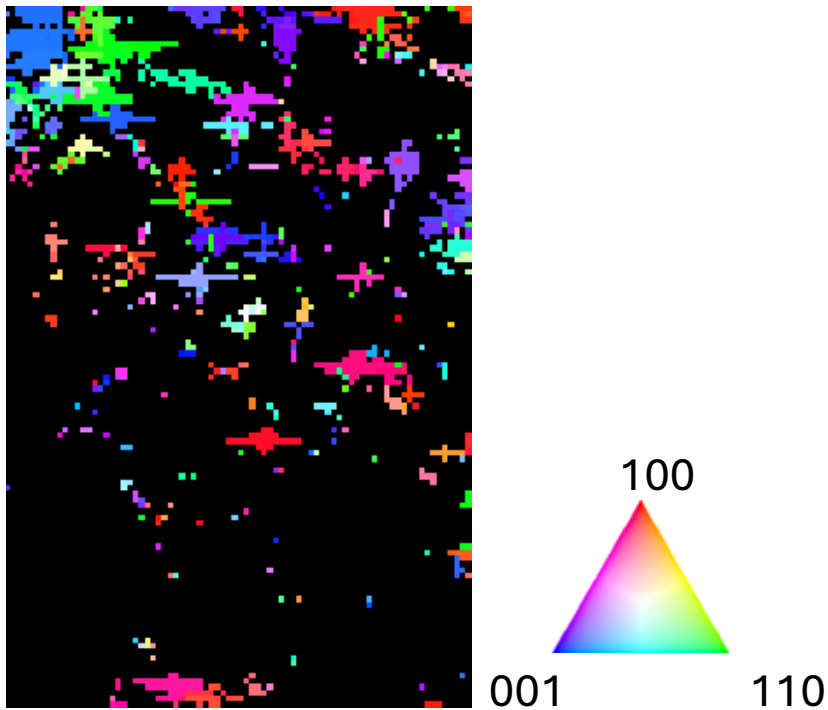
RRUFF XRD references for forsterite, augite, diopside, calcite, and merrillite.



XRD raster subsection used for manual texture analysis and