Near-infrared Spectroscopic Study of Nontronites and Ferruginous Smectite

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Abstract:
The existence of life on planets such as Mars depend upon the presence of water. This water may not necessarily be as liquid or crystalline water but may be as interlayer water such as is found in smectitic clays. One group of smectites, relevant to the search for interplanetary life are those which have a high iron content, known as nontronites. Near-IR reflectance spectroscopy has been used to show the presence of water and hydroxyl units in these minerals. Three near –IR spectral regions are identified: (a) the high frequency region between 6400 and 7400 cm^{-1} attributed to the first overtone of the hydroxyl stretching mode (b) the 4800-5400 cm^{-1} region attributed to water combination modes and (c) the 4000-4800 cm^{-1} region attributed to the combination of the stretching and deformation modes of the FeFeOH units of nontronite. Two types of hydroxyl groups were identified using near-IR spectroscopy: hydroxyl units coordinated to the iron and hydroxyl groups from water in the nontronite structure. The first hydroxyls are characterised by several bands: firstly in the 7055 to 7098 cm^{-1} region assigned to the first overtone of the AlFeOH stretching unit, secondly in the 6958-6878 cm^{-1} region attributed to the FeFeOH unit. The overtone of the hydroxyl stretching frequency of water was observed at around 6800 cm^{-1}. These observations show that nontronites can be a source of water that may support life.

Key words: Mars, nontronites, ferruginous smectite, infrared spectroscopy, near-infrared spectroscopy, water

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1. Introduction

The search for life on Mars is endless and many publications are based upon the search for water on Mars [1-6]. It is possible that water is retained in the polar ice caps [1]. Estimates of the amount of water retained and lost from Mars have been made [2-3]. The role of particular minerals such as carbonates in the evolution of Mars's oceans has been forthcoming [4-5] Indeed, the stability of hydroxylated minerals on exposure to UV radiation on Mars has been made [6]. Scientific evidence that water on Mars in the form of lakes and rivers is overwhelming. Whilst there is little evidence of water is such forms existing on Mars at the present time, water may be retained in crystals and in minerals. It is possible that minerals such as smectites may exist on the planets such as Mars, known commonly as the "red planet". If so, then such minerals may be able to retain water either in the form of intercalated water or as hydroxyls bonded to the octahedral cations in the clay minerals.

Nontronites are an unusual set of clay minerals such that the structure is based upon octahedral iron as opposed to octahedral aluminium or magnesium. Nontronites are a subset of the minerals known as smectites, which expand upon contact with water and other solvents. Smectites may be either dioctahedral or trioctahedral, depending on whether the octahedral sheet is filled with 2 out of 3 positions with a trivalent cation or fully filled with a divalent cation. Among this group of clay minerals are the dioctahedral aluminium based clays known as montmorillonites. When iron substitutes for the aluminium in the octahedral sheet, then ferruginous montmorillonites are obtained. When the aluminium is completely replaced with iron, then these ferruginous montmorillonites are known as nontronites. These minerals have the capacity to retain water to high temperatures [7]. It is probable that these minerals exist on the planet Mars.

Mid-IR infrared spectroscopy has been used extensively for the study of clay minerals including smectites and nontronites [8-10]. Far-IR has been only used to a limited extent to determine vibrations of layer silicates below 400 cm^{-1} [11]. Some Raman spectra of some layer silicates including chlorites, phlogopites, muscovites and lepidolites have been obtained [12]. No Near-IR spectra of nontronites have been reported. The colour of these minerals varies from green through to reddish brown. The near-IR runs into the visible part of the spectrum above about 9,500 cm^{-1} and as a consequence some absorption may be observed in this region from the nontronites. The objective of this paper is to report the near-IR spectra of these high-iron containing smectites and to identify the forms of water in these minerals.

2. Materials and Methods

2.1 Clay Mineral samples

The clay minerals used are The Clay Minerals Society standards: the ferruginous smectite SWa-1, and the nontronite NG-1 from Hohen-Hagen, Germany [13]. Samples from Wards scientific labelled nontronite from Spokane (from Washington State) and a ferruginous smectite were also used. The calcium exchanged, < 1 μm portions were used. Samples were analysed for purity by X-ray diffraction. Quartz is the predominant impurity found in both the ferruginous smectite and the nontronite. Infrared spectroscopy was also used to detect low levels of other phases, particularly kaolinite and amorphous phases.

