

SYSTEMATICS OF THE 1.0 μm ABSORPTION BAND IN REFLECTANCE SPECTRA OF ACTINOLITE. J.F. Mustard, C.M. Pieters, and S. F. Pratt, Dept. Geol. Sci, Box 1846, Brown University, Providence RI, 02912.

Introduction Visible to near-infrared reflectance spectra are an important tool for remote analysis of surface composition in terrestrial and extraterrestrial geologic investigations. Compositional information is derived from the position, shape, and strength of absorption bands caused by electronic processes associated with transition metal ions (i.e. Fe^{2+}) and overtones of fundamental stretching and bending modes in such ions as OH^- . Mineral groups displaying solid solution between Fe-rich and Mg-rich endmembers commonly exhibit systematic variations in the position and shape of Fe^{2+} absorptions related to the proportion of Fe to Mg in the minerals. Well studied examples include the important mineral groups olivine (1), and pyroxene (2,3). Another group of minerals which exhibit Fe-Mg solid solution, but have not been investigated in detail using reflectance spectra, are the amphiboles. Amphiboles are common terrestrial minerals, present in many different types of geologic terrain, and most commonly form in metamorphic environments where water or equivalent fluorine or chlorine are available. Given the evidence for possible abundant water during the early history of Mars (4) and the long history of volcanism (5), such minerals may also be expected in Martian geologic terrain. Reflectance spectra measured of the calcic amphibole actinolite, shown in Figure 1, exhibit distinct variations in the position of a Fe^{2+} absorption feature centered near 1.0 μm . The purpose of this investigation is to examine the relationship of the position of this absorption to chemical composition.

Sources of Absorptions in Calcic Amphibole Spectra The spectra of the calcic amphiboles shown in Figure 1 are dominated by an intense band centered near 1 μm and a broad band centered near 2.4 μm which has several narrow sharp absorption bands superimposed on it. Detailed analysis of the 1.0 and 2.4 μm bands by Goldman and Rossman (6,7) indicate that the broad bands arise from d-d orbital transitions of Fe^{2+} located in the highly distorted M(4) site. Although Ca^{2+} is the principle ion residing in the calcic amphibole M(4) site, it is rare to have a full complement of calcium ions in the structure and Fe^{2+} preferentially fills vacancies in the M(4) site over Mg (8). Absorptions associated with Fe^{2+} in the M(1), M(2), and M(3) sites occur between 0.8 and 1.2 μm , but are much less distinct because these sites are more symmetric than the M(4) site. The broad band centered near 0.7 μm is due to $\text{Fe}^{2+}/\text{Fe}^{3+}$ intervalence charge transfer (9). The sharp bands at 1.4 μm and between 2.3 and 2.5 μm are due to vibrational overtones of OH^- .

The variations observed in the position of the 1 μm band in the reflectance spectra of actinolite shown in Figure 1 indicates the crystal field stabilization energy (CFSE) of the M(4) site is varying. By analogy with studies of trends in the 1.0 and 2.0 μm bands of pyroxenes (2), it is hypothesized that the position of the 1.0 μm band in actinolite is associated with the proportion of Fe to Mg and Ca in the minerals. This hypothesis is supported by studies of Fe-Mg-Mn amphiboles using optical absorption and Mossbauer spectroscopies. Goldman (10) showed with Mossbauer spectroscopy that the quadrupole splitting (and hence M(4) distortion) was negatively correlated with $\text{Fe}/(\text{Fe}+\text{Mg})$ ratios while optical absorption measurements by Burns (9) showed that all Fe^{2+} absorption bands move to longer wavelengths with increasing Fe, in agreement with the results of Goldman (10).

Methods and Analyses All reflectance measurements were made from 0.35 to 2.6 μm with a wavelength sampling resolution of 0.005 μm . Reflectance measurements were obtained using bulk powder for samples 1 and 2 which are relatively homogeneous. Since samples 3-6 are very heterogeneous, we have isolated the reflectance properties of the actinolite in the samples by measuring spectra from actinolite rich zones in thin section using a method which effectively sends the beam diffusely through the sample and corrects for the optical properties of the thin section glass and glue. Variations in thin section sample thickness contribute to the differences in the depths of the 1.0 and 2.4 μm absorption bands for the spectra shown for samples 3-6. Chemical analyses shown in Table 1 were obtained with an electron microprobe.

Discussion Variations of the 1.0 μm band minimum relative to the $\text{Mg}/(\text{Mg}+\text{Fe}+\text{Ca})$ ratio (Mg^*) are shown in Figure 2. If the hypothesis that the ratio of Fe to Mg and Ca controls the CFSE of the M(4) site, and therefore the position of the 1.0 μm band minimum is true, then an inverse relationship between Mg^* and band minimum would be expected. Although the data shown in Figure 2 indicate that there might be a weak relationship, it is not a clear trend. This is not an unexpected result since chemical substitution in the tremolite-actinolite mineral series, and in amphiboles in general, occurs for a wide variety of cations. This complexity precludes a simple relationship between absorption band position and Mg^* , although more data may clarify the issue. There are, however several important aspects of the calcic amphibole spectra analyzed here relevant to the interpretation of remotely acquired data. The 1.0 μm band in actinolite becomes much less distinct as the Mg^* decreases and absorptions due to Fe in the M(1,2,3) sites dominate. Also if there is sufficient Ca or equivalent ion to fill the M(4) site (i.e. 2.0 ions/unit structure), the 1.0 and 2.4 μm bands would be absent from the spectra. Therefore the presence of these absorptions is indicative of a low Fe amphibole with less than 2.0 ions/unit structure. It should be noted that, the shape and position of the 1.0 and 2.4 μm bands in these amphiboles is, to a first order, very similar to Fe^{2+} absorptions in high-Ca pyroxenes since the distortion of the amphibole M(4) site is similar to the M(2) site in pyroxenes. However, not only are the amphibole bands more widely separated, but the amphiboles also exhibit diagnostic hydroxyl bands at 1.4 and between 2.3 and 2.5 μm . Given broad spectral coverage at high spectral resolution, high-ca pyroxene should be readily distinguished from calcic amphibole if OH^- bands due to other minerals or alteration do not interfere with the exact mineral assignment.