superimposed Raman and XRD grids.

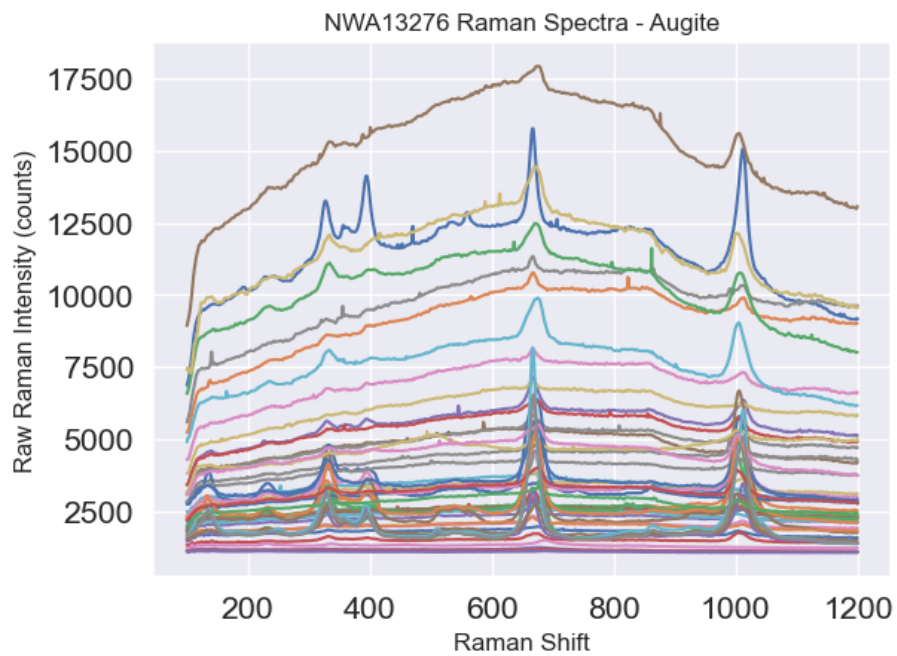
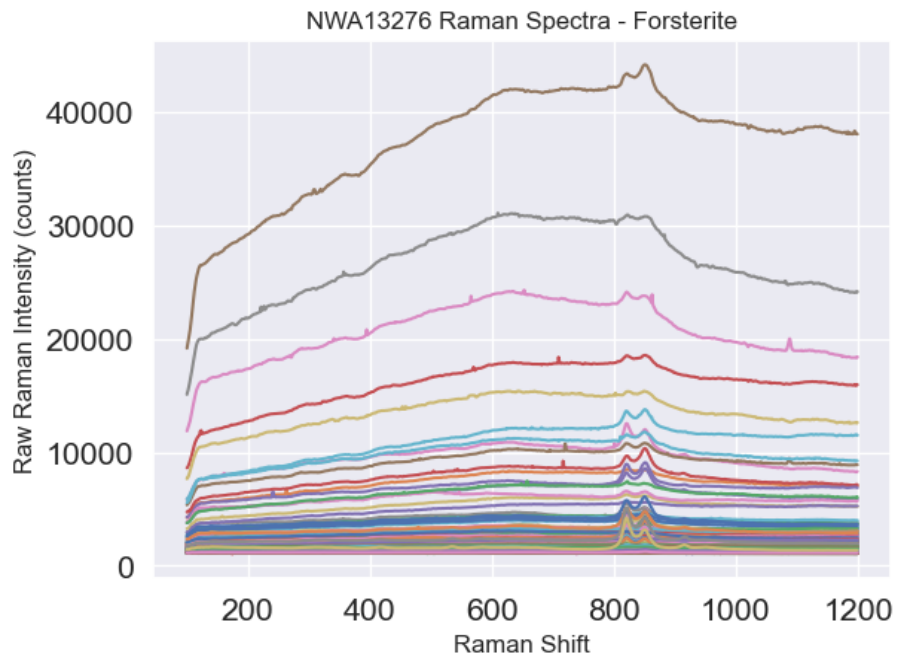


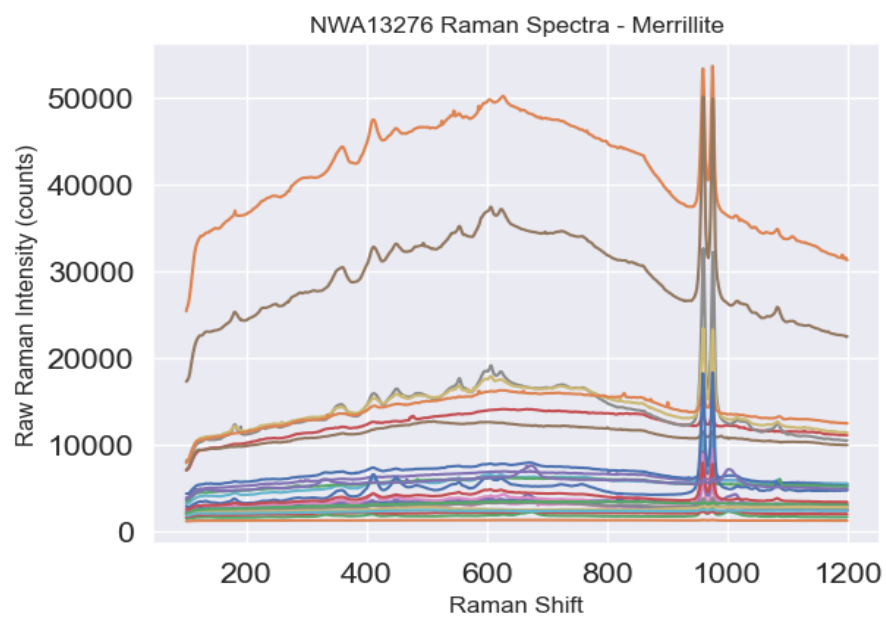
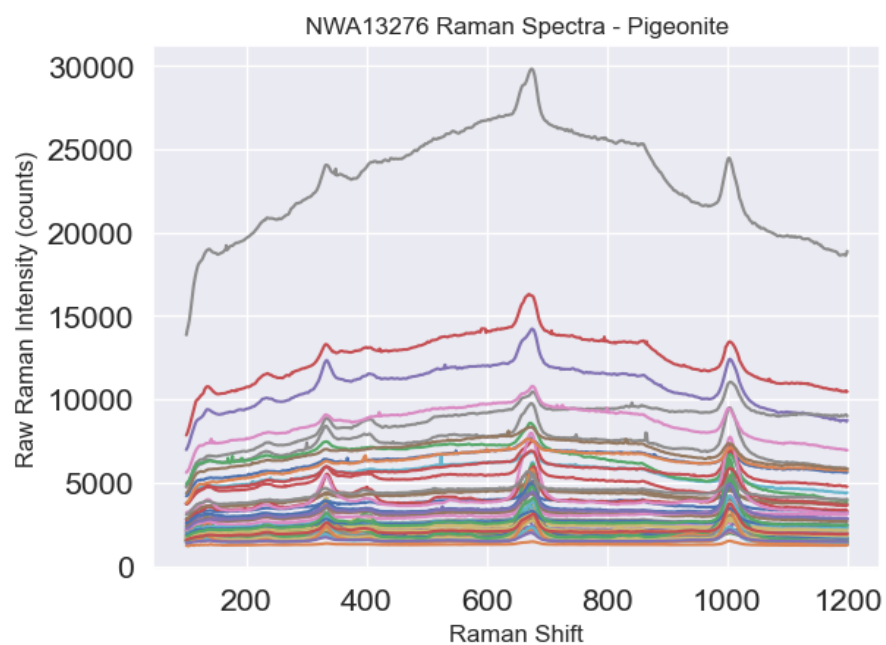
