Effect of halite and calcite coatings on thermal infrared spectra with implications for Mars exploration

Jeffrey A. Berger

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EFFECT OF HALITE AND CALCITE COATINGS ON THERMAL INFRARED SPECTRA WITH IMPLICATIONS FOR MARS EXPLORATION

by

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ABSTRACT

Knowing the occurrence and distribution of soluble ionic salts allows us to model the aqueous history and geochemical conditions of surface solutions on Mars. Salts deposited as coatings are particularly important for attaining this knowledge because the thermal infrared (TIR) remote sensing method for determining mineral abundance is limited to the top few hundred micrometers of the surface. To better understand the TIR properties of salt coatings, we investigated the effects of coating thickness and texture on the TIR reflectance spectra of halite- and calcite-coated glasses. We evaluated salt coating textures that could occur on Mars: 1) continuous, uniformly thick layers of salt without exposed substrate; 2) discontinuous particulate salt coatings with variable thickness and exposed substrate. Salt-coated glasses have spectral features attributable to the substrate and the coating. Partially transmissive coatings decrease the intensity of substrate absorption bands as thickness increases. This decrease in intensity is exponential for continuous and coarse particulate (< 50 µm) halite coatings and linear for fine particulate halite coatings (< 2 µm). All halite coating textures and continuous calcite
coatings have spectral features indicating nonlinear mixing of the coating and substrate spectra. Therefore, coatings may result in significant challenges to modeling mineral abundances on Mars using a linear deconvolution algorithm for TIR spectra. An exception is fine particulate calcite coatings (< 8 µm), which are effectively optically thick and display linear spectral mixing. We find that halite coatings can cause an increase in a reflectance minimum (emissivity maximum) found previously to be useful for identifying chloride deposits on Mars. Continuous and coarse particulate halite coatings that are thicker and cover more substrate increase the reflectance minimum and are easier to detect in remotely sensed TIR spectra. Fine particulate halite does not increase the reflectance minimum and is not detectable by the method.
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1. INTRODUCTION

Aqueous processes are difficult to track on Mars because liquid water is not stable for extended periods of time at current surface conditions. Nonetheless, evidence of the activity of water is recorded in soluble ionic solids like carbonates, halides, and sulfates. These salts have been found in Martian meteorites [e.g., Bridges et al., 2001] and inferred from the chemical compositions of soils, rocks, and coatings on the Martian surface [Clark and Van Hart, 1981; summarized by Ming et al., 2008]. Knowing the composition, occurrence, and distribution of salts allows us to model the aqueous history and geochemical conditions of surface solutions on Mars [e.g., King et al., 2004; Tosca et al., 2005, 2006]. Models predict that highly soluble halide salts (e.g., halite) are likely to precipitate later than less soluble carbonate salts (e.g., calcite) that form early in the precipitation sequence. Therefore, understanding the distribution and relationships between these two salt types is important for investigating the history of surface solutions on Mars.

Salts on Earth commonly accumulate as coatings via aqueous processes. Coatings related to aqueous weathering have been identified on Mars [Squyres et al., 2004; Clark et al., 2005; Haskin et al., 2005] and they are particularly important to thermal infrared (TIR) remote sensing because the technique effectively measures only the top few hundred micrometers of the surface. Developing TIR spectroscopic methods for identifying and characterizing salt coatings will improve knowledge of Mars’ aqueous history and help the search for areas with high potential for habitability and preservation of extant or extinct life [Farmer and Des Marais, 1999; Foster et al., 2010].
1.1. Chloride salts on Mars

Chloride salts are found in Martian meteorites [e.g., Bridges et al., 2001] and their presence is inferred from high Cl concentrations detected in rocks on Mars with X-ray techniques [Clark et al., 2005; Gellert et al., 2006; Knoll et al., 2008]. Geochemical modeling of weathering and brine evolution also predicts the presence of chloride salts on the Martian surface [King et al., 2004; Tosca et al., 2005; Tosca and McLennan, 2006]. Results from the alpha-particle X-ray spectrometers on the Mars Exploration Rovers show that chlorides may contribute to rock coatings on Mars [Haskin et al., 2005; Clark et al., 2005; Knoll et al., 2008]. In addition, orbital TIR observations show that chloride-bearing deposits on Mars may be widespread, although concentrated in locally low-lying areas and in some sinuous channels and small craters [Osterloo et al., 2008, 2010; Glotch et al., 2010]. Chlorides are challenging to detect with IR remote sensing techniques because they are transmissive and spectrally featureless over the TIR spectrum [Eastes, 1989]. However, Osterloo et al. [2008] recognized that chlorides may impart diagnostic TIR spectral slopes and decreased spectral contrast, and this method was used to find putative chlorides on Mars [Glotch et al., 2010; Osterloo et al., 2010]. In this study, we investigate the reflectance spectra of halite coatings to evaluate the chloride-related negative slope in emission spectra. Reflection spectroscopy is useful for this because it does not require the assumptions about temperature made for emission spectroscopy. As a result, the absolute TIR reflectance of halite and halite-coated materials can be measured [cf. Lane and Christensen, 1998].
1.2. Carbonate salts on Mars

Carbonates are found in Martian meteorites [Gooding et al., 1991; Bridges et al., 2001] and predicted in geochemical models of aqueous processes [King et al., 2004]. Recently, evidence of carbonates on Mars’ surface has been growing. Carbonates were identified as a small component (~2 to 5 weight %) in orbital TIR [Bandfield et al., 2003] and near-infrared data [Ehlmann et al., 2008], and at a much larger proportion (16 to 34 weight %) in an outcrop investigated by the Mars Exploration Rover Spirit, where carbonates are hypothesized to be nodules associated with hydrothermal processes [Morris et al., 2010]. Scanning calorimetry and wet chemistry experiments also indicate the presence of carbonates in soils at the Phoenix landing site [Boynton et al., 2009; Kounaves et al., 2010]. The spectral properties of carbonates contrast with chlorides because they have characteristic absorption bands in thermal infrared [Salisbury et al., 1991] and chlorides do not.

1.3. Important role of coating texture on TIR spectra

Different geologic processes may result in salt deposits with different textures. Volcanic aerosol deposition, hydrothermal deposits, precipitation from a brine, efflorescence, eolian reworking, and freezing can result in a wide range of particle sizes, roughness, mixing, packing, cementation, and disaggregation. These textural factors affect TIR properties, changing TIR spectra predictably [e.g., Hunt and Vincent, 1968; Vincent and Hunt, 1968; Eastes, 1989; Salisbury et al., 1991; Christensen et al., 2000a; Cooper and Mustard, 2002]. Few studies have examined the textural effects of coatings [Crisp and Bartholomew, 1992; Christensen and Harrison, 1993; Johnson et al., 2002], which add complications due to the layering of materials, potentially causing nonlinear
spectral behavior [Hapke, 1993] not captured by models that determine mineralogy using TIR spectra [e.g., Ramsey and Christensen, 1998].

The role of coatings on the TIR investigations of Mars have been studied in terms of palagonitic dust [Crisp and Bartholomew, 1992; Johnson et al., 2002], clay powders and loess [Johnson et al., 2002], silica [Crisp et al., 1990; Kraft et al., 2003], desert varnish [Christensen and Harrison, 1993], and in natural volcanic settings [Crisp et al., 1990; Minitti et al., 2007]. Several trends relevant to this study were identified in these works. First, partially transmissive coatings that are nearly continuous over the substrate cause a nonlinear decrease in the TIR signal of the substrate [Kraft et al., 2003]. Second, when optically thick patches of coating dominate over thin, partially transmissive patches, then the TIR signal of the substrate decreases linearly with increasing coating thickness [Christensen and Harrison, 1993]. Finally, fine particulate coatings reduce the contrast of the substrate’s absorption bands as coating thickness and coverage increases, acting as a near-blackbody component [Crisp and Bartholomew, 1992; Johnson et al., 2002].

