

CLASSIFICATION OF IRON BEARING PHYLLOSILICATES BASED ON FERRIC AND FERROUS IRON ABSORPTION BANDS IN THE 400-1300 NM REGION. L. Stewart¹, E. Cloutis¹, J. Bishop², M. Craig¹, L. Kaletzke¹, K. McCormack¹, ¹ Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada R3B 2E9, l.stewart@uwinnipeg.ca, ²SETI Institute and NASA AMES Research Center, 515 N. Whisman Rd., Mountain View, CA 94043, USA.

Introduction: This project was undertaken to determine whether iron absorption bands in the 0.4-1.3 μ m region can be used to discriminate different phyllosilicates and to provide insights into structural differences. Water bearing minerals such as these play an important role in reconstructing the climatic and geological evolution of Mars. OMEGA recently detected nontronite, chamosite and montmorillonite on the surface of Mars [1].

Experimental Procedure: Reflectance spectra of various phyllosilicates (<45 μ m grain size) were measured at the RELAB facility at Brown University. Spectra were measured from 0.3-2.6 μ m with 5 nm resolution, at $i=0^\circ$, $e=30^\circ$, relative to halon, and corrected for minor irregularities in halon's reflectance in the 2-2.5 μ m region. Band minima were determined by fitting a third order polynomial to data points on either side of a visually determined minimum. A number of the absorption features discussed below occur as inflection points. In these cases the point of maximum slope change was taken as the band "minimum".

The phyllosilicates included in this study have been grouped based on their structural formulae. The difference between the two major groups is the structure of their tetrahedral layers. We also split them into subgroups - dioctahedral and trioctahedral. In trioctahedral minerals, all three octahedral sites are filled, whereas in dioctahedral minerals only two of the three sites are filled. This grouping helps determine whether there is a relationship between absorption band wavelength positions of Fe^{3+} and/or Fe^{2+} with phyllosilicate structure as well as whether it is possible to determine the type of phyllosilicate or group on the basis of iron absorption bands.

Results (1): Double Layer Dioctahedral Phyllosilicates: Double layer dioctahedral phyllosilicate spectra are presented in Figure 1 and include nontronite, glauconite, and celadonite.

The nontronite sample contains 22.08 wt. % Fe^{3+} and 0.79 wt. % Fe^{2+} . Given the low abundance of Fe^{2+} , the spectrum exhibits clear evidence only for Fe^{3+} spin forbidden bands at 0.37, 0.48, 0.65, 0.95 μ m [2,3].

The glauconite sample contains more Fe^{2+} than the nontronite (1.51 wt. %) and 16.06 wt. % Fe^{3+} . Fe^{3+} results in absorption bands at 0.37, 0.45, and 0.65 μ m. The band at 0.75 μ m is a charge transfer band between

the $Fe^{3+} - Fe^{2+}$. The absorption bands at 0.95 and 1.15 μ m are both due to crystal field transitions in octahedrally coordinated Fe^{2+} ; such bands are common feature of Fe^{2+} -bearing phyllosilicates. However, when abundant Fe^{2+} is present, its 0.95 μ m band can obscure the Fe^{3+} band also located in this region [2].

The third sample in this group is celadonite and it contains 18.19 wt. % and 3.57 wt. % Fe^{3+} and Fe^{2+} , respectively. The Fe^{3+} gives rise to spin-forbidden absorption bands at 0.34 and 0.37 μ m. The $Fe^{3+}-Fe^{2+}$ charge transfer band is located near 0.75 μ m, and very broad bands due to Fe^{2+} are present near 0.95 and 1.13 μ m. An additional Fe^{3+} band at 0.95 μ m is likely, but is concealed by the strong Fe^{2+} bands in this region.

Results (2): Double Layer Trioctahedral Phyllosilicates: Chamosite, clinochlore, and saponite are trioctahedral double layer phyllosilicates, and their reflectance spectra are shown in Figure 2.

Our chamosite contains 2.82 wt. % Fe^{3+} and 1.91 wt. % Fe^{2+} . These low iron abundances translate into weak absorption bands. From Burns' research on nontronite [2], we can infer causes for the absorption bands in the other phyllosilicates. The typical bands illustrated by Fe^{3+} and Fe^{2+} are present in chamosite's spectrum. There are very minor Fe^{3+} bands at 0.45 and 0.6 μ m. $Fe^{3+}-Fe^{2+}$ charge transfer is also represented by a minor absorption band at 0.75 μ m. The Fe^{2+} double band feature is again present near 0.9 and 1.15 μ m.

Clinochlore has 4.23 wt. % and 5.96 wt. % Fe^{3+} and Fe^{2+} , respectively. Fe^{3+} bands are present at 0.4 and 0.45 μ m. The charge transfer feature is present at 0.7 μ m. The double Fe^{2+} absorption bands are present at 0.92 and 1.12 μ m. Removal of a straight line continuum across this region suggests that an additional band is present near 0.95 μ m, attributable to Fe^{3+} .

The Fe^{3+} content in saponite is much greater than in the chamosite and clinochlore (14.25% Fe^{3+} and 3.94% of Fe^{2+}). The deep and broad absorption bands at the lower wavelength end (0.42, 0.47, 0.65 μ m) exemplify the high abundance of Fe^{3+} . The $Fe^{3+}-Fe^{2+}$ charge transfer band is located near 0.74 μ m. The double Fe^{2+} bands occur near 0.9 and 1.1 μ m.

Results (3): Single Layer Phyllosilicates: Figure 3 shows spectra of three trioctahedral single layer phyllosilicates (serpentine, cronstedtite, and berth-

ierine), as well as a dioctahedral single layer phyllosilicate (hisingerite).