K-means clustering left versus principal component analysis. PCA performs better.

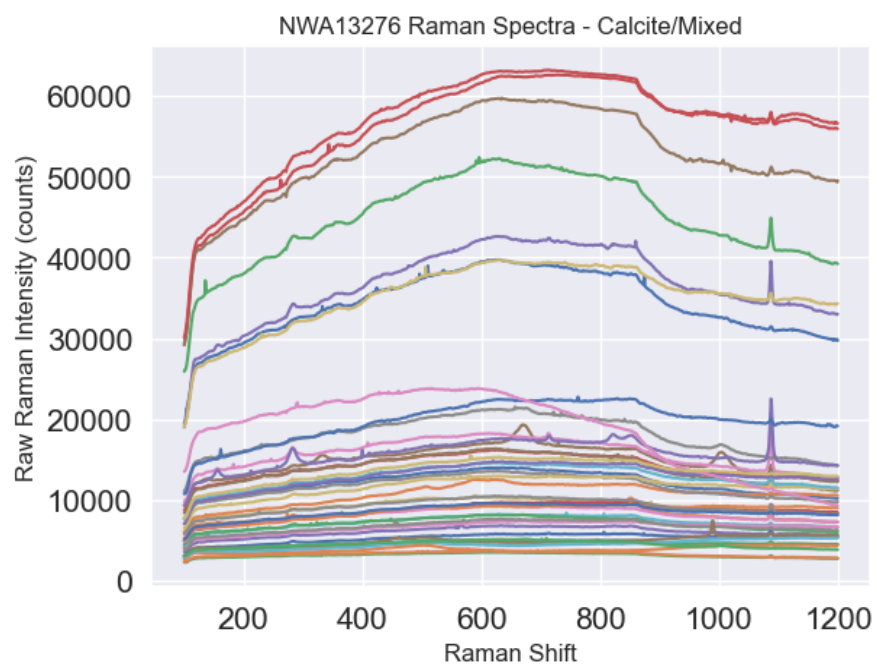
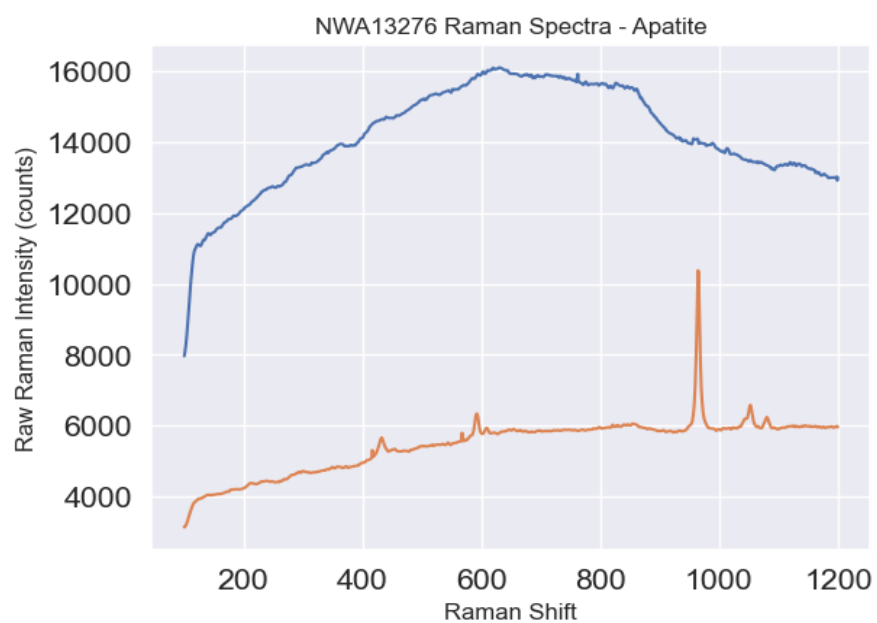


