

THE MID- AND FAR-INFRARED EMISSION SPECTRA OF CHLORIDE MINERALS. J. L. Mitchell¹ and P. R. Christensen¹, ¹Arizona State University (201 E. Orange Mall, Tempe, AZ 85281, julie.l.mitchell@asu.edu)

Introduction: Geomorphologic and geochemical evidence indicate that the surface of Mars was once exposed to large quantities of liquid water. Evaporation of natural bodies of water on Earth results in the precipitation of a specific sequence of minerals. This precipitation sequence is determined by the relative solubilities of the dissolved minerals, where carbonates are less soluble than sulfates, and sulfates are less soluble than chlorides. As a result, chlorides are the last minerals to precipitate from natural waters; the identification of chlorides on Mars, therefore, indicates regions where the last liquid water may have existed on the martian surface. [1] Chlorides are therefore high-priority targets for studies of ancient Mars.

Background: The crystal structures of anhydrous chlorides are unique among evaporite minerals in that they vibrate only in the far-infrared (FIR). In the mid-infrared (MIR), they are characterized by a lack of spectral absorption features and peak emissivities less than one; this results in featureless, sloping mid-infrared spectra. Chlorides have been identified on Mars by this unique MIR emission spectrum [2, 3], however the exact type of chloride mineral cannot be determined with MIR spectra only.

Martian chlorides also have similar morphologies to chloride deposits on Earth; meter-scale polygonal fractures have been observed by numerous orbiting instruments [4, 5]. A variety of sub-meter textures are observed on Earth [6]; these textures can provide additional information about the environmental conditions at the time of evaporation. These textures may have substantial effects on chloride spectra as a function of grain size, cementation, and compression.

While chlorides are featureless in the wavelength range of the Thermal Emission Imaging System (THEMIS, 6.5-15 μm) currently orbiting Mars [7], future instruments will be sensitive to longer wavelengths. The purpose of this study is to fully characterize the spectral features of a suite of chloride minerals and textures in mid- and far-infrared emission. By quantifying the spectral properties of a suite of chloride compositions and textures, we provide scientific context for future far-infrared spectral analyses of the martian surface.

Methods: Three types of samples were analyzed as part of this study: pressed pellets of three reagent-grade chloride minerals, synthetic textures of a fixed composition (halite/NaCl), and field samples from a chloride-rich playa in the Mojave Desert. Synthetic textures were grown from a 300 g/L NaCl brine at var-

ying evaporation rates. A summary of the samples is shown in **Table 1** below.

MIR emission spectra (4000 – 400 cm^{-1} , CsI beamsplitter) were collected at a spectral resolution of 2 cm^{-1} at Arizona State University. MIR (4000 – 400 cm^{-1} , KBr beamsplitter) and FIR emission spectra (600 – 50 cm^{-1} , solid state beamsplitter) were collected at Stony Brook University. All spectra were collected using the techniques developed by [8].

Table 1. Summary of chloride samples from which spectra were collected for this study. (ST = synthetic texture)

Type	Sample Name	Composition
Pressed Pellet	NaCl W3	NaCl (halite)
Pressed Pellet	KCl W3	KCl (sylvite)
Pressed Pellet	CaCl ₂ W2	CaCl ₂
ST	Efflorescent Crust	NaCl
ST	<180 μm Grains	NaCl
ST	>180 μm Grains	NaCl
ST	Small Cubes	NaCl
ST	Lab Aggregate	NaCl
ST	Pyramid (raft)	NaCl
ST	Large Crystal	NaCl
Field	Pulverized Polygonal Halite	NaCl
Field	Cleaned Polygonal Halite	NaCl
Field	Massive Salt	Unknown

Results: MIR emission spectra of all samples were featureless except for minor transmission-like features due to water (at 1627 cm^{-1}), sulfate (1110 cm^{-1}), and/or potassium nitrate (a known contaminant in reagent-grade KCl powders, 1402 cm^{-1}), which have been seen in other studies [9-11]. FIR emission spectra are shown below in **Figures 1-3** for each sample type. Variations in absorption band location, depth, and the location of the first Christiansen feature were measured and compared for each sample.

Pressed Pellets. The fundamental absorption features for NaCl are visible as one large absorption at $\sim 180 \text{ cm}^{-1}$ (transverse stretch) and a more shallow absorption (longitudinal stretch) at 260 cm^{-1} . Similarly for KCl, the transverse mode is at 154 cm^{-1} and the longitudinal mode is at 216 cm^{-1} . Because CaCl₂ is orthorhombic instead of isometric, its absorption features are shallower than those of NaCl or KCl, though still in the FIR (168 and 237 cm^{-1} , respectively).