Previous TIR studies of thin coatings emphasize silicate materials and do not include halide or carbonate salts. Halides are spectrally distinct from silicate materials because they are transmissive and spectrally flat. Ca-carbonate has a strong absorption band (~1485 cm\(^{-1}\)) offset from bands common in silicate rocks (~700-1250 cm\(^{-1}\)) from asymmetric stretching of O-Si-O units (summary in Dalby and King [2006]) as well as a weaker absorption (~880 cm\(^{-1}\)). Analyses of the contrasting spectral features of halides and carbonates and their TIR properties as coatings will likely improve the understanding of coating effects on TIR.
1.4. Goals of this study

Here, we examine the TIR spectroscopic properties of halite- and calcite-coated surfaces as a function of coating texture and thickness. We present TIR reflectance and emission spectra of halite coatings on glass substrates and TIR reflectance spectra of calcite coatings on glass substrates. We evaluate the following questions: 1) What is the nature of the spectral mixing of the coating and substrate (i.e., linear or nonlinear)? 2) Is there a difference in the spectral signatures of different salt coating textures? and 3) At what thickness does the coating effectively mask the substrate’s TIR signature? Finally, we discuss our findings in terms of improving methods for detecting salts on Mars.
2. METHODS

2.1. Substrate preparation

Glass substrates were used to ensure compositional homogeneity and to avoid complications related to crystallographic orientation and roughness because those variables are known to affect infrared spectra [Bennett and Porteus, 1961; Salisbury et al., 1991; Hapke, 1993]. Both basaltic and albitic glasses were prepared with the goal of investigating coatings on substrates with different spectral features. Basaltic glasses have spectral bands related to asymmetric stretching of the Si-O molecule at ~960 – 1000 cm\(^{-1}\) [Dufresne et al., 2009] whereas albitic glasses have a major spectral band at ~1040 – 1085 cm\(^{-1}\) and a shoulder at ~1180 – 1225 cm\(^{-1}\) [Lee et al., 2010]. Unweathered basalt (Broken Tank 2, Socorro, NM) and albite (Bancroft, ON) were ground into powders using a steel mill, mixed with a lithium-tetraborate flux at a sample to flux ratio of 9:1 then melted in a Pt crucible at 1100 °C. Nominally flat glass substrates were formed by pouring the mixed molten material into disk-shaped molds (40 mm inner diameter). The lithium-tetraborate flux was required to reduce the viscosity sufficiently so that a flat surface formed. The flux resulted in an absorption band at ~1365 cm\(^{-1}\), which overlaps with the carbonate band at ~1500 cm\(^{-1}\). To simplify the interpretation of the spectral mixing, calcite coatings were also investigated with Na-Ca-Si-O glass (microscope slide) as a substrate. This glass substrate has no bands in the vicinity of carbonate bands.

2.2. Coating preparation

Coating textures were designed to determine the thermal infrared spectral properties of different halite and calcite coatings that could occur on the surface of Mars. The textures were 1) continuous, 2) coarse particulate, and 3) fine particulate. Continuous
coatings cover the substrate entirely with a smooth layer of uniform thickness and particulate coatings have more variable thickness and may have partially exposed substrate. We now discuss the methods used to produce the coating textures with target coating thicknesses of ~1 – 200 µm.

2.2.1. Halite coating preparation

Continuous halite coatings were prepared by pressing dry, reagent grade NaCl particles (< 125 µm) with 8 tons of force for 5 to 8 minutes into solid wafers. Thinner coatings were formed by pressing < 2 µm powders obtained by chemical vapor deposition of halite on glass (below). The wafers were placed on the basaltic Li-tetraborate glass substrate for TIR measurements. A dust-free, planar contact with the surface was confirmed by optical microscopy. Optically thick (~1 mm) NaCl windows (Thermo-Fisher) were also examined.

Coarse particulate halite coatings were produced immediately before TIR analysis by dusting < 125 µm halite particles over a basaltic Li-tetraborate glass substrate through a 125 µm mesh. The same material was placed in a sample holder > 1 mm deep, and loosely packed and leveled at the surface for TIR analysis as an optically thick halite particulate.

Fine particulate halite coatings were formed by chemical vapor deposition (CVD), where halite was vaporized by a heated filament and condensed as particles (< 2 µm) on the surface of the substrate. To minimize larger “bombs” and uneven sputtering we used a single piece of halite (< 10 mm across) that had been melted. Samples were returned to the CVD chamber multiple times to produce thicker coatings.
2.2.2. Calcite coating preparation

Continuous calcite coatings were prepared in the same manner as the halite continuous coatings, except with reagent grade CaCO$_3$ particles (< 8 µm) and a Na-Ca-Si-O glass substrate.

Fine particulate calcite coatings were prepared from a mixture of reagent grade calcite and deionized water. The suspended calcite particles were deposited as a coating on the glass substrate via evaporation at ~150° C. The CaCO$_3$ particulate was also placed in a sample holder > 1 mm deep, loosely packed, and leveled at the surface for IR analysis as an optically thick calcite particulate.

2.3. Sample characterization

2.3.1. Thermal infrared reflection spectroscopy

TIR spectra were collected at the University of New Mexico in specular reflectance mode using a Nicolet Nexus 670 Fourier Transform infrared spectrometer with a Continuµm microscope, Globar source, KBr beamsplitter, and MCT-A* detector. The spectral region 4000 to 650 cm$^{-1}$ (2.5 – 15.3 µm) was measured with 4 cm$^{-1}$ resolution and 100 to 200 scans. With the sample in a dry-air purged compartment, micro-reflectance TIR measurements were collected over a 100 x 100 µm spot size. Before each sample was measured, background measurements were collected on gold. For the continuous halite- and calcite-coated samples, as well as the fine particulate halite-coated samples, three spectra were collected for each sample from three separate spots.
2.3.2. Thermal infrared emission spectroscopy

Thermal emission spectra were collected for the fine particulate halite coatings because they had the appropriate areal extent (> 1 cm) and were considered to be durable enough to survive shipping. Emission measurements were made at the Image Visualization and Infrared Spectroscopy (IVIS) Laboratory, at the University of Pittsburgh. The IVIS Nexus 870 spectrometer uses a KBr beamsplitter, and a deuterated triglycerine sulfate (DTGS) detector with a spectral range of 2000 to 400 cm\(^{-1}\) (5.0 – 25.0 µm). Each sample disc was placed onto a round, 3.8 cm copper sample holder that was painted with high emissivity paint to maintain the blackbody environment around the sample. Each holder and sample was then placed into an 80 °C oven for 24 hours, so that the heated sample could serve as the TIR source. Prior to sample analysis, spectra were acquired from two blackbody sources that are precision controlled to 70 °C and 100 °C. Blackbody spectra allow for any instrument and environmental energy to be quantified and removed, as these energy sources can impart unwanted features into emission spectra, as well as lower the signal-to-noise ratio [Ruff et al., 1997]. Following blackbody spectra acquisition, each sample and its sample holder were removed from the oven and placed on a blackbody-painted heating stage. The heating stage maintains a sample temperature of approximately 80 °C. Having a consistent sample temperature that lies within the two blackbody source temperatures is an important factor in attaining accurate emissivity spectra [Ruff et al., 1997]. The entire heating stage/sample holder assembly was then raised into a temperature-controlled blackbody chamber. This chamber eliminates downwelling radiation, and maintains a constant blackbody environment for the sample during spectrum acquisition. Emission spectra were collected of each sample.
over 256 scans, at a spectral resolution of 4 cm$^{-1}$, and averaged. Raw data were then converted to absolute emissivity spectra via Fourier transform, as described in Ruff et al. [1997].

### 2.3.3. Coating thickness and morphology

Coatings were characterized for their thickness and morphology using scanning electron microscopy, optical microscopy, and for continuous coatings, a reflectance TIR technique. A JEOL 5800LV Scanning Electron Microscope (SEM) at the University of New Mexico was used, operating at 15 – 20 kV. To analyze the samples without applying conductive coatings, scans were collected in backscattered electron mode (BSE) in a low vacuum of 40 Pa. Parallax was achieved with a second offset BSE detector. To measure thickness ($x$) in the SEM, the samples were tilted to an angle $\theta$ ($\sim$30 – 50°) and imaged (100 – 400x). The inclined thickness ($x_\theta$) was measured $> 50$ times using ImageJ software. Measurements were made across the edge including the highs and lows in the coating, then thickness was calculated using $x = x_\theta / \sin \theta$. Error was taken to be one standard deviation from the mean of the measurements.

Optical microscope measurements were used to determine the thickness of the coarse particulate halite coatings because the samples were not adhered to the surface so the SEM could not be used. Thickness was measured at 150x by recording the focused height positions of the motorized microscope stage at the top of the coating and at the substrate. Testing this method resulted in a minimum accuracy error of $\pm 3$ µm. Measurements were repeated 2 – 3 times to determine precision errors and the greatest error is reported.
To determine the thickness of the continuous coatings we took advantage of the interference of infrared light through coatings (Figure 1). IR light reflected through continuous coatings may result in periodic waveforms (interference waveforms) in IR spectra [e.g., Swanepoel, 1983; Marquez et al., 1992; Teolis et al., 2007]. At near-normal incidence, an IR beam can reflect at both the air/coating and coating/substrate interfaces. The two reflected beams have different optical path lengths, and are thus shifted out of phase by a length equal to the thickness of the coating. As the wavelength of the incident beam increases, the reflected beams shift in and out of phase, causing an oscillation in the reflected intensity. After the Fourier transform function is applied to the spectrometer data, the oscillating reflectance results in interference waveforms in the IR spectra with maxima at wavelengths where the beams are in phase. The coating’s thickness (x) can be determined from the wavelengths (λ) and real refractive indices (n) at two adjacent maxima (Figure 1) by

\[ x = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \]  

(Eq. 1)  

[Marquez et al., 1992]. Interference waveforms were present in the spectra of all of the samples with continuous coatings provided they were sufficiently thin to transmit IR through the coating. Coating thicknesses were calculated by this method for the halite coatings, as n is relatively constant over the TIR spectrum. This has an advantage over SEM measurements because the thickness is measured at the actual TIR analysis spot.
Figure 1: Schematic of the interference of TIR reflected from a coated surface. (a) TIR reflected at the air/coating interface ($R_1$) has a different optical path length than TIR reflected at the coating/substrate interface ($R_2$). This causes $R_1$ and $R_2$ to be out of phase by the distance $x$ (the thickness of the coating), causing interference in the TIR signal. (b) The interference oscillates as a function of wavenumber, resulting in local maxima in the TIR spectrum when $R_1$ and $R_2$ are in phase. The coating thickness can be calculated with $\lambda$ and $n$ at two adjacent maxima with Eq. 1.