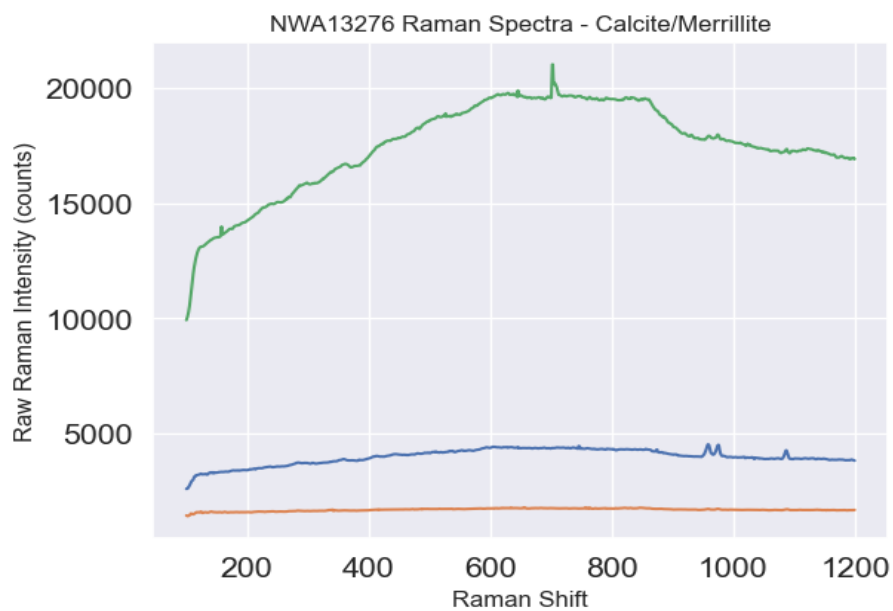
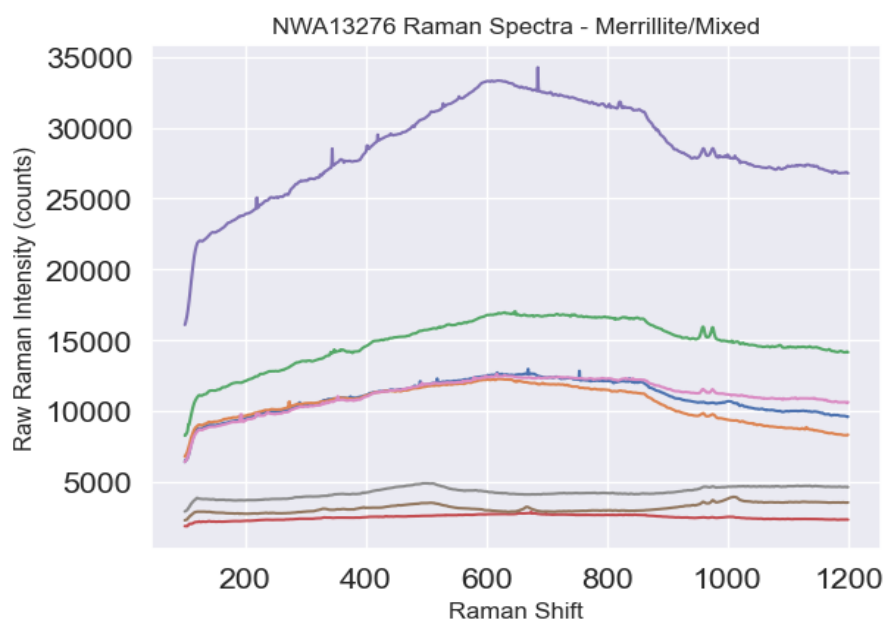
Laue diffraction measurements indicated homogeneous orientation vectors for all detected calcite crystals in