

Derivation of the Midinfrared (5.0-25.0 μm) Optical Constants of Hydrous Carbonate and Sulfate. Ted L. Roush and James B. Orenberg (San Francisco State Univ. & NASA Ames Research Center), and James B. Pollack (NASA Ames Research Center)

BACKGROUND: There is ample theoretical and observational evidence suggesting liquid water was once stable at the surface of Mars [*e.g.* 1, 2, 3, 4]. Because water is essential to the evolution of life [5], it is important to understand the types of environments in which the liquid water was present. For example, if water were present early in Mars' history, then this raises the possibility that biological activity may have evolved only to eventually become extinct as liquid water became scarce. Alternatively, if liquid water were stable only later in Mars' history, then it becomes problematic to envision mechanisms by which biological activity evolved and remained viable without water until more favorable conditions existed. Even without biological activity, atmospheric carbon dioxide dissolved in water can assist the chemical weathering of primary igneous minerals producing common secondary phases such as hydrates, carbonates and sulfates [*e.g.* 4]. While the identification of hydrates, carbonates, and sulfates on Mars cannot provide direct evidence of biological activity, it can provide significant information regarding the presence and duration of an environment that would support the presence of liquid water at the surface. The specific mineralogy of these secondary phases can provide insight into the environments of their formation [6]. For example, slow precipitation that occurs in large standing bodies of water, *e.g.* oceans or lakes, commonly results in the formation of calcite, magnesite, dolomite, siderite, and rhodochrosite [6]. Rapid precipitation that occurs in ephemeral bodies of water, *e.g.* hypersaline lakes or playas, can result in the formation of all of the above phases as well as aragonite, vaterite, hydrated carbonates, alkali carbonates, bicarbonates, and other poorly ordered phases [6].

Absorption features identified in recent near-infrared spectra of Mars have been interpreted as being due to bicarbonate and bisulfate located in the mineral scapolite [7]. Spectral data returned by the Mariner 6 and 7 spacecraft have been interpreted as remaining consistent with the presence of hydrated carbonates [8]. Additionally, airborne thermal infrared spectra of Mars have been interpreted as implying the presence of carbonates, sulfates and hydrates [9]. Modeling of the thermal infrared data relied upon the optical constants of calcite anhydrite and a mixture of water in basalt because of their availability [9]. The derived abundances of carbonate and sulfate were 1-3% and 10-15% by volume [9]. However, the observed complexity and positions of the bands suggested other carbonate-, and sulfate-bearing species [9]. We have already derived optical constants for hydrous and anhydrous silicates [10] and we now apply these techniques to the derivation of the optical constants of hydrous carbonate and sulfate.

EXPERIMENTAL: A suite of carbonate and sulfate samples were collected from mineralogical supply houses. All of these samples were initially investigated using standard transmission spectroscopy techniques that involved dispersing a small amount of the sample in a KBr pellet. The transmission spectra of all samples were acquired and the carbonate and sulfate that provided the best comparison to the bands seen in the thermal infrared spectra of Mars were selected as a sub-set for derivation of their optical constants. The carbonate was

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dypingite with the structural formula $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ [11] and the sulfate was fibroferrite, having the structural formula $\text{Fe}^{3+}(\text{OH})\text{SO}_4 \cdot 3\text{-}5\text{H}_2\text{O}$ [12]. Because these samples consisted of fragile fine-grained masses that are not suitable for preparing polished surfaces, pressed pellets of the pure materials were prepared, similar to the clays previously studied [10]. The Fresnel reflectances of these tablets were measured (relative to aluminum mirror) using a Fourier transform infrared (FTIR) spectrometer and standard attachment at 4 cm^{-1} resolution from 4000 to 400 cm^{-1} ($2.5\text{-}25.0 \mu\text{m}$). As with our previous work for clays [10], we rely upon dispersion analysis to describe the real (n) and imaginary (k) indices of refraction as the contributions due to a sum of classical oscillators.

$$n^2 - k^2 = \epsilon_{\infty}^2 + \sum_{i=1}^n \frac{4\pi\rho_i\lambda^2(\lambda^2 - \lambda_i^2)}{(\lambda_i^2 - \lambda^2)^2 + \Gamma_i^2\lambda^2} \quad (1)$$

$$2nk = \sum_{i=1}^n \frac{4\pi\rho_i\lambda^3\Gamma_i}{(\lambda_i^2 - \lambda^2)^2 + \Gamma_i^2\lambda^2} \quad (2)$$

where $4\pi\rho_i$, Γ_i , and λ_i are the strength, width, and central wavelength of each oscillator, and ϵ_{∞} is the high frequency dielectric constant. Fresnel's equations for non-normal incidence were used to relate n and k to the near-normal reflectance measured in the laboratory. Nonlinear least squares techniques were used to minimize the differences between the calculated and observed spectra. Results of the analyses for dypingite and fibroferrite will be presented.

REFERENCES: [1] Pieri, D.C. (1980) *Science*, **210**, 895. [2] Squyers, S.W. (1989) *Icarus*, **79**, 229. [3] Baker, V.R. *et al.* (1992) *Mars*, Univ. Arizona Press, 493. [4] Fanale, F.P. *et al.* (1992) *Mars*, Univ. Arizona Press, 1135. [5] McKay, C.P. *et al.* (1992) *Mars*, Univ. Arizona Press, 1234. [6] Gaffey, S.J. (1989) *LPSC XX*, 323. [7] Clark, R.N. *et al.* (1990) *JGR*, **95**, 14,463. [8] Calvin, W.M. & T.V.V. King (1990) *LPSC XXI*, 153. [9] Pollack *et al.* (1990) *JGR*, **95**, 14,595. [10] Roush *et al.* (1991) *Icarus*, **94**, 191. [11] Raade, G. (1970) *Am. Mineral.*, **55**, 1,457. [12] Palache *et al.* (1951) *Dana's System of Mineralogy*, 7th Ed., v.II, 614, New York, Wiley

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