2.3.4. Surface roughness

Surface roughness of the glass substrates was measured with an Alpha Step direct contact stylus profilometer in the Center for High Technology Materials at the University of New Mexico. The instrument detects surface topography variations with a diamond-tipped stylus while a stage moves the sample linearly beneath the stylus on an optically flat reference surface. The vertical resolution of the stylus is better than 10 nm. Measurements were made over a length of 20 mm, recording $1.66 \times 10^4$ data points for a horizontal resolution of 1.20 µm.

The coatings were too fragile to measure roughness with direct contact profilometry. Estimates of the size of surface roughness features were determined by measuring pits and asperities in SEM micrographs with ImageJ software.
To estimate the optical smoothness of the substrates and continuous coatings, roughness values were tested against the Rayleigh criterion [Hapke, 1993]. Using the average angle of incidence of the FTIR spectrometer ($\theta = 25.7^\circ$) and the wavelength ($\lambda$), the vertical deviations of the surface ($h$) below which interference due to phase changes of reflected waves are negligible is $h < \frac{\lambda \sec \theta}{8}$. 
3. RESULTS

3.1. Substrate and coating materials

3.1.1. Glass substrates

All glass substrates were nominally flat, with measured root mean squared variations in surface topography of < 0.380 μm. This roughness value is considered optically smooth using the Rayleigh criterion at wavelengths above 2.8 μm (below 3570 cm$^{-1}$).

We anticipated that the basaltic and albitic glass substrates would have different major spectral bands (see section 2.1). However, the lithium-tetraborate flux significantly affected the structure of the glasses, producing spectral bands in both compositions at ~1365 cm$^{-1}$ and ~975 cm$^{-1}$ and a shoulder at ~775 cm$^{-1}$ (Figure 2a). The lack of basaltic and albitic spectral signatures reflects an increase in more depolymerized Si$_6$O$_{18}^{12-}$ and Si$_2$O$_6^{4-}$ structural units that have bands at 950 cm$^{-1}$ and 980 cm$^{-1}$ respectively [Dalby and King, 2006] that contribute to an overall band at ~975 cm$^{-1}$. The band at ~1365 cm$^{-1}$ is likely due to B-O asymmetric stretching in BO$_3$ [Krogh-Moe, 1965]. Both spectra have a reflectance minimum at 1580 cm$^{-1}$. The albitic glass has higher reflectance over the absorption bands consistent with its lighter color.

The Na-Ca-Si-O glass spectrum has a band at ~1055 cm$^{-1}$ and a shoulder at ~775 cm$^{-1}$ (Figure 2b). A reflectance minimum is apparent at ~1260 cm$^{-1}$. 
Figure 2: Reflectance spectra of (a) uncoated albitic and basaltic Li-tetraborate glass substrates and (b) Na-Ca-Si-O glass substrate.

3.1.2. Halite and calcite endmember coating materials

Reflectance spectra of optically thick reagent grade halite are featureless and have an increasing slightly positive slope toward higher wavenumbers (Figure 3a). The halite particulate (<125 µm) decreases in reflectance over the spectrum due to particle size effects [e.g., Aronson et al., 1966; Hunt and Vincent, 1968; Lane and Christensen, 1998] and roughness [Bennett and Porteus, 1961]. The spectrum of the optically thick pressed calcite reagent has a strong absorption band at ~1485 cm\(^{-1}\) and a sigmoidal band at ~880 cm\(^{-1}\) (Figure 3b). These stronger characteristic calcite absorption bands decrease in contrast in the fine particulate (< 8 µm) spectrum due to particle size effects [e.g., Aronson et al., 1966; Hunt and Vincent, 1968; Mustard and Hays, 1997]. The calcite also
has a reflectance minimum at 1620 cm\(^{-1}\) and absorptions at \(~1795\) and \(~2515\) cm\(^{-1}\). All four absorptions are caused by \(\text{CO}_3^{2-}\) groups [Farmer, 1974]. The unidentified doublet at \(~2925\) cm\(^{-1}\) may be related to contamination.

**Figure 3:** Reflectance spectra of optically thick (a) halite and (b) calcite endmembers. (a) The reflectance of the halite particulate (<125 µm) decreases over the spectrum due to particle size effects and roughness. (b) The calcite absorption bands at \(~1485\) cm\(^{-1}\) and \(~880\) cm\(^{-1}\) decrease in contrast in the calcite fine particulate (<8 µm) spectrum due to particle size effects. The doublet at \(~2925\) cm\(^{-1}\) may be related to unidentified contamination.

### 3.2. Halite coatings

#### 3.2.1. Continuous halite coatings

The continuous halite coatings are flat and laterally continuous layers of salt (Figure 4). The pressed particulates fused to produce coatings that are optically...
transparent and of uniform thickness. Mean coating thicknesses ranged from 12 to 137 µm from SEM measurements and from 19 to 164 µm from interference waveform calculations (Table 1). Non-vertical deviations at the edges of the coatings likely caused additional error in SEM thickness measurements. We conclude that thicknesses calculated from interference waveforms are more accurate than the SEM measurements, and all thickness values discussed further are from the interference method when available. Roughness features on the coating surfaces average to less than ~1 µm in height, as measured in SEM micrographs. By the Rayleigh criterion, roughness at this scale is considered optically smooth at wavelengths greater than 7.2 µm (less than 1387 cm⁻¹). Thus, the roughness of the coatings may affect the band contrast at shorter wavelengths (higher wavenumbers).

Figure 4: SEM micrographs of continuous halite coating wafers with thicknesses of (a) 120 µm and (b) 31 µm. The samples are tilted 30°, showing the edge of the coating.

All continuous halite-coated sample spectra show periodic waveforms due to interference of the infrared through interaction with the salt coating (Figure 5). Interference waveforms are distinguishable from absorption bands by their narrower wavenumber range (< 120 cm⁻¹). The waveforms are also superimposed on the absorption bands. In some cases, an air gap between the coating and substrate caused a second
interference waveform. The reflectance of the bands at ~1365 cm\(^{-1}\) and ~975 cm\(^{-1}\) decreases as the thickness of the coating increases. At the glass reflectance minimum at 1580 cm\(^{-1}\), the halite coating causes an increase in reflectance from 0% to as much as 6%, although the values do not systematically correlate with thickness.

Figure 5: Offset reflectance spectra of continuous halite coatings on a basaltic Lithetaborate glass substrate with mean coating thicknesses above each spectrum. The % reflectance of the ~1365 and ~975 cm\(^{-1}\) features (vertical lines) decreases with increasing coating thickness. Absolute reflectance at the minimum at 1580 cm\(^{-1}\) is shown next to the vertical dashed line, showing higher reflectance at that feature with the addition of a halite coating.
Table 1: Summary of results for the halite-coated samples. Basaltic Li-tetraborate glass substrates were used (exceptions are indicated). See text for explanations of the errors.

<table>
<thead>
<tr>
<th>Coating texture</th>
<th>Sample name</th>
<th>SEM mean thickness (µm)</th>
<th>Interference thickness (µm)</th>
<th>OLM thickness (µm)</th>
<th>Areal coverage of coating (%)</th>
<th>Calculated substrate fraction $\beta$ (Eq. 4)</th>
<th>Calculated substrate fraction $\alpha_{97.5}$ (Eq. 3)</th>
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<td>a6$^*$</td>
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<td>0.81 ± 0.02</td>
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</tr>
</tbody>
</table>

$^*$A second interference waveform in the spectra of these continuously coated samples indicates that an air gap < ~3 µm was present between the coating and substrate. This gap did not measurably affect thickness measurements or the calculation of $\beta$.

$^2$Albitic Li-tetraborate substrate.
3.2.2. Coarse particulate halite coatings

The coarse particulate halite coating consists of scattered aggregates of subhedral to anhedral halite particles < 125 µm in diameter. The cubic habit dominant in the NaCl reagent was likely diminished due to the dry grinding and sieving process used to form the < 125 µm particulate. SEM thickness measurements were not possible because the dry coating process did not adhere the halite to the substrate. Thus, only optical light microscope thickness measurements were feasible (Table 1). Uncoated exposures of the substrate were present in the TIR field of view, and the areal coverage of the coating was estimated from optical light images of the TIR spot (Table 1).