The ferruginous smectite SWa-1 from the Source Clays Repository (SCR) of The Clay Minerals Society (Grant County, Washington) has a structural formula of

$$(M^{+}_{0.95})[Al_{1.10}Fe_{2.61}Mg_{0.25}][Si_{7.40}Al_{0.60}]O_{20}(OH)_4.$$

The nontronite from Hohen Hagen, Germany (CMR NG-1) has a structural formula:

$$(M^{+}_{0.95})[Al_{0.86}Fe_{3.08}Mg_{0.05}][Si_{7.12}Al_{0.11}Fe_{0.76}]O_{20}(OH)_4.$$

The difference in the composition of the ferruginous smectite and nontronite is minimal. It should be noted some of the Fe (≈18%) might be incorporated in the tetrahedral layers. Most of the layer charge originates from the tetrahedral layer with a charge of -0.91 and –0.18 on the octahedral layer. The interlayer charge is –1.09. For nontronite, the charges on the octahedral and tetrahedral layers are -0.08 and -0.92 with an interlayer charge of –0.99. It is generally accepted that nontronite contain Fe predominantly in the trivalent state [14-17]. The two minerals are very similar in formulation, the major difference being in the iron content. The iron content of SWa-1 is 24.4 wt % and for NG-1 is 32.2 wt %.

The Uley (NAu-1) nontronite (sample 1) has a formula of $[M^{+}_{1.05}][Al_{0.26}Fe_{3.71}Mg_{0.03}][Si_{6.97}Al_{1.03}]O_{20}(OH)_4$ and the Uley (NAu-2) nontronite (sample 2) has a formula of $[M^{+}_{0.83}]$ $[Al_{0.42}Fe_{3.43}Mg_{0.04}]$ $[Si_{7.52}Al_{.06}Fe_{.42}]$ $O_{20}(OH)_4$. The above chemical compositional analyses were conducted on ignited, Ca-saturated purified fractions (nominally <0.15 μm) of each nontronite.

2.2 Mid-Infrared and Near-infrared spectroscopy (NIR)

The samples were dried to remove any adsorbed water and stored in a desiccator before measurement in the spectrometers. The sample (1mg) was finely ground for one minute, combined with oven dried spectroscopic grade KBr having a refractive index of 1.559 and a particle size of 5-20 mm (250mg) and pressed into a disc using 8 tonnes of pressure for five minutes under vacuum. The spectrum of each sample was recorded in triplicate by accumulating 64 scans at 4 cm^{-1} resolution between 400 cm^{-1} and 4000 cm^{-1} using the Perkin-Elmer 1600 series Fourier transform infrared spectrometer equipped with a LITA detector.

The NIR spectroscopy analyses were performed on a Perkin Elmer System 2000 NIR-FT Raman spectrometer equipped with a Spectron Laser Systems SL301 Nd:YAG laser operating a wavelength of 1064 nm. For the samples, 32 scans using DRIFT spectroscopic techniques were accumulated at a spectral resolution of 16 cm^{-1} using a mirror velocity of 0.2 cm^{-1}/s to get an acceptable signal/noise ratio. This FT-Raman spectrometer operating in the Near-IR functions as a Near-IR spectrometer as well as an FT Raman spectrometer. One of the advantages of this instrument is that one may scan from 3000 to 8000 cm^{-1}. This means that the hydroxyl stretching, combination and overtone bands are measured simultaneously.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

3. Results and Discussion

Nontronites are characterised by hydroxyl stretching, deformation and translation modes, which are associated with the ferric iron. The mid-IR spectra for a series of nontronites and ferruginous smectite as detailed in the experimental section above are shown in Figures 1 and 2. The spectral details are reported in Table I. Ferruginous smectites where the aluminium is only partially replaced by Fe^{3+}, show stretching bands at 3596 cm^{-1}, attributed to the FeAlOH stretching vibration. Nontronites show the equivalent band at 3560 cm^{-1}, due to the FeFeOH stretching vibration. The hydroxyl deformation vibrations are observed at 914 cm^{-1} and around 880 cm^{-1} for the ferruginous smectites and are assigned to the AlAlOH and FeAlOH vibrations [14,16]. For nontronites bands are observed at ~870 and 850 cm^{-1} [15]. Bands in the 800 to 400 cm^{-1} are attributed to firstly the hydroxyl translation modes associated with the Si-O-Fe or Si-O-Al vibrations and to the flexing vibrations of the Fe-O-Si units [17].

Near infrared spectroscopy has been often termed: 'proton' infrared spectroscopy, as it fundamentally measures the overtone and combination bands associated with the hydroxyl modes detailed above. These hydroxyl overtone bands may arise from either the water in the interlayer spaces of the nontronite and from the hydroxyls associated with the octahedral Fe^{3+}. In ferruginous smectites and nontronites, which contain both adsorbed water and coordinated water, the hydroxyl bands in the mid-IR arise from both water and the iron smectites. In the near-IR such band are well separated. Three regions are observed in the near IR of the nontronites. These may be defined as (a) the high frequency region between 6400 and 7400 cm^{-1} as shown in Figure 3; (b) the 4800-5400 cm^{-1} region as illustrated in Figure 4 and (c) the 4000-4800 cm^{-1} region (Figure 5) [17].