Synthetic Textures. The NaCl transverse mode showed a systematic increase in band depth with particle size. The efflorescent crust, which had the finest

particle size, had the shallowest transverse absorption, while the largest particle size – the large crystal – had the deepest absorption. The effects of compression (i.e. the pressed pellet) and cementation (i.e. the lab aggregate) resulted in deeper absorptions for those samples than would be expected based on particle size alone. The shape of the transverse absorption was increasingly asymmetric with decreasing particle size. No variation in the location of the first Christiansen feature was observed as a function of texture.

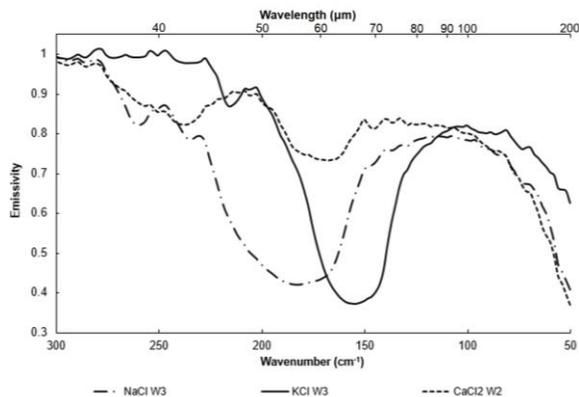


Figure 1. FIR emissivity spectra of chloride pressed pellets.

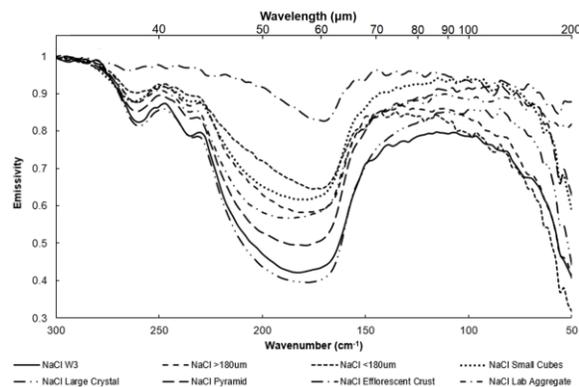


Figure 2. FIR emissivity spectra of synthetic textures.

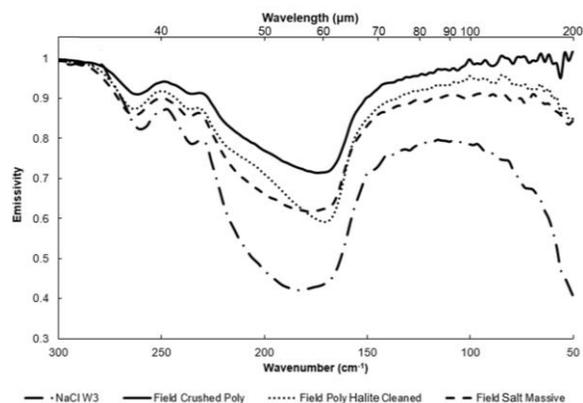


Figure 3. FIR emissivity spectra of field samples.

Field Samples. The polygonal halite samples had absorption features in the same locations as the synthetic halite samples. Additionally, they showed similar variations in transverse absorption depth with particle size as the synthetic samples. The unknown-composition “Massive Salt” sample was shown to be primarily halite, though some component of antarcticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) may also be indicated.

Discussion: The presence of contaminants with fundamental absorptions in the MIR is relatively straightforward, since such materials show up as distinct transmission-like features when mixed with chlorides. Variations in composition between chloride species are shown to be resolvable in the FIR. Large variations in texture are also resolvable; however, the effects of compression and cementation complicate the interpretation of texture based on the transverse absorption feature alone. Field samples show that variations in both texture and composition can be resolved when the variations are great. However, the effects of mixed chlorides can potentially make compositional constraining difficult (i.e., the Massive Salt sample).

The technology exists to study the FIR on Mars, as evidenced by the recent flight of a FIR emission-sensitive instrument (OTES) on the OSIRIS-REx mission. This study shows that sending such an instrument to Mars can provide significant scientific return solely by the investigation of martian chloride deposits. As the first target for such an instrument, we recommend the Terra Sirenum region, which includes both the largest chloride deposit on Mars [2, 3] and recent evidence of seafloor-like hydrothermal activity [12]. Understanding the compositional and textural variations of chloride minerals on Mars will provide new insights into the period when liquid water last existed in large volumes on the martian surface, including the provenance of such water (hydrothermal/groundwater upwelling/surface runoff) and the potential habitability of such environments during Mars’ ancient history.

Acknowledgements: The authors would like to thank Tim Glotch, Deanne Rogers, and the graduate students in Earth and Space Sciences at Stony Brook University for their incredible assistance in collecting and calibrating the chloride spectra.

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