TIR measurements of coarse particulate halite coatings were collected for coating thicknesses of 4 to 94 µm. Aggregates of smaller particles < 50 µm were targeted for TIR measurements because larger halite grains > 100 µm occur in aggregate with finer particles and clinging fines, yielding flat reflectance spectra indicative of optically thick coverage and/or particle size effects. Reflectance spectra of the coarse particulate halite coatings show a trend toward decreasing glass band contrast at ~1365 and ~975 cm\(^{-1}\) with increasing coating thickness (Figure 6). Spectra also flatten and decrease in reflectance over higher wavenumbers as coating thicknesses increase. There is a larger decrease in the reflectance value for the substrate absorption features than for the featureless parts of the spectrum. The three thickest coatings do not follow this trend closely; the 85 µm thick coating has lower reflectance than the 94 µm thick coating. The glass reflectance minimum at 1580 cm\(^{-1}\) increases with increasing coating thickness.
Figure 6: Reflectance spectra of coarse particulate halite-coated basaltic Li-tetraborate glass, with the mean thickness of the coating in the legend. The % reflectance of the ~1365 and ~975 cm\(^{-1}\) features (vertical lines) decreases with increasing coating thickness. Spectra also flatten and decrease in reflectance over higher wavenumbers. The glass reflectance minimum at 1580 cm\(^{-1}\) (vertical dashed line) increases in reflectance with increasing halite coverage.

3.2.3. Fine particulate halite coatings

The fine particulate halite coatings consist of very fine-grained, cryptocrystalline halite particles with a size fraction < 2 µm distributed uniformly over the glass surfaces (Figure 7). Halite particles formed low-density aggregates and “fairy castles” that increasingly aggregated into thicker hummocky topography as more material was deposited (Table 1). The coating is cohesive and adhered to the substrate such that it is not disturbed by movement. The substrate is partially exposed in patches through the thinner discontinuous coatings, while the substrate is exposed through thicker coatings only in small, scattered holes. For all samples, the exposed substrate has a dusting of fine halite particles.
The reflectance of the fine particulate halite-coated glass samples decreases across the full spectrum as the thickness of the coating increases (Figure 8). There is a larger decrease in the reflectance value for the substrate absorption features than for the featureless parts of the spectrum. The reflectance minimum at 1580 cm\(^{-1}\) is essentially constant (~0\%) with increasing coating thickness. Two spectra (8 µm and 21 µm coatings) do not preserve the same relative band heights at ~1365 and ~975 cm\(^{-1}\) as seen in the other spectra (Figure 8a).

![SEM micrographs of fine particulate halite coatings](image)

**Figure 7:** SEM micrographs of fine particulate halite coatings that are (a, b) ~8 µm thick and (c, d) ~94 µm thick. Arrows indicate the halite coating and glass substrate. The glass substrate is partially exposed beneath the thinner, lighter-toned coatings (a, b), while the thicker coating has no exposed glass (c, d). The edges of the coatings are shown in (a) and (c), which are tilted 40° and 52°, respectively.
Figure 8: Reflectance spectra of fine particulate halite-coated (a) albitic and (b) basaltic Li-tetraborate glasses. Reflectance at the ~1365 and ~975 cm$^{-1}$ features (vertical lines) and for the gentle rise out to higher wavenumbers decreases as mean coating thickness increases. The reflectance minimum at 1580 cm$^{-1}$ (dashed vertical line) remains constant with $R \approx 0\%$ for all spectra. Mean coating thicknesses are given in the legends.

Emission spectra of the fine particulate halite-coated glasses have absorption bands at ~975 cm$^{-1}$ and ~1365 cm$^{-1}$ and an emissivity maximum at ~1580 cm$^{-1}$ (Figure 9). These correspond with the positions of the features seen in reflectance (Figure 8). The thickest two halite coatings cause a greater decrease in the absorption band contrast than the thinner coatings. As the thickness of fine particulate coatings increases, the emissivity tends to increase over the absorption bands at ~1365 cm$^{-1}$ and ~975 cm$^{-1}$, consistent with the reflectance data. Compared to reflectance, however, the relationship between decreasing band contrast and increasing coating thickness is less clear. The emissivity...
maximum at ~1580 cm\(^{-1}\) does not change with increasing coating thickness except for one spectrum, which decreases in emissivity (96 µm coating).

![Figure 9: Representative TIR emission spectra of fine particulate halite-coated albitic Li-tetraborate glasses, with mean coating thicknesses in the legend. Absorption bands at ~1365 cm\(^{-1}\) and ~975 cm\(^{-1}\) (vertical lines) and an emissivity maximum at ~1580 cm\(^{-1}\) (dashed vertical line) correspond with the positions of the features in reflectance (Figure 8). The thickest two halite coatings cause a greater decrease in the absorption band contrast than the thinner coatings.](image)

3.3. Calcite coatings

3.3.1. Continuous calcite coatings

The continuous calcite coatings are very tightly packed and uniformly thick (Figure 10a). Coating thicknesses ranged from ~5 to 273 µm (Table 2). All coatings had roughness features < 2.5 µm in height, which fails the Rayleigh criterion for smoothness over the TIR spectrum and may cause drops in band contrast.
Figure 10: SEM micrographs of (a) a continuous calcite coating tilted up 50° showing the edge of the coating and (b) the fine particulate calcite-coated sample.

Table 2: Summary of results for the calcite coatings on Na-Ca-Si-O glass. See text for explanations of the errors. Calculation of $\alpha$ and $\beta$ was not possible for the continuous calcite coatings due to interference waveforms.

<table>
<thead>
<tr>
<th>Coating texture</th>
<th>Sample name</th>
<th>SEM mean thickness (µm)</th>
<th>Areal coverage of coating (%)</th>
<th>Calculated substrate fraction $\beta$ (Eq. 4)</th>
<th>Calculated substrate fraction $\alpha_{1055}$ (Eq. 3)</th>
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The TIR reflectance spectra of the continuous calcite-coated samples (Figure 11) have absorption bands at $\sim$1485 cm$^{-1}$ and $\sim$880 cm$^{-1}$ that correspond to the bands of the optically thick calcite (Figure 3b). The calcite band at $\sim$1485 cm$^{-1}$ increases in overall reflectance and changes shape with decreasing coating thickness. When calcite coatings are $< 141$ µm, interference waveforms are apparent in the spectra in the vicinity of the Na-Ca-Si-O glass absorption band at $\sim$1055 cm$^{-1}$ and shoulder at 775 cm$^{-1}$. These
waveforms increase in amplitude and wavelength with decreasing coating thickness. Interference waveforms are not evident with the 141 and 273 \( \mu m \) coatings.

**Figure 11**: Representative offset reflectance spectra of continuous calcite coatings on Na-Ca-Si-O glass, with mean coating thicknesses above each spectrum. The calcite band (~1485 \( cm^{-1} \)) and shoulder (~1415 \( cm^{-1} \)) increase in overall reflectance and change shape with decreasing coating thickness. When calcite coatings are < 141 \( \mu m \), interference waveforms are apparent in the spectra in the vicinity of the glass absorption band at ~1055 \( cm^{-1} \) and shoulder at ~775 \( cm^{-1} \).

### 3.3.2. Fine particulate calcite coatings

Evaporating the mixture of calcite reagent and deionized water on the glass substrates resulted in thin layers of < 8 \( \mu m \) particulates of euhedral to subhedral calcite rhombohedra (Figure 10b). The coatings adhered to the glass. Two coatings were prepared by this method; one was generally thinner (calev1) than the other (calev2).
Within the two samples, a small range of coating thicknesses (~5-18 µm) was observed (Table 2). However, due to error, only two overall thicknesses are distinguishable: 1) two coatings ~17 µm thick and 2) all other coatings ~5 to 9 µm thick. The thinnest coatings consisted of one layer of the particulate, while thicker coatings had about two to four layers of particulate in aggregates.

Possible relationships between fine particulate calcite coating thickness and the intensity of the Na-Ca-Si-O glass absorption band (~1055 cm\(^{-1}\)) were not resolvable due to error in the coating thickness (Figure 12). However, the band decreases predictably in intensity with increasing areal coverage of the coating. As areal coverage increases, spectral features of calcite particulate (< 8 µm; Figure 3b) dominate the spectra.

![Figure 12: Representative reflectance spectra of fine particulate calcite coatings on Na-Ca-Si-O glass, with mean thickness (and areal coating % coverage) in the legend. The calcite TIR absorption band at ~1485 cm\(^{-1}\) is attenuated here due to particle size effects. The intensities of the Na-Ca-Si-O glass absorption band (~1055 cm\(^{-1}\)) and shoulder (~775 cm\(^{-1}\)) change unpredictably as coating thickness increases, but decrease with increasing areal coverage of the coating.](image-url)
4. DISCUSSION

Our results successfully show that salt coatings have a major role in changing the TIR signal of coated material. Furthermore, we showed that different textures result in distinct spectral properties linked mainly to particle size and partially exposed substrate. In this section, we expand on previous theoretical TIR models of layered materials to examine the spectral properties of halite and calcite coatings. We then apply these models to our results to better understand 1) the effects of coating thickness and composition on transmission of the substrate TIR signal; 2) the influence of exposed substrate on TIR spectra; and 3) how the spectral mixing of the coating and substrate might differ from a linear model. Finally, we discuss our findings in terms of remote sensing applications for exploring Mars.