The first region is attributed to the overtones of the hydroxyl stretching modes observed in the mid-IR at around 3560 cm^{-1}. Figures 6 and 7 illustrate the band components in the spectral profile of this region for the Hohen-Hagen nontronite and the clay minerals standard of ferruginous smectite. Table II summarises the results of the analyses of the near-IR spectra. Three bands are observed for each of the profiles in this spectral region. The band with the highest wavenumber is assigned to the first overtone of the Al-FeOH vibration. The band is observed in the 7056 to 7098 cm^{-1} region. The band is most intense for the ferruginous smectite. A second band is observed at around 6965 cm^{-1} and is assigned to the first overtone of the FeFeOH stretching vibration. The third band is significantly broader and is observed at around 6840 cm^{-1}. It is considered that this band is due to the overtone of the hydroxyl stretching frequencies of water coordinated to the clay mineral. Figure 3 displays the first hydroxyl overtone of the ferruginous smectites and nontronites. The first observation is that the spectra for the ferruginous smectites are different from that of the nontronites. The ferruginous smectites are characterised by an intense band at

7070 cm^{-1}, whereas the nontronites principal band is at 6965 cm^{-1}. The spectra of the two newly discovered Australian nontronites known as Uley (NAu-1) nontronite and the Uley (NAu-2) nontronite fit well with the spectra of the other nontronites. In Figure 3, spectrum c resembles that of the Garfield nontronite (spectrum f). Spectrum d seems to be like a combination of spectra (a) and (f). Thus the similarity of the Near-IR spectra of the Uley nontronites to some of the standards confirms the use of these minerals as clay standards to replace the now unobtainable Hohen-Hagen nontronite. The region around 7000 cm^{-1} is useful for the identification of water, which may arise through the 'microbiological' dehydroxylation of the nontronites.

Water in clay minerals is readily observed by studying the infrared spectrum of the water deformation modes centred on 1630 cm^{-1}. This band has proven most sensitive to changes in the structural environment of the water. Water, which is coordinated to cations in clays, occurs around 1680 cm^{-1}, water in the hydration sphere of cations around 1650 cm^{-1} and adsorbed water at 1630 cm^{-1}. The water in the Hohen-Hagen nontronite shows two bands at 1680 and 1632 cm^{-1} with relative areas of 44.0 and 55.0 %. The first band is attributed to water coordinated to the interlayer cation. The second band is attributed to adsorbed water. A similar feature is observed for the Garfield nontronite but the ratio of the two bands is now 19.5 to 80.5 %. For the ferruginous smectites bands are observed at 1670 and 1635 cm^{-1} with relative intensities of 39.5 and 60.5 %. The Uley green nontronite shows two bands at 1672 and 1635 cm^{-1} with relative areas of 23.3 and 58.0 %. An additional band is observed at 1613 cm^{-1} and is attributed to weakly hydrogen bonded interlayer water. Such a band component analysis is typical of smectites. The water-bending region is different for the Uley brown nontronite. Two bands are observed at 1654 and 1630 cm^{-1} with relative areas of 21.9 and 78.1 %. Three principal bands are observed in the second region of the near-IR spectra. These bands are attributed to water combination bands (Figures 8 and 9) [17]. Three major bands are observed at around 5240, 5200 and 5120 cm^{-1}. The first band at 5240 cm^{-1} is attributed to the combination of water bands arising from the coordinated water with the deformation frequency of 1680 cm^{-1}. The second band at 5200 cm^{-1} is ascribed to the combination of the stretching and deformation modes arising from the interlayer water with a bending frequency of 1630 to 1640 cm^{-1}. The spectra of this region are almost identical for all the samples studied in this work. The spectra for the ferruginous smectites show greater bandwidths in the component bands. This is the region for the identification of interlayer water and coordinated water.

