

THERMAL INFRARED SPECTROSCOPY OF HALITE-COATED GLASSES – AN EVALUATION OF CONTINUOUS VERSUS DISCONTINUOUS COATINGS. J. A. Berger¹, P. L. King¹, T. S. Kunkel¹, M. N. Spilde and J. A. Crisp² ¹Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131. ²Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109.

Introduction: Discoveries of evaporite minerals on Mars [e.g., 1-7] and in Martian meteorites [8-9] are evidence of aqueous processes that may have deposited evaporites as cements and coatings on rocks and sedimentary materials. Martian rocks show chemical changes with depth from the rock surface, indicating the presence of coatings composed of salts, clays, and/or silica [6, 7]. Halide salts with Cl and Br, identified on Mars [6, 7], likely precipitated from brines. Knowing the occurrence and distribution of these products of aqueous alteration will clarify interpretations of Mars' aqueous history. However, methods to find halide salts using remote sensing techniques, like thermal infrared (TIR), have been developed only recently because halides have subtle TIR absorption features [10, 11]. The high emissivity and near-featureless TIR spectra of chlorides may contribute higher emissivity to chloride-bearing Martian deposits [10]. Further, chlorides could cause incorrect temperature derivations, introducing a spectral slope [10]. The purpose of this study is to examine the effects of thin chloride salt coatings on the TIR energy of underlying substrates as a function of both the coating coverage (discontinuous versus continuous) and coating thickness.

Methods: To investigate the effects of salt coatings on TIR spectra, NaCl-coated basaltic and albitic glasses were prepared for analysis by TIR micro-reflectance (*R*-TIR). Smooth, flat glass substrates were produced by melting either powdered basalt or albite with Li-tetraborate flux. Albitic and basaltic glass substrates were sputter-coated with pure NaCl to thicknesses of ~9-120 μm to form a discontinuous coating. Basaltic glass substrates were covered with salt wafers, prepared by pressing NaCl powder into fused solids (~15-135 μm thick), to form a continuous coating.

Salt coatings were characterized for their thickness using a Scanning Electron Microscope (SEM). Samples were tilted to ~30°, then the actual thickness (*h*) was calculated from measurements of the inclined thickness (*x*) by $h = x/\sin 30^\circ$. Errors on the coating thicknesses were estimated to be the standard deviation of ~45 thickness measurements.

TIR spectra were collected in specular reflectance mode using a Nicolet Nexus 670 Fourier Transform infrared spectrometer with a Continuum microscope, Globar source, KBr beamsplitter, and MCT-A* detector. With the sample in a dry-air purged compartment, μ -*R*-TIR measurements were collected over a 100 μm^2

spot, from 650 to 4000 cm^{-1} (2.5-15.3 μm), with 4 cm^{-1} resolution and 200 scans. Spectra were evaluated with OMNIC software.

Results: *SEM observations.* The discontinuous coatings consist of a layer of NaCl condensate distributed somewhat uniformly over the surface. Clustering of particles <2 μm formed rough and discontinuous coatings (Fig. 1a). In contrast, the continuous NaCl coatings are smooth with even thickness (Fig. 1b).

TIR observations. The spectra of the uncoated glasses show two bands, rather than one related to Si-O-Si asymmetric stretching at ~975 cm^{-1} [12], due to modification of the glass structure by the Li-tetraborate flux (Fig. 2). For the discontinuously-coated glasses, the *R*-TIR decreases across the spectrum as the thickness of the coating increases (Fig. 2a). The ~975 cm^{-1} band decreases to ~4% of the uncoated peak with a discontinuous coating of $95 \pm 21 \mu\text{m}$. Discontinuous coatings show a positive slope change at higher wavenumbers with increasing thickness.

For the continuously-coated glasses the *R*-TIR decreases as the thickness of the coating increases (Figure 2b), and there is a positive slope change at higher wavenumbers. All continuously-coated samples show interference fringing (periodic waveforms) due to multiple reflections of the infrared beam within the salt coating. The ~975 cm^{-1} band decreases to ~3% of the uncoated peak at a continuous thickness of $116 \pm 12 \mu\text{m}$. However, significant errors in band height measurements result from the interference fringing.

Discussion: Both continuous and discontinuous NaCl coatings >100 μm thick attenuate the ~975 cm^{-1} band of the glass substrate by >95%. Thinner coatings exhibit different spectral effects between the 2 coating types. These effects are modeled below.

Modeling. Assuming Kirchoff's Law, reflectance (*R*) spectra are related to emission (ϵ) spectra by $\epsilon = 1 - R$ [13]. Unlike ϵ , in *R*-TIR the beam travels through the coating twice, complicating comparisons to emissivity measurements [14]. Nonetheless, TIR should behave similarly in ϵ and *R*, so we tested previous models based on emissivity. Christiansen and Harrison [14] suggest that a discontinuous coating may be modeled with:

$$\epsilon_{mix} = \epsilon_1 \alpha - \epsilon_2 (1 - \alpha) \quad (1)$$

where ϵ_{mix} is the observed emissivity, ϵ_1 is the emissivity of the substrate, ϵ_2 is the emissivity of the

coating, and α is the fraction of substrate in the mixture. Thus, increasing the coating thickness decreases the fraction of substrate in the R -TIR spectra linearly. Following [14], continuous coatings may be modeled by:

$$\varepsilon_{mix} = \varepsilon_1 e^{-kx} + \varepsilon_2 (1 - e^{-kx}) \quad (2)$$

where k is the absorption coefficient and x is the thickness of the coating. In this case, the fraction of substrate is e^{-kx} and will decrease exponentially in R -TIR spectra as coating thickness increases.