4.1. Models for understanding coatings

To provide a basis for understanding our laboratory spectra (and by extension remote sensing data), we now examine theoretical spectral fitting methods. First, we build on previous theoretical models [Christensen and Harrison, 1993; Ramsey and Christensen, 1998] that are constrained by knowing the endmember spectral features. Then we present a new model that only relies on knowing the substrate spectral features and uses an iterative approach to calculate the coating and other features. These two models provide a spectral measure for calculating the relative contribution of the substrate to the spectrum of a coated sample, referred to here as the ‘substrate fraction.’ Knowing the substrate fraction, we assess the spectral mixing of the substrate and coating with respect to coating thickness and texture. The substrate fraction also allows the generation of model spectra to test linear spectral mixing models.
4.1.1. Theoretical model based on linear endmember spectral mixing (α model)

Linear models are typically not applied to layered materials because radiative transfer models are often more appropriate [e.g., Hapke, 1993; Smith et al., 2000]. Linear models [e.g., Ramsey and Christensen, 1998] used to determine mineral abundances from remotely sensed TIR spectra of Mars [e.g., Bandfield et al., 2000; Christensen et al., 2000; Hamilton et al., 2003] must assume a minimal contribution from layered phases (e.g., coatings are assumed to be optically thick). Our results confirm that partially transmissive coatings have significant effects on TIR spectra, and interpretations of remotely sensed spectra will benefit from refined assumptions about coatings. For this reason, we test a linear spectral mixing model to assess the implications of incorrectly assuming that salt coating effects are minimal.

An emissivity model of coatings, previously applied to desert varnish by Christensen and Harrison [1993], was investigated to constrain the effects of coatings on reflectance spectra. The model describes the emissivity of a salt-coated substrate by the linear function

\[ \epsilon_{\text{sample}} = \alpha \epsilon_{\text{substrate}} + (1 - \alpha) \epsilon_{\text{salt}} \]  \hspace{1cm} (Eq. 2)

where \( \epsilon_{\text{sample}} \) is the emissivity of the coated sample, \( \epsilon_{\text{substrate}} \) is the emissivity of the substrate, \( \epsilon_{\text{salt}} \) is the emissivity of the coating, and \( \alpha \) is the fraction of substrate emissivity in the sample spectrum [Christensen and Harrison, 1993]. We adapted the model to reflection spectroscopy by substituting emissivity (\( \epsilon \)) for reflectance (\( R \)) according to Kirchhoff’s law: \( \epsilon = 1 - R \) [Hapke, 1993]. The ‘substrate fraction’ (\( \alpha \)) can be used to evaluate how the coated sample reflectance (\( R_{\text{sample}} \)) may be a linear mixture of the substrate reflectance (\( R_{\text{substrate}} \)) and the salt reflectance (\( R_{\text{salt}} \), according to
\[ R_{sample} = aR_{substrate} + (1 - a)R_{salt}. \]  \hspace{1cm} (Eq. 3)

We note that reflectance processes involve the IR light traveling through the coating twice, while emission processes only involve one pathway through the coating; strictly speaking, \( a \) in Eq. 3 would be halved to account for the doubling of distance through the coating. However, the form of the equation is similar to Eq. 2 and we use \( a \) in favor of simplicity.

Values for \( a \) were calculated using the measured sample reflectance for \( R_{sample} \) and the appropriate endmembers for \( R_{substrate} \) (Figure 2) and \( R_{salt} \) (Figure 3). The substrate fraction \( a \) can be calculated for every channel in the spectrum, but this procedure was most informative when \( a \) was determined at the largest substrate absorption bands: \(~975\text{ cm}^{-1}\) for Li-tetraborate glass (\( a_{975} \)) and \(~1055\text{ cm}^{-1}\) for Na-Ca-Si-O glass (\( a_{1055} \)).

When multiple spectra were collected for one sample, \( a \) was determined for all spectra and one standard deviation for those values is reported as error. Fitting the model to the substrate bands was highly uncertain when interference waveforms appeared in the spectra, and \( a \) was not calculated for these samples.

4.1.2. Theoretical model based on linear spectral mixing of an endmember + unknown (\( \beta \) model)

A second method for calculating the substrate fraction uses the factor \( \beta \) and another form of Eq. 3:

\[ R_{sample} = \beta R_{substrate} + R_{salt+other}. \]  \hspace{1cm} (Eq. 4)

Determining the substrate fraction with Eq. 4 requires iterations of \( \beta \) because \( R_{salt+other} \) is not known. With the measured \( R_{sample} \) and endmember \( R_{substrate} \), a module in the OMNIC
FTIR microscope software enables the determination of $\beta$ with Eq. 4 using a graphical interface that allows the user to adjust $\beta$ values. If 100% of the spectral contribution of the substrate can be removed from $R_{\text{sample}}$ by a certain value of $\beta$, then $R_{\text{salt+other}}$ is the sum of the spectral features not attributable to the substrate. This includes a fraction of $R_{\text{salt}}$, interference waveforms, and other features that may be in $R_{\text{sample}}$ (e.g., related to roughness). The method was verified using spectra without interference waveforms, and values for $\alpha$ and $\beta$ were, in most cases, within error (Tables 1, 2). Comparing the $\alpha$ and $\beta$ values provides a test for the validity of the $R_{\text{salt}}$ endmember selected for the $\alpha$ model: if the values are the same, then $(1 - \alpha)R_{\text{salt}} = R_{\text{salt+other}} \pm \text{error}$.

4.1.3. Theoretical model based on radiative transfer theory

Another model for layered materials [Schanda, 1986; Christensen and Harrison, 1993] incorporates radiative transfer theory, which states that radiance propagating through an absorbing medium will attenuate by the factor $e^{-4\pi k x/\lambda}$, where $k$ is the imaginary part of the complex refractive index ($k$ describes absorption), $x$ is the distance traveled in the medium, and $\lambda$ is the wavelength [Hapke, 1993]. Converted to reflectance with Kirchhoff’s law, the model is

$$R_{\text{sample}} = e^{-8\pi k x/\lambda} R_{\text{substrate}} + (1 - e^{-8\pi k x/\lambda}) R_{\text{salt}}.$$  \hspace{1cm} (Eq. 5)

Note that the exponent contains the factor 8 in reflectance (rather than 4 in emission and transmission) because the radiation propagates through the coating material twice.

For this study, simplification of the radiative transfer model (Eq. 5) was necessary. The attenuation of TIR by a coating can be predicted if $k$ and $\lambda$ are known. However, the precise determination of $k$ was impractical with our rough/particulate
samples because in reflectance, $k$ must be estimated knowing all of the scattering components [Hapke, 1993], which varied due to microscale features. Modeling the continuous coatings was also impractical due to interference waveforms. Despite that, our results can be qualitatively compared to the model. The factor $e^{-8\pi k x / \lambda}$ in Eq. 5 has the same mathematical relationship to $R_{\text{sample}}$, $R_{\text{substrate}}$ and $R_{\text{salt}}$ as the factor $\alpha$ in Eq. 3, so it is also the ‘substrate fraction.’ We can then compare our results to the radiative transfer model using values of $\alpha$ (and the equivalent $\beta$) [cf. Christensen and Harrison, 1993]. Specifically, Eq. 5 predicts that, as the coating thickness ($x$) increases, the substrate fraction $\alpha$ and $\beta$ will decrease exponentially.

4.2. Coating thickness and substrate fraction

Changes in the substrate fraction as a function of coating thickness illustrate the spectral mixing models described above [Christensen and Harrison, 1993]. If increasing the coating thickness decreases the substrate fraction linearly, the linear mixing model (Eq. 3) may be more appropriate to describe the spectral mixing. According to the radiative transfer model (Eq. 5), an increase in coating thickness ($x$) will decrease the substrate fraction exponentially. $\beta$ values are shown below because it was not possible to calculate $\alpha$ for all samples.

The continuous halite coatings show an exponential decrease in $\beta$ with increasing coating thickness (Figure 13a). The coarse particulate halite coating follows a similar exponential behavior (Figure 13b). For these two coating textures, the radiative transfer model (Eq. 5) would likely be more appropriate to describe the mixing of the coating and substrate spectra than the linear mixing model (Eq. 3).
The fine particulate halite coatings display spectral properties that are distinct from the continuous and coarse particulate halite coatings. Thicker coatings of the fine particulate result in reflectance spectra that are lower than both the glass and halite endmembers, indicating that halite is an inappropriate endmember (Figure 8). As demonstrated in other studies, fine particles coating a surface cause a drop in reflectance that approaches a blackbody spectrum, where $R = 0\%$ at all wavelengths [Crisp and Bartholomew, 1992; Johnson et al., 2002]. Following this, a synthetic blackbody spectrum was used as the coating endmember to calculate $\alpha$. The good correlation of the resulting $\alpha$ with $\beta$ (which is calculated without knowing $R$ of the coating) is evidence that the blackbody spectrum is a more appropriate coating endmember than halite for these fine particulate coatings. As the thickness of the fine particulate halite coatings increases, the fraction of the glass substrate in the spectra decreases linearly (Figure 13c). The linear relationship between substrate fraction and coating thickness suggests that Eq. 3 is a more appropriate model than Eq. 5 and that the fine particulate halite coating spectra are linear mixtures of blackbody and glass.