NWA 13276 and vindicated a high degree of mosaicism for the rest of the meteorite.

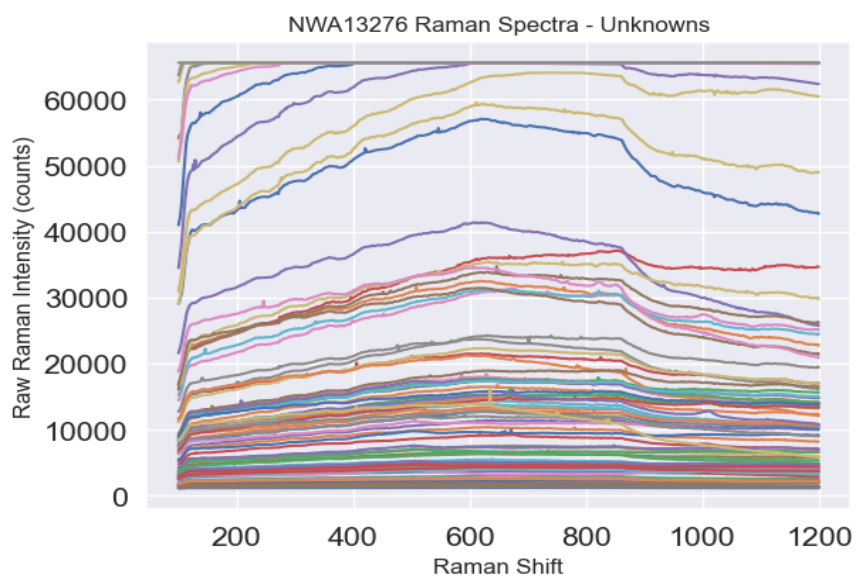
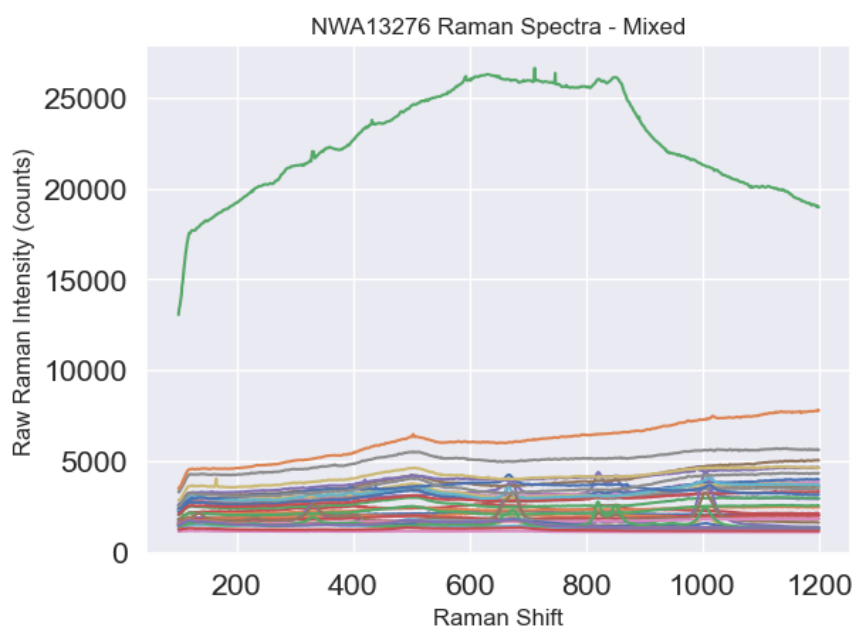
