H₂O/OH-ASSOCIATED ABSORPTION BAND DEPTH RELATIONSHIPS IN MINERAL REFLECTANCE SPECTRA.

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Introduction: A number of planetary objects have been spectrally imaged in wavelength regions which enable the detection of absorption features associated with OH and/or H_2O, specifically the 1.4, 1.9, and 2.8 µm regions. Specific targets for which spectral data across one or more of these wavelength regions is available include Mars [1], asteroids [2], and Galilean satellites [3]. The presence of absorption features associated with OH/H_2O are interpreted in various ways, some of which may not be fully justified by the data.

The spectral reflectance properties of a number of materials of planetary interest are being re-examined in order to determine the relationship between absorption band depths in the 1.4, 1.9, and 2.8 µm regions. This analysis will eventually be extended to include compositional data and more sophisticated spectral analysis for the various samples. This paper deals with the relationships between depths of the 1.4 and 1.9 µm overtone and combination bands and the 2.8 µm OH stretching fundamental. The goal is to determine whether the detection of absorption bands in any one of these regions can be used to predict absorption band behavior in the other wavelength regions.

Experimental Procedure: This analysis focuses on the spectral properties (specifically band depths) of OH/H_2O-related absorption bands for the follow groups of minerals: pyroxenes, olivines, troilites, clays, palagonites, and sulphates. All of the spectra used in the analysis were measured at the RELAB spectrometer facility at Brown University [4]. The spectral data were acquired as follows: 0.3-2.6 µm spectra were measured at i=30° and e=0°, with 5 nm spectral resolution relative to halon; 2.5-26 µm were measured at i=30° and e=30°, with 4 cm⁻¹ spectral resolution relative to brushed gold. The spectra were merged in the 2.5-2.6 µm region [4].

Band depths for the 1.4 and 1.9 µm regions were measured using a straight line continuum tangent to the reflectance spectrum on either side of the absorption band. Band depths in the 2.8 µm region were measured relative to the region of maximum reflectance in the 2.0-2.7 µm region. Band depth was calculated as $1 - R_b/R_c$ [5], where R_b is the reflectance at the band minimum (position of minimum reflectance) and R_c is the reflectance of the continuum at the same wavelength position as R_b.

Results: Absorption features seen in the 1.4 µm region are normally attributable to combinations and overtones of O-H stretching fundamentals, although contributions from overtones of the H-O-H bending fundamental at 6.1 µm are also possible [6]. The 1.9 µm absorption band is attributed to a combination of an O-H stretch and H-O-H bend [6]. The 1.4 and 1.9 µm bands are generally discriminated from electronic transition bands on the basis of their shape (usually narrow) and the presence of multiple associated OH/H_2O absorption bands.

The fact that the 1.4 and 1.9 µm absorption features can be attributed to different types of OH and H-O-H stretching and bending fundamentals is reflected in the fact that there is a high degree of scatter when 1.4 and 1.9 µm band depths are compared for the various minerals used in this study (Figure 1). While some of this scatter is attributable to differences in band depths which can be assigned to differences in absolute OH and/or H_2O, reflectance in the 1.4 and 1.9 µm regions for some minerals, this scatter persists when only spectra with roughly equivalent reflectances in the 1.4 and 1.9 µm region are used.

Much of the scatter is due to differences in terms of the relative proportions of OH and H_2O present in the various samples. Those that contain appreciable free or adsorbed water (H_2O) will have more intense 1.9 µm bands than minerals which contain predominantly structural OH, because OH does not contribute absorption bands in the 1.9 µm region.

Another source of scatter arises from the fact that in many spectra the 1.4 and/or 1.9 µm absorption features are composed of two or more partially overlapping absorption bands [6]. The way in which band depth is measured here does not accurately account for these overlapping bands.

In spite of these limitations, the data are useful for deriving some general observations concerning the relationship between the 1.4, 1.9, and 2.8 µm OH/H_2O absorption bands. Figure 2 shows the relationship between the depths of the 1.4 and 2.8 µm absorption features. It can be seen that the 2.8 µm feature can have band depths on the order of 95% even for spectra for which the 1.4 µm band has depths of a few percent or less. Band depths in excess of 80% in the 2.8 µm region are seen in some spectra which do not exhibit a measurable 1.4 µm band. These are generally associated with pyroxene and olivine which are considered to be anhydrous minerals.

The situation is similar for the 1.9 µm region (Figure 3). Once again, 2.8 µm band depths in excess of 50% may be present with no associated evidence for a 1.9 µm absorption feature. In the case of pyroxenes, the 1.9 µm band falls in a region of low overall reflectance, being located near the center of the pyroxene Band II [7].

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Discussion: Many investigators associate a 2.8 µm band with the presence of "abundant" water or widespread hydration. However, all pyroxene and olivine spectra included in this study exhibit a 2.8 µm absorption band, including samples which exhibit no evidence of alteration, either visually, compositionally, or on the basis of X-ray diffraction. In fact it is difficult to find anhydrous mineral spectra which do not exhibit a 2.8 µm absorption feature. While we have not determined the nature of the water (or OH) which causes these absorptions, it may be some combination of adsorbed water, minor alteration (undetected by standard analytical methods) and/or fluid inclusions.

In terms of planetary observations, Rivkin et al. [2] has used the presence of an absorption feature in the 3 µm region of some M-class asteroids to argue for evidence of hydration. However band depths in the 3 µm region of these spectra are less than 50%, consistent with terrestrial mafic silicates and meteoritic troilites. Thus these asteroids could conceivably be composed of anhydrous minerals with the absorption feature in the 3 µm region due to fluid inclusions in the mafic silicates or hydrated IDPs accreted onto the surface [8].

Reflectance spectra of Mars which cover the 3 µm region exhibit an absorption feature in this region with a depth of up to 60% [1,9]. This is generally not accompanied by measurable absorption bands in the 1.4 and 1.9 µm region which can be attributed to OH/H_2O in the optically sampled surface (although it should be noted that acquiring reliable surface spectra in these wavelength regions is extremely difficult). Nevertheless, the depth of the 2.8 µm band, and lack of associated features near 1.4 and 1.9 µm is not unreasonable and is consistent with many mafic silicates which are deemed to be anhydrous by other criteria (see above). It may also be consistent with palagonitic materials in equilibrium with Martian surface conditions, a possibility which we are actively investigating.

References: [1] Erard S. et al. (1991) *Proc. LPSC, 21,* 437-455. [2] Rivkin A.S. et al. (2000) *Icarus, 145,* 351-368. [3] Fanale F.P. et al. (2000) *JGR, 105,* 22,647-22,655. [4] RELAB User's Manual (1999) Brown U. [5] Clark R.N. and Roush T.L. (1984) *JGR, 89,* 6329-6340. [6] Clark R.N. et al. (1990) *JGR, 95,* 12,653-12,680. [7] Cloutis E.A. and Gaffey M.J. (1991) *JGR, 96,* 22,809-22,826. [8] Fraundorf P. et al. (1983) *LPSC, 14,* 207-208. [9] Murchie S. et al. (1993) *Icarus, 105,* 454-468.

Figure 1. Relationship between 1.4 and 1.9 µm band depths in various minerals. **Figure 2.** Relationship between 1.4 and 2.8 µm band depths. **Figure 3.** Relationship between 1.9 and 2.8 µm band depths.