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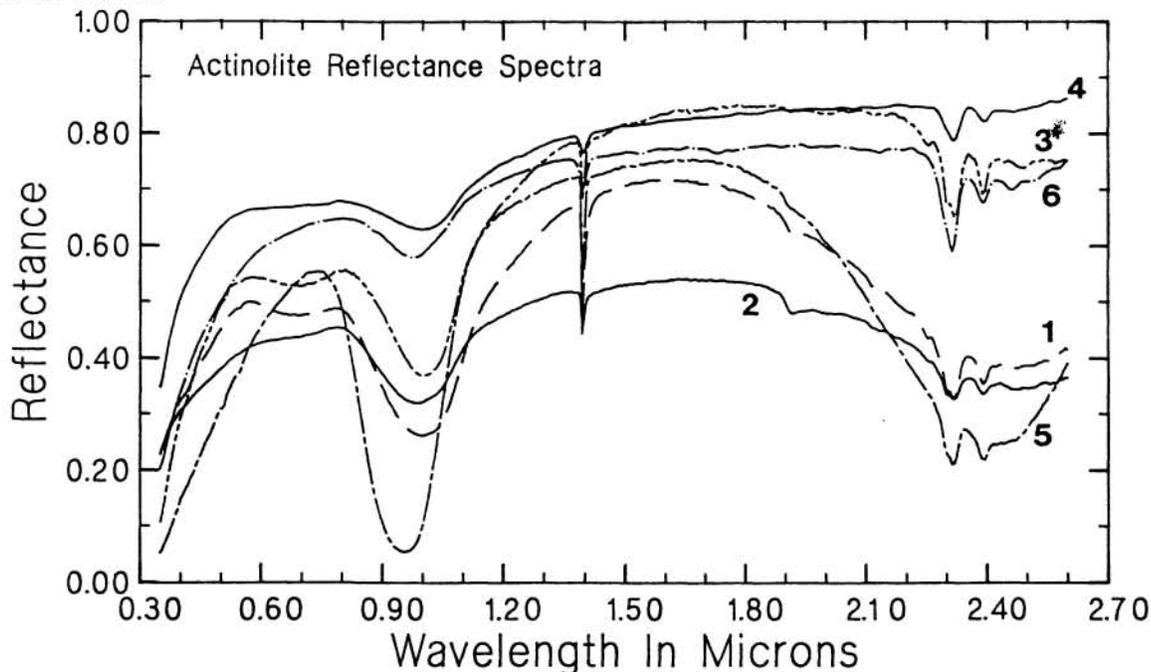


Figure 1. Bidirectional reflectance spectra of actinolite samples. Chemical compositions are given in Table 1 where the number of the spectrum corresponds to the chemical analysis number. Spectra 1 and 2 are from bulk powders while spectra 3-6 are from thin sections using a method described in text.

Table 1. Microprobe Composition of Actinolite

	1	2	3	4	5	6
SiO ₂	56.45	56.54	56.04	55.61	57.05	56.12
Al ₂ O ₃	1.50	1.91	1.16	0.40	0.45	0.30
MgO	22.00	22.10	21.10	18.97	22.61	21.78
NaO	0.08	0.37	0.55	0.09	0.07	0.15
TiO	0.02	0.09	0.02	0.02	0.02	0.00
CaO	11.90	12.21	11.97	12.77	11.58	12.26
K ₂ O	0.04	0.02	0.04	0.02	0.01	0.02
FeO†	5.38	4.83	6.28	8.93	5.55	5.93
MnO	0.29	0.15	0.32	0.14	0.22	0.24
Cr ₂ O ₃	0.24	0.06	0.07	0.17	0.03	0.01
Cl	0.00	0.00	0.00	0.01	0.01	0.00
Total	97.91	98.27	97.56	97.11	97.60	96.78
† Total Fe given in FeO						
Mg*	0.655	0.658	0.635	0.57	0.664	0.643
Mg* = Mg/(Mg+Fe+Ca)						
1.0 μm minimum	0.995	0.985	1.0	1.01	0.955	0.975

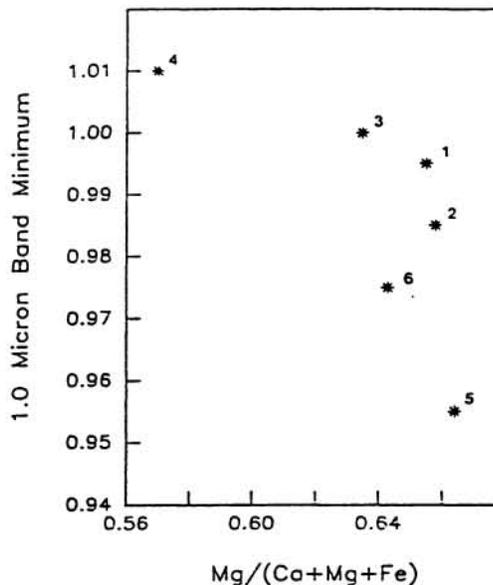


Figure 2. 1.0 μm absorption band minimum as a function of Mg/(Mg+Fe+Ca) ratio. Numbers correspond with numbered spectra shown in Figure 1 and chemical analyses in Table 1