Olivine, augite, pigeonite, merrillite, apatite, calcite, mixed, and unknown Raman spectra from the meteorite raster.

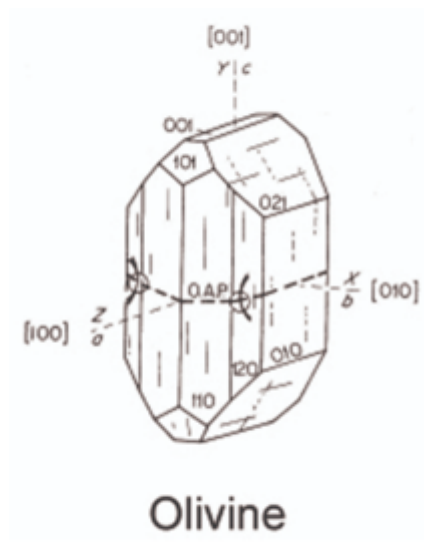
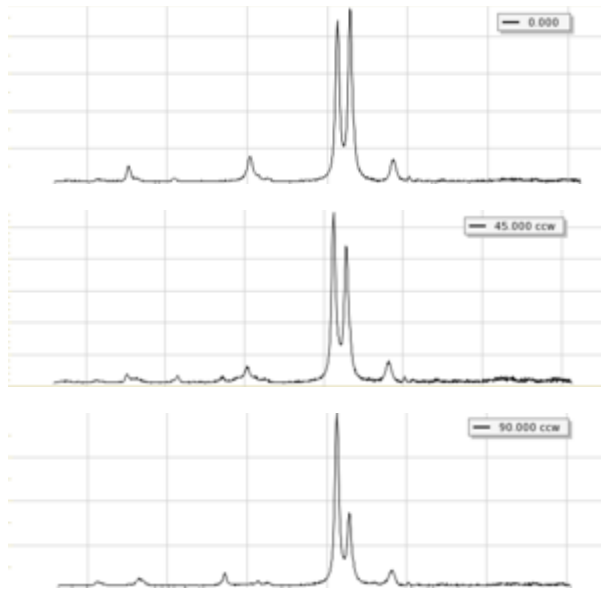