A similar trend is apparent in the emission spectra, but the same thickness reduces the substrate fraction by about half the amount seen in reflectance (Figure 13c). This difference is consistent with the fact that reflected TIR transmits through the coating twice, while emitted TIR transmits through the coating once. Compared to reflectance, the linear relationship between substrate fraction and increasing coating thickness is less certain. The emission spectroscopic method may be less sensitive to small differences in coating thickness. Or, the larger field of view on the emission spectrometer (~1 x 1 cm)
may have included small variations in thickness or a different amount of exposed substrate not seen in the reflection spectrometer field of view.

Unlike the halite coatings, the fine particulate calcite coatings do not have a clear functional relationship between substrate fraction and coating thickness (Figure 14). $\alpha$ values (Table 2) were calculated using the fine particulate calcite endmember (Figure 3b). The agreement of $\beta$ values with these $\alpha$ values supports the use of the fine particulate calcite endmember for the model. It is notable that the calcite fine particulate ($< 8 \, \mu m$) does not have a blackbody spectrum, while the halite fine particulate ($< 2 \, \mu m$) has blackbody spectral properties.
Figure 13: Substrate fraction ($\beta$ for reflectance, $\alpha$ for emissivity in c) as a function of halite coating thickness. (a) Continuous and (b) coarse particulate halite coatings cause a nonlinear decrease and (c) fine particulate halite coatings cause a linear decrease in the substrate fraction as coating thickness increases. Because reflected TIR transmits through the coating twice, $\beta$ values for reflectance are \sim half the $\alpha$ values for emitted radiance, which transmits through the coating once (c). Open symbols in (a) designate samples that had a < 3 $\mu$m air gap between the coating and substrate. Best-fit linear regression lines are shown with equations.
4.3. Considerations for exposed substrate

4.3.1. Relationship between coating coverage and exposed substrate area

The areal coverage of a coating is an important but complex consideration for TIR studies of coatings. As coatings grow and increase in thickness, the area of coverage usually increases. This is a feature in common with natural coatings and is shown in previous work on spectral features of coatings [Crisp and Bartholomew, 1992; Johnson et al., 2002]. Spallation of the coating, however, can act against this trend [Christensen and Harrison, 1993]. Particle size and differences areal distribution due to coating deposition processes are also factors. For example, a thin coating of fine, evenly distributed particles can obscure the TIR signal from a substrate more than a thick, patchy coating [e.g., Christensen and Harrison, 1993; Crisp and Bartholomew, 1992; Crisp et al., 1990; Johnson et al., 2002]. We see an example in this study with the coarse particulate halite coatings, where an ~85 µm thick coating with 100% coverage attenuates the substrate absorption bands more than a ~94 µm thick coating with 68% coverage (Table 1, Figure
Although we did measure areal coverage of the coatings in this study (Table 1, 2), we did not control for all areal factors in most samples. Instead, we examined this effect in select samples where both area and thickness were controlled (section 4.3.2). The results of analyses of these samples allow us to make some qualitative conclusions about the effect of exposed substrate on TIR spectra.

4.3.2. Role of exposed substrate on TIR signal of coatings

Optical microscope images of TIR spots were used to determine areal coverage of halite and calcite coatings. Images of TIR spots were cropped to the aperture size and the coating and substrate were separated into a binary image from which a histogram was used to calculate the areal coating coverage. Dispersion and other effects at the edges of the aperture and the edges of the coating material introduce error that was not quantified here. However, this error should be similar for all TIR measurements within each sample set, so relative spectral behaviors are not likely to be significantly impacted. Fine particulate halite coating coverage was determined from SEM micrographs and the coverage at the TIR spot was not measured.

Continuous halite coatings

Natural continuous coatings are likely to occur in areas separated by substrate (patches). To investigate the effects of having exposed substrate within the same field of view as the continuous coatings, we placed a 42 ± 2 μm thick continuous wafer on the basaltic Li-tetraborate glass substrate. Multiple analyses were made at the edge of the coating. For each measurement, the sample was moved so that the edge of the coating moved through the TIR field of view, exposing a progressively greater area of substrate. This achieved a range of areal coverages (Table 1).
TIR measurements of the continuous halite-coated sample show spectral changes as areal coverage is progressively decreased (Figure 15). Note that the reflectance of the uncoated basaltic Li-tetraborate glass is 28% less than the uncoated endmember (Figure 2a) because the TIR spot was focused on the top of the coating, causing a drop in the substrate TIR signal. As with the continuous halite coatings, due to the interference waveforms, the substrate fraction was estimated by Eq. 4 to find $\beta$ (Table 1). $\beta$ decreases exponentially as the areal coverage of the coating increases up to ~50%, then increases exponentially as the coating coverage continues to decrease to 0% (Figure 16). Exponential least squares fitting yields higher $R^2$ values, however, linear fits cannot be ruled out. The reflectance minimum at 1580 cm$^{-1}$ is also affected, increasing in reflectance with increasing coating coverage (see section 4.5). The dip in total reflectance at 50% is likely due to shadowing and/or dispersion at the edge of the coating. Orienting the edge of the coating horizontally, vertically, and diagonally in the square TIR field of view resulted in the same dip in reflectance.

Spectral differences introduced by both exposed substrate and vertical relief (roughness) at the edge of the coating underline the importance of texture in the study of the TIR properties of coatings. Of particular importance to finding chlorides with remote sensing techniques is the decreasing reflectance minimum at 1580 cm$^{-1}$ with the addition of exposed substrate (see section 4.5). Figure 15 also demonstrates that interference waveforms occur with ~31 to 100% coating coverage. “Patchy” discontinuous coatings are more likely than continuous coatings in the meter- to kilometer-wide fields of view in remote sensing. Our results show that a thin, uniformly thick coating has the potential to cause interference in TIR spectra when the coating is patchy.
Figure 15: Reflectance spectra of a ~42 µm thick patchy halite coating on basaltic Li-tetraborate glass with the areal coating coverage in the legend. (a) The spectra display interference waveforms and decrease in reflectance at ~1365 and 975 cm\(^{-1}\) with decreasing coating coverage. (b) The reflectance increases again as the coating coverage drops below ~50%. The reflectance minimum at 1580 cm\(^{-1}\) increases with increasing coating coverage.

Figure 16: Substrate fraction (\(\beta\)) versus areal coverage of the 42 µm thick continuous halite coating. Equations for two lines fit by linear regression are shown.
**Fine particulate calcite coatings**

For the fine particulate calcite coatings, exposed substrate is the source of glass spectral features, which decrease linearly as a function of areal coverage of the coating (Figure 17) and not as a function of thickness (Figure 14). Coatings ~5 to 9 µm thick attenuate the glass band at ~1055 cm\(^{-1}\) by 99% when the areal coverage is ~100%, indicating that the coating is optically thick. Increasing the area of the coating decreases the substrate fraction linearly. This behavior is in agreement with the linear spectral mixing model (Eq. 3).

![Figure 17: Substrate fraction (β) as a function of fine particulate calcite coating areal coverage. The calcite fine particulate behaves as if optically thick, and variation in substrate fraction is thus due primarily to exposed substrate, which mixes linearly with the calcite. Depression below the 1:1 line may be due to shadowing of the substrate at the coating edges.](image)

4.4. **Linear spectral mixing model applied to coatings**

Under many conditions, the TIR spectrum of a geologic sample is a linear mixture of the spectra of mineral endmembers in the sample [Ramsey and Christensen, 1998]. The spectral mixing is in proportion to areal abundance, which can be extended to modal abundance [Ramsey and Christensen, 1998]. These assumptions are the basis for analyses
of TIR spectra in remote sensing applications [e.g., Bandfield et al., 2000; Christensen et al., 2000; Hamilton et al., 2003]. While layered materials are generally treated with radiative transfer models (e.g., Eq. 5 and section 4.2) [Hapke, 1993], we believe it is useful to test our results against the linear mixing model because it is commonly used to investigate remotely sensed spectra after subtraction of atmospheric components [e.g., Smith et al., 2000]. Furthermore, as our results for rough coatings show that $k$ may vary in a complex manner making it challenging to appropriately apply radiative transfer models.

In this section, we use the two-endmember linear mixing model (Eq. 3) adapted from an emissivity model [Christensen and Harrison, 1993; Ramsey and Christensen, 1998] to model the reflectance spectra of salt-coated glasses. Model spectra were calculated using the closest fitting endmembers (Figures 2, 3) and $\beta$ values (Tables 1, 2).

4.4.1. Linear spectral mixing model for continuous coatings

We attempted fitting the linear spectral mixing model (Eq. 3) to the spectra of the continuous halite-coated samples (Figure 18). Testing the fit of the model to the measured spectra is complicated by the interference waveforms in the spectra. However, an interference-free curve can be approximated as the curve that passes through the inflection points of the waveforms [Swanepoel, 1983; Marquez et al., 1992]. Error could not be quantified with this method; we considered a good fit to be a model curve that was within 2-5% reflectance of the interference-free curve. The halite particulate endmember was used because it provided a closer fit to the data than the smooth halite endmember (Figure 3a). The fit of modeled spectra of thinner coatings is difficult to evaluate due to interference waveforms. For the thicker coatings, the model fits the shape of the
measured spectra but deviates from the spectral slope. Overall, the model underestimates the reflectance minimum ($R_{\text{min}}$) at 1580 cm$^{-1}$ and overestimates the slope at higher wavenumbers. $R_{\text{min}}$ will be discussed further in section 4.5.