To test these models, the fractions of substrate (α , e^{-kx}) in the coated glass spectra were estimated by fitting blackbody (a proxy for a flat, featureless NaCl spectrum) and uncoated glass spectra linearly to the peak at $\sim 975 \text{ cm}^{-1}$. For spectra with ringing, e^{-kx} was determined by subtracting the uncoated glass from the coated glass spectra. The fraction of the uncoated endmember that yielded the flattest spectrum after subtraction represented e^{-kx} . Eqs. 1 and 2 fit the experimental data: 1) increasing the thickness of discontinuous coatings corresponds to a linear decrease in the substrate's spectral component (Fig. 3a) and 2) increasing the thickness of continuous coatings corresponds to an exponential decrease in the substrate's spectral component (Fig. 3b).

Summary. Both discontinuous and continuous coatings result in decreased R -TIR band heights. Discontinuous coatings cause a linear decrease in R -TIR Si-O bands as coating thickness increases. Continuous coatings cause an exponential decrease in R -TIR Si-O bands as coating thickness increases. Emissivity-based models adequately describe these spectral effects. At higher wavenumbers, increasing the thickness of both continuous and discontinuous coatings results in more positive slopes. Continuous coatings also show significant interference fringing.

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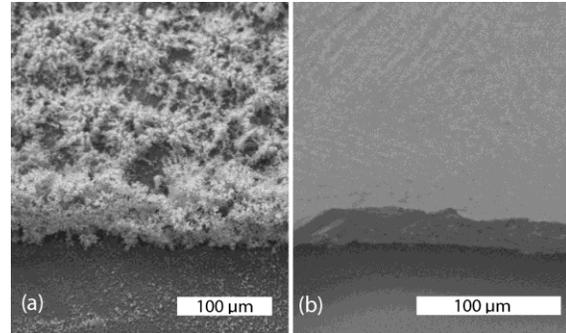


Figure 1: SEM micrographs of glass with (a) discontinuous NaCl coating and (b) continuous NaCl coating. The samples are tilted up 30° , showing the edge of the salt and the glass substrate.

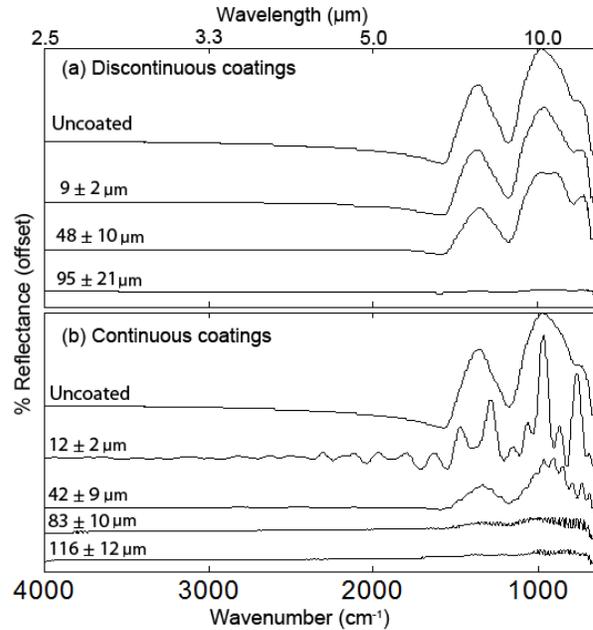


Figure 2: R -TIR spectra of (a) discontinuous & (b) continuous NaCl-coated basaltic glass. Coating thicknesses are given on the left for each spectrum.

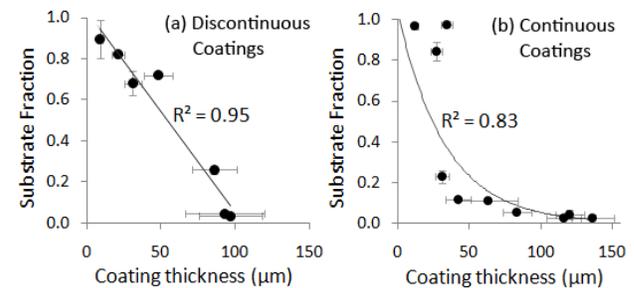


Figure 3: (a) Discontinuous coatings decrease the substrate fraction (α) in spectra linearly as NaCl coating thickness increases, following eq. 1 [14]. (b) Continuous coatings decrease the substrate fraction (e^{-kx}) in spectra exponentially as NaCl coating thickness increases, following eq. 2 [14].