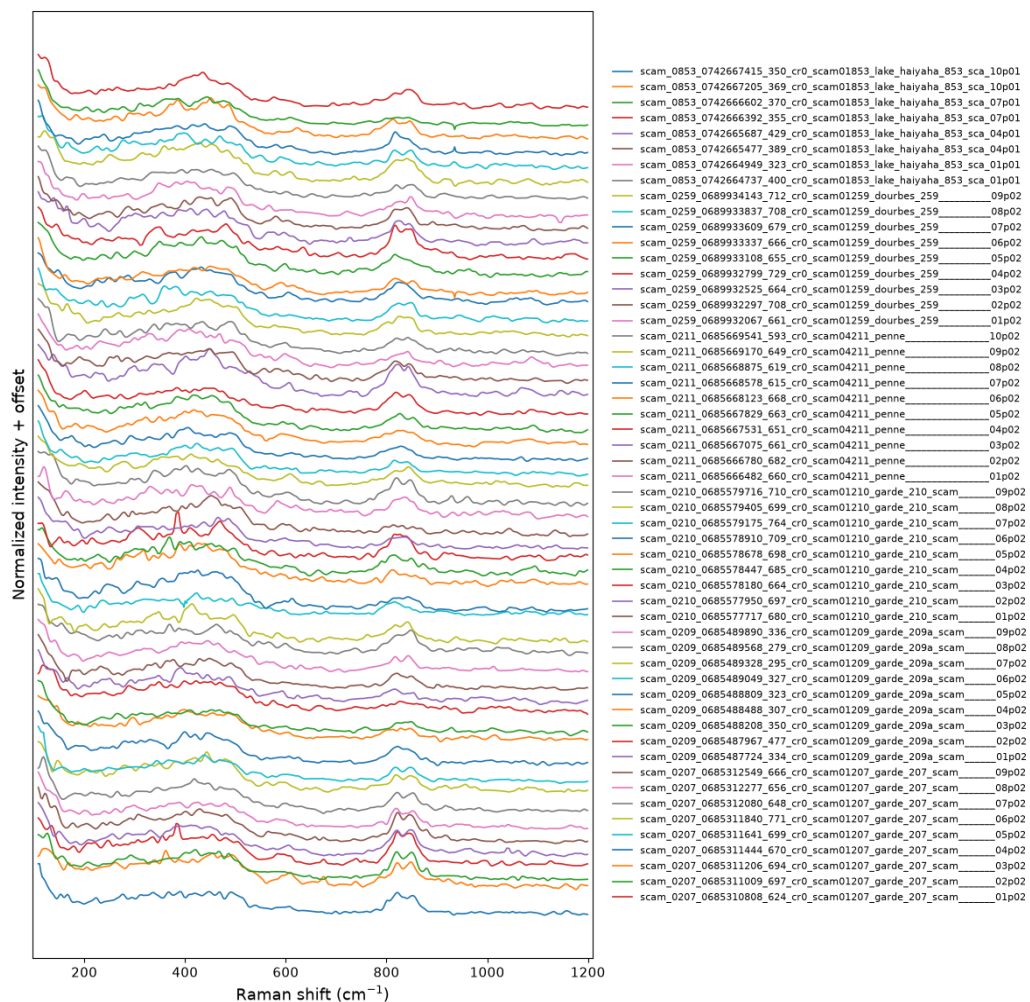




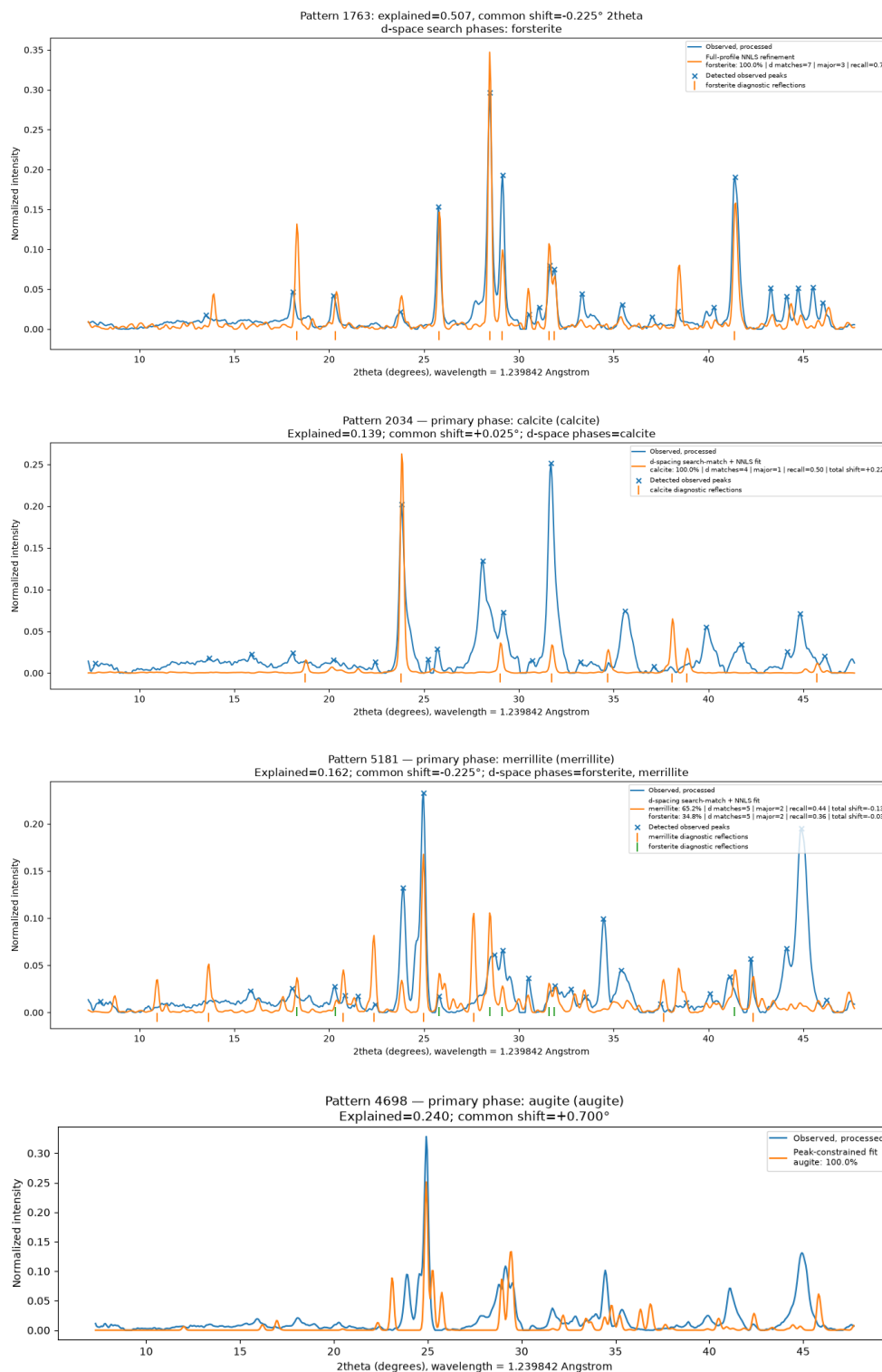


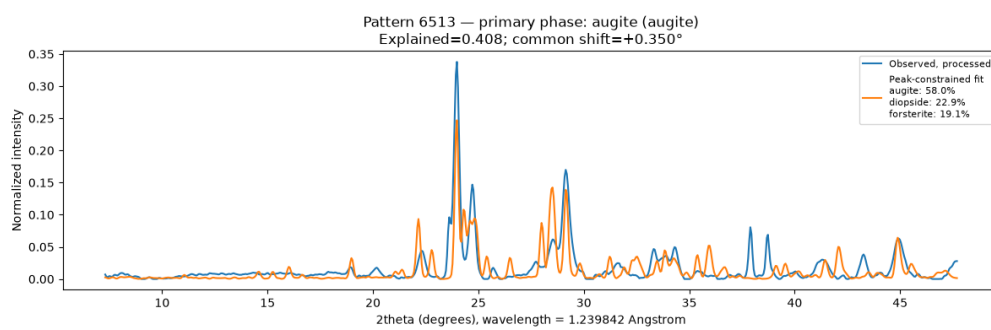
Polarized Raman of olivine doublet from RRUFF.

Perseverance SuperCam Raman Spectra - Olivine Seitah Formation



Representative XRD patterns fit using pseudo-Rietveld automated loop





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