The poor fitting to the continuous halite coating spectra is likely due to the simplicity of the linear model. As indicated by the exponential drop in substrate fraction with increasing thickness (Figure 13a), the radiative transfer model (Eq. 5) is more appropriate (but again, very challenging to apply especially in a remote sensing situation). In addition, the glass substrate endmember spectrum was measured in air ($n = 1$), but the actual reflectance from the coated glass surface was at an interface with halite ($n = 1.4 – 1.5$), which will result in a small difference in reflectance. These wavelength-dependent factors are not negligible, as evidenced by the poor fit of the linear model.
Figure 18: Linear spectral mixing models of continuous halite coatings using basaltic Lithetaborate glass and halite particulate endmembers. Reflectance at $1580\ \text{cm}^{-1}$ is underestimated for thinner coatings and the slope at higher wavenumbers fits poorly with the measured spectra.

Although the linear spectral mixing model was not applied to the continuous calcite coatings due to interference waveforms (preventing the calculation of $\alpha$ and $\beta$), it is clear that the calcite and glass spectra do not mix linearly. As the coating thickness decreases, the calcite absorption band does not decrease (Figure 11). This conflicts directly with the linear mixing model, which predicts that the calcite bands will decrease by the factor $(1 - \alpha)$, approaching the low reflectance of the glass substrate at $\sim1485\ \text{cm}^{-1}$. Optical thickness and its wavelength dependence are important factors in this non-linear mixing. A coating’s “optical thickness” is the thinnest length a coating can be without transmitting TIR from the substrate. In wavenumber regions where a coating absorbs
TIR, optical thickness is lower than flat, transmissive regions \cite{Crisp1990}, causing spectral mixing of the substrate and coating to vary over the spectrum \cite{Hapke1993}. The strong reflectance of the thinnest calcite coatings at \( \sim 1485 \text{ cm}^{-1} \) suggests that the coating is optically thick in this wavenumber region with coatings as thin as \( \sim 5 \mu\text{m} \). The increase in reflectance and appearance of interference waveforms at \( \sim 1055 \text{ cm}^{-1} \) is evidence that TIR reflected from the glass substrate is transmitting through the calcite coatings \( < 141 \mu\text{m} \) thick in this lower wavenumber region. These observations are consistent with variations in optical thickness over the spectrum \cite[cf.]{Crisp1990}. The relative contributions of the calcite coating and glass substrate to the spectrum will thus vary nonlinearly as a function of wavelength, yielding spectra the linear mixing model cannot describe.

### 4.4.2. Linear spectral mixing model for coarse particulate coatings

Most of the spectral features of the coarse particulate halite-coated glasses are modeled well by the linear mixing model (Figure 19). The halite particulate endmember provided the best fit. In all cases, the relative peak heights (\( \sim 1365 \) and \( \sim 975 \text{ cm}^{-1} \)) are preserved and \( R_{\text{min}} \) at 1580 \text{ cm}^{-1} \) is close to the measured reflectance. With greater thickness, the slope of the model deviates from the measured spectra at higher wavenumbers.

Spectra of thinner coarse particulate halite coatings fit the linear mixing model, but the exponential decrease in substrate fraction as thickness increases (Figure 13b) also agrees with the nonlinear radiative transfer model. As seen with the addition of exposed substrate to a continuous coating (section 4.3.2), substrate exposed through the coarse particulate diminishes the nonlinear, wavelength-dependent effects of the halite coating.
(e.g., high $R_{\text{min}}$ at low thickness, attenuated reflectance at higher wavenumbers). As the thickness of the coarse particulate increases, the areal coverage increases and the nonlinear spectral properties of the coating become increasingly apparent as the model deviates over the higher wavenumbers. Overall, the observed spectra show the combined effects of reflection of TIR off exposed glass and coated glass, with the relative spectral contributions changing as a function of both coating thickness and areal coverage.

Figure 19: Linear spectral mixing models of coarse particulate halite coatings using basaltic Li-tetraborate glass and particulate halite endmembers. The model was calculated with the substrate fraction $\beta$. The linear model fits the spectral shape well at all thicknesses, but thicker coatings cause a deviation in slope at higher wavenumbers.
4.4.3. Linear spectral mixing model for fine particulate coatings

*Fine particulate halite coatings*

The fine particulate halite coatings were modeled using a glass substrate mixed with particulate halite and synthetic blackbody endmembers (Figure 20). Relative to the halite endmember model, the blackbody endmember model fits the measured spectra better and more consistently at different thicknesses. Unlike the halite endmember model, the blackbody endmember model accurately predicts the observed near-zero reflectance at the $R_{\text{min}}$ at 1580 cm$^{-1}$ (see section 4.5). Both models differ from the measured spectra over the glass bands, which do not maintain proportional peak heights at ~1365 and ~975 cm$^{-1}$. In addition, the models display higher reflectance at higher wavenumbers, although this effect is less pronounced in the blackbody endmember model.

As discussed in section 4.2, the fine particulate halite coatings exhibit blackbody spectral properties that are also evident, with exceptions, in the linear spectral mixing model. Due primarily to particle size effects, the fine particulate halite coating has lower reflectance than the coarse particulate halite coating [cf. Lane and Christensen, 1998] and lowers the reflectance of the substrate [Crisp and Bartholomew, 1992; Johnson et al., 2002]. Differences between the modeled and measured spectra are similar to those seen in the continuous and coarse particulate halite coatings (e.g., different slope at higher wavenumbers) and indicate non-linear spectral mixing.
Figure 20: Linear spectral mixing models of fine particulate halite coatings using basaltic Li-tetraborate glass with particulate halite (hal) and simulated blackbody (bb) endmembers. The blackbody endmember yields a better fit, however, relative peak heights at ~1365 and ~975 cm\(^{-1}\) are not preserved and the slope at higher wavenumbers does not fit well for thinner coatings. The reflectance minimum at 1580 cm\(^{-1}\) is well-modeled by the blackbody endmember and not the particulate halite endmember.

Fine particulate calcite coatings

Applied to the fine particulate calcite coatings, the linear spectral mixing model yields a good fit for all spectra (Figure 21). The fine particulate calcite was used as the coating endmember. No differences between the modeled and measured spectra clearly result from increases in coating thickness.

We proposed in section 4.3.2. that the increase in the strength of substrate spectral features (e.g., band at ~1055 cm\(^{-1}\)) were attributable to decreases in the coating areal coverage rather than decreases in coating thickness. We also proposed that this was
evidence that the coating was optically thick. In theory, an optically thick coating will closely follow a linear mixing model, where the areal coverage of the coating is proportional to the fraction of coating in the spectrum \((1 - \alpha)\) \cite{Christensen and Harrison, 1993}. The close fit of the linear mixing model supports (but does not confirm) the hypothesis that the fine particulate calcite coating is optically thick. In cases where the endmember spectra are known, and the presence of an optically thick coating is recognized, the areal coverage of the coating may be modeled.

Figure 21: Linear spectral mixing models of fine particulate calcite coatings using Na-Ca-Si-O glass and fine particulate calcite endmembers. The good fit of the model to the measured spectra indicates linear spectral mixing, which is evidence that the calcite coating is effectively optically thick at thicknesses as low as \(\sim 5\mu m\).
4.5. Effect of halite coatings on the reflectance minimum

Reflectance minima ($R_{\text{min}}$) are a useful spectral feature for determining the TIR properties of a sample and for identifying unknown phases [Hapke, 1993]. These features are caused by the Christiansen effect, where the index of refraction $n$ of the surrounding medium is equal to $n$ of the sample, resulting in zero reflectance and unit emissivity [Hapke, 1993]. Because the flat TIR spectra of chlorides have a reflectance of $\sim 4 \text{ – } 10\%$ and no distinct $R_{\text{min}}$ (Figure 3a), the principle of linear spectral mixing predicts that the addition of halite to a sample will increase reflectance where minima may occur in the sample. Our results show that the addition of a halite coating can increase reflectance at the substrate’s $R_{\text{min}}$, however, particle size effects are an important consideration.

Continuous halite coatings increase reflectance of the substrate at $R_{\text{min}}$, but without a clear correlation with coating thickness (Figure 22a). Absolute reflectance values could not be determined reliably for all continuously coated samples at $R_{\text{min}}$ due to interference waveforms. Nevertheless, all of the continuous coating spectra are similar in that reflectance at $R_{\text{min}}$ does not vary widely from the $\sim 4 \text{ – } 10\%$ range of optically thick halite. In contrast, the introduction of exposed substrate into the field of view does cause the reflectance at $R_{\text{min}}$ to decrease below that of optically thick halite (Figure 22b).

The coarse particulate halite coatings cause an increase in reflectance at $R_{\text{min}}$ as thickness increases, with the maximum reflectance approaching that of the particulate halite endmember (Figure 22a). This is not seen with the fine particulate halite coatings, which cause no change in reflectance at $R_{\text{min}}$ (Figure 22a). The lack of reflectance from the fine particulate halite coating is consistent with other theoretical and experimental
studies that show a decrease in reflectance with very fine particles coating a substrate [Crisp and Bartholomew, 1992; Johnson et al., 2002].