Our serpentine sample contains 3.04 wt. % Fe^{3+} and 1.78 wt. % Fe^{2+} . Absorption bands are present at 0.45, 0.75, 0.95, and 1.1 μm . [2] attributes the 0.45 μm band to Fe^{3+} , however according to [4] it is caused by Fe^{2+} and is a spin-forbidden transition; both however agree on the 1.1 μm band being attributable to Fe^{2+} .

Our sample of cronstedtite contains 63.51 wt. % Fe^{3+} and 15.96 wt. % Fe^{2+} . The broad band at 0.39 μm is due to Fe^{3+} . The continuum-removed spectrum suggests that two bands are present: at 1.0 and 1.25 μm . These bands are at greater wavelengths than usual, perhaps due to the higher iron content, a difference in structure, or from the way the continuum was constructed. These two bands are likely attributable to Fe^{2+} crystal field transitions.

The berthierine contains 30.59% Fe^{3+} and 15.96% Fe^{2+} . The Fe^{3+} -caused bands are at 0.35 and 0.48 μm . There is an Fe^{3+} - Fe^{2+} charge transfer band near 0.7 μm and two Fe^{2+} crystal field bands at 0.9 and 1.2 μm .

The analytical data for hisingerite indicates 30.53% Fe^{3+} and 0% Fe^{2+} , although a small amount of Fe^{2+} (below the analytical detection limit (~ 0.1 wt. %)) may be present. The Fe^{3+} bands are at 0.45 and 0.95 μm . The weak band at 0.7 μm is suggestive of Fe^{2+} - Fe^{3+} charge transfer. The weak bands at 0.9 and 1.08 μm are most consistent with the presence of Fe^{2+} .

Conclusions: In spite of the fact that the three phyllosilicate subgroups differ in terms of structure and/or octahedral site occupancies, there appear to be no systematic differences within or between groups in terms of iron-associated absorption band wavelength positions. When Fe^{3+} is present, spin forbidden absorption bands arise between 0.35-0.5, and near 0.65 and 0.95 μm . If Fe^{2+} is present spin allowed absorption bands can be seen near 0.7 (Fe^{2+} - Fe^{3+} charge transfer), 0.9 and 1.1 μm . Thus, Fe^{3+} and Fe^{2+} absorption bands show up in the same specified regions regardless of their grouping. It is possible that when considering other absorption bands (i.e., OH, H_2O , metal-OH) along with the iron bands there may be a way to “fingerprint” phyllosilicates via spectra analysis.

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References: [1] Poulet F. et al. (2005) *Nature*, 438, 623-627. [2] Burns R.G. (1993) *Mineralogical Applications of Crystal Field Theory 2nd Edition*, Cambridge U. Press. [3] Clark R. N. et al. (1990) *JGR*, 95,

12,666-12,676. [4] Hunt, G.R. and Ashley R. P. (1979) *Mod. Geol.*, 74, 1613-1629.

Table 1	Absorption Bands (μm)					
Samples	Fe^{III}			Fe^{III} - Fe^{II}	Fe^{II}	
Double Layer-Dioctahedrals						
Nontronite	0.37	0.48	0.65	0.95		
Glauconite	0.37	0.45	0.65		0.75	0.95 1.15
Celadonite	0.34	0.37			0.75	0.95 1.13
Double Layer-Trioctahedrals						
Chamosite	0.45	0.6			0.75	0.9 1.15
Clinochlore	0.4	0.45	0.95		0.7	0.92 1.12
Saponite	0.42	0.47	0.65		0.74	0.9 1.1
Single Layer-Dioctahedral						
Hisingerite	0.45	0.95			0.7	0.9 1.08
Single Layer-Trioctahedrals						
Serpentine	0.45				0.75	0.95 1.1
Cronstedite	0.39					1 1.25
Berthierine	0.35	0.48			0.7	0.9 1.2

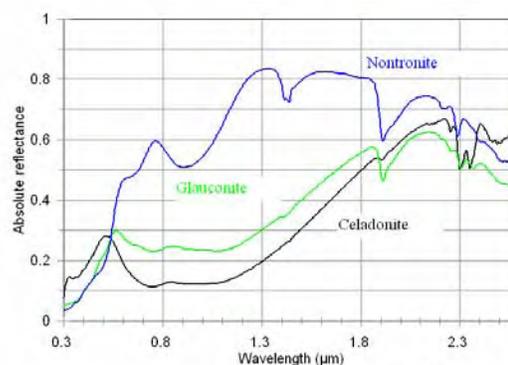


Figure 1

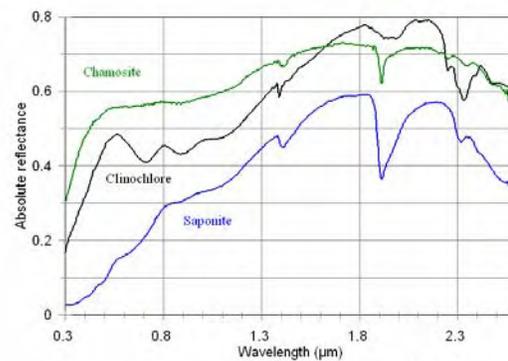


Figure 2

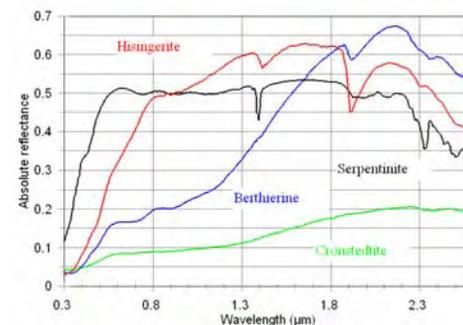


Figure 3