Similar properties are seen in the emission spectra of the fine particulate halite coatings (Figure 9). In emission spectroscopy, emissivity maxima ($\varepsilon_{\text{max}}; \varepsilon = 1$) generally occur at the same wavelengths as $R_{\text{min}}$. However, $\varepsilon_{\text{max}}$ is also affected by increasing $k$, which may shift the feature to longer wavelengths than corresponding $R_{\text{min}}$ [Hapke, 1993]. Such a shift of the emissivity maximum was not observed in the emission spectra of the fine particulate halite coatings studied here. Emission spectra of the fine particulate halite coatings also do not change in emissivity at $\varepsilon_{\text{max}}$, which is consistent with the reflectance spectra. This property has important implications for detecting chloride deposits on Mars (section 4.6.2.).

Figure 22: Absolute reflectance of halite-coated glasses at the minimum $R$ feature ($\sim 1580 \text{ cm}^{-1}$) related to coating thickness, areal coverage, and texture.

4.6. Applications to remote sensing

Our laboratory results cannot be directly applied to remotely sensed spectra from Mars because we have not discovered a solution for deconvolving spectra that is unique to coated materials on remote bodies. Our results predict a decrease in substrate band
contrast with increasing coating thickness, but band contrast is also affected by roughness [e.g., Bennett and Porteus, 1961] and particle size effects [e.g., Aronson et al., 1966; Hunt and Vincent, 1968; Lane and Christensen, 1998]. Our results predict an increase in the reflectance minimum (decrease in emissivity maximum). This feature is also affected by composition and by assumptions about the thermal properties of the surface [Osterloo et al., 2008]. Despite these limitations, our study provides a framework for future studies that use ‘ground truth’ methods for satellite measurements on Earth. Ground truth field data will constrain coating texture and composition, lateral extent, and surface thermal properties. This will enable studies to determine if there is an averaging effect of coating texture on the scale of a remote sensing pixel, possibly defining regional terrains with coatings. In addition, studies that compare areas with salts as a rock, cement, or coatings will help us understand the specific properties that coatings impart to remote sensing data.

We have discovered that the TIR properties of halite and calcite coatings impact remote sensing techniques in two important ways. First, salt coatings, when optically thin (transmissive), result in nonlinear spectral mixing between the coating and substrate. Second, the effects of halite coatings on reflectance minima (emissivity maxima) provide constraints on a method for identifying chloride deposits developed by Osterloo et al. [2008].

4.6.1. **Nonlinear spectral mixing**

The non-linear spectral mixing shown here for coated material has the potential to introduce error to mineral abundance determinations. A linear deconvolution algorithm [Ramsey and Christensen, 1998] is used to determine mineral abundances from remotely
sensed TIR spectra of Mars [e.g., Bandfield et al., 2000; Christensen et al., 2000; Hamilton et al., 2003], based on the principle that spectra of mineral endmembers mix linearly in proportion to areal abundance. The linear models investigated here were adapted from the same principles, and show that halite and calcite coatings cause nonlinear spectral properties (section 4.1.). Nonlinear spectral mixing introduces error in the linear deconvolution, and can cause the algorithm to fail [e.g., Ramsey and Christensen, 1998].

We found features attributable to nonlinear spectral mixing in all coated sample spectra except the fine particulate calcite coating, which had optically thick properties. Our results provide evidence that the nonlinear effects are minimized with the addition of exposed substrate (Figure 15, Figure 19). Although a blackbody endmember provided a better fit than a halite endmember for modeling the fine particulate halite coating, the spectra still had nonlinear features (Figure 20). These wavelength-dependent features of the TIR spectra of coated materials may alter TIR spectra such that linear deconvolution models have increased error in identifying spectral endmembers.

4.6.2. Identifying chloride deposits on Mars

The spectral features of halite-coated glasses shown here have implications for a method for finding chloride deposits on Mars developed by Osterloo et al. [2008]. More than 600 chloride-rich deposits, distinguishable by their low-contrast, sloping emission spectra from orbital observations (TES, THEMIS), have been mapped in the southern highlands of Mars [Osterloo et al., 2008, 2010; Glotch et al., 2010]. The geologic context, morphology, and thermal properties of many of the sites provide supporting lines of evidence that chloride-rich deposits exist [Osterloo et al., 2008, 2010; Glotch et al.,]
Osterloo et al. [2008] argue that two TIR spectral features indicate the presence of chlorides: 1) the relatively flat spectra lacking the broad basaltic absorption band of regional materials (centered at ~1080 cm$^{-1}$) and 2) the slope toward lower wavenumbers not seen in regional materials. The flattened spectra are likely due to the flat, featureless spectra of chlorides (Figure 3a). The authors attribute the spectral slope to an error in the calculation of the emission spectrum from incorrectly calibrated radiance measured by the spectrometer. Emissivity is calculated from the ratio of radiance from the sample to blackbody radiance at the same temperature [Ruff et al., 1997]. When the surface temperature is not known, it is necessary to assume that the sample emissivity equals one (emissivity maximum) at some point in the spectrum, which is reasonable for most rock-forming minerals with TIR absorption features [Ruff et al., 1997]. The surface temperature may then be derived from the sample radiance and an emission spectrum is generated [Ruff et al., 1997]. As a consequence of this assumption, emission spectra of samples with a maximum emissivity < 1 are calculated at the incorrect temperature, which causes a negative slope in the spectra [Osterloo et al., 2008]. Chlorides do not have unit emissivity in TIR, and their presence will potentially lower an emissivity maximum such that a negative slope appears in the spectrum [Osterloo et al., 2008].

The reflectance spectra of halite coatings may be used to evaluate the chloride-related negative slope in emission spectra because reflection spectroscopy does not require the assumptions about temperature made for emission spectroscopy. As a result, the absolute TIR reflectance of halite and halite-coated materials can be measured [cf. Lane and Christensen, 1998]. Increases in the glass substrate reflectance minimum ($R_{\text{min}}$) at 1580 cm$^{-1}$ correspond to decreases in the emissivity maximum that cause a spectral
slope. Because an assumed emissivity of 0.95 removes the slope [Osterloo et al., 2008], we propose that a reflectance of ~5% at $R_{\text{min}}$ will cause a detectable slope in emission spectra, assuming Kirchhoff’s law. As the reflectance at $R_{\text{min}}$ approaches zero, detectability decreases.

As discussed in section 4.5., the behavior of $R_{\text{min}}$ is related to halite coating thickness and texture (Figure 22). Continuous halite coatings may be detectable over a range of thicknesses, but the addition of exposed substrate decreases detectability as reflectance at $R_{\text{min}}$ decreases. Coarse particulate halite coatings increase in detectability with increasing thickness. Fine particulate halite coatings do not increase reflectance at $R_{\text{min}}$, so they are not detectable by this method. Emission spectra of the fine particulate halite coatings, which were measured at a known temperature, show no decrease in the emissivity maximum (with one exception). This confirms that fine particulate halite coatings do not decrease the emissivity of the emissivity maximum, making the halite undetectable. In addition, the blackbody properties of the fine particulate may make the halite indistinguishable from other very fine-grained materials.
5. CONCLUSIONS

Our investigation demonstrates the effects of salt coatings on the TIR signal of coated material. We showed that coating thickness, texture, and composition are important factors to consider when evaluating spectra of coatings. We conclude that:

1. Halite- and calcite-coated glasses have spectral features attributable to both the substrate and coating, and the substrate spectral features weaken with increasing coating thickness. The thickness at which the coating becomes optically thick is dependent on the coating’s optical properties: halite is partially transmissive to reflected TIR when < 150 µm thick, and calcite is optically thick at ~5 µm in the region of the strong absorption band (~1485 cm\(^{-1}\)) but otherwise partially transmissive to TIR reflected through < ~140 µm.

2. The spectral mixing of the coating and substrate indicates both linear and nonlinear behaviors related to the textural parameters. The continuous halite and calcite coatings have nonlinear spectral mixing consistent with radiative transfer models for layered materials. The addition of exposed substrate appears to dampen the nonlinear effects of the coatings on the spectra, agreeing more closely with linear modeling.

3. Spectral signatures of the different salt coating textures are primarily linked to exposed substrate and particle size effects. Exposed substrate strengthens substrate features. Though not studied rigorously here, particle size effects agree with previous studies showing that very fine particulate coatings act as a blackbody component.
4. The nonlinear spectral mixing of the coating and substrate may alter TIR spectra such that linear deconvolution models used to determine mineral abundances for the surface of Mars have increased error in identifying spectral endmembers.

5. Halite coatings, with the exception of fine particulates, increase the reflectance minimum (and decrease the emissivity maximum) of the glass substrate in a manner that increases chloride detectability in remotely sensed TIR emission spectra of Mars using the method of Osterloo et al. [2008]. Detectability decreases as coating thickness and areal coverage decrease. Fine particulate halite coatings do not increase the reflectance minimum, and are not detectable by this method.
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