Spectra in the 4000 to 4500 cm^{-1} region are attributed to the combination bands of the stretching, bending and translation modes of the FeFeOH and AlFeOH units. Two major bands are observed at around 4370 and 4160 cm^{-1} with bands of lesser intensity at 4470 and 4100 cm^{-1} (Figures 10 and 11). The first band at ~4370 cm^{-1} is assigned to the combination of the hydroxyl stretching and bending modes of the FeFeOH units. Spectra a and b are the spectra from two different ferruginous smectites and is clear that the spectra occur at higher frequencies than that of the nontronites. This is the result of the combination of the FeAlOH stretching and deformation frequencies, which occur at higher wavenumbers than that of the FeFeOH vibrations. This band for the Uley samples occurs at lower frequencies than for the nontronites from Spokane and Hohen-Hagen. The second principal band is ascribed to the combination of the hydroxyl stretching and hydroxyl translation modes. This band shows sensitivity to the nontronite structure. It is suspected that the band may be useful for determining the strength of interlayer bonding, although such a concept requires further investigation.

Conclusions

If life exists on Mars or other planets, then this life may depend on the presence of water. Such water may not be present as liquid water but could be involved as interlayer water in clay minerals. This water may take two forms (a) interlayer water and (b) water formed from the hydroxyls of minerals such as nontronites.

In this work we have used near-IR spectroscopy to show the presence of both of these types of 'water' molecules (a) coordinated water which produces bands in the 5200 cm^{-1} region and (b) the overtone and combination bands of the hydroxyls of nontronites and the related mineral ferruginous smectite. The near-IR technique used in this study is that of reflectance and whereas this technique may be useful for studying the infrared spectra from Mars, infrared emission techniques may prove more useful. Importantly near-IR spectroscopy enables distinctions between ferruginous smectites and nontronites to be easily made, as in the Near-IR the spectra occur at different frequencies.

Acknowledgments

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Table I Infrared absorption bands of nontronite and iron containing smectites

Ferruginous Smectite		**Nontronites**					**Suggested assignments**
This work	Previous work [8-10]	Spokane (Washington State)	Hohen-Hagen (Germany)	Uley NAu-1 (South Australia)	Uley NAu-2 (South Australia)	Previous work [8-10]	
3596	3620						Al FeOH stretch
		3558	3597	3572	3568	3560	FeFeOH stretch
3434	3410	3429	3432	3414	3419	3400	Water OH stretch
3233	3215	3230	3232	3244	3244	3210	cation-H_2O
3070			3047				cation-H_2O
1635	1630	1630	1628	1630	1630	1625	HOH bends
1100	1090	1101	1077	1121	1110	1110	Si-O stretch
1022	1027	1020	1039	1033	1024	1020	Si-O stretch
	914						AlOH deformation
873	876		880	872	867		AlOH deformation
801	843	852		838	853	850	AlFeOH deformation
770	788	815	793	823	819	816	Quartz impurity
		781	788	788	785 751	782	Quartz impurity

689	695	677	693	676	676	677	Quartz impurity
	625						FeFeOH translation
491	519	583			594	595	FeFeOH translation
461	478	490	487	496	493	490	Si-O-Fe
433	464	460	458		452	450	Si-O-Si
	449			433		431	Si-O-Fe
	427	423	429		423		

Table II. Band component analysis of the NIR spectra of nontronites and ferruginous smectites

Fe Smectite cm^{-1}	Fe Smectite cm^{-1} (Wards)	Hohen-Hagen cm^{-1}	Spokane (Washington State)	Nontronite (Garfield) (Washington County)	Uley NAu-1 (South Australia)	Uley NAu-2 (South Australia)	Suggested Assignment
7055	7069	7056	7068	7098	7060	7082	Overtone OH-stretch (1) (2x) AlFe-OH
6977	6958	6965	6965	6978	6962	6974	Overtone OH-stretch (1) (2x) FeFe-OH
6705	6835	6843	6846	6766	6825	6819	Overtone OH-stretch (1) (2x) crystal H_2O
5249	5243	5247	5248	5233	5249	5244	H_2O combination (librational 1+ deform 1+ stretch 1)
5213	5158	5206	5215	5074	5195	5187	H_2O combination (deform 1+ stretch 1)
5159/5033	5038	5120/4951	5123/4986	4818	5069	5070	H_2O combination (deform 2 + stretch 1) crystal H_2O
5033		4951	4986				H_2O combination (deform 2 + stretch 1) crystal H_2O
4472	4457	4470	4508	4370	5073	4531	Combination OH-stretch and OH deform. of Fe FeOH
4362	4372	4264	4370	4152	4351	4374	Combination OH-stretch and OH translation of Fe FeOH
4186	4165	4164	4161	4054	4174	4162	Combination OH-stretch and OH translation of Fe FeOH
4100	4100	4111	4072				Combination OH-stretch and OH translation of Fe FeOH

List of Tables

List of Figures

Table 1 Infrared absorption bands of nontronite and iron containing smectites

Ferruginous Smectite		Nontronites					S as
This work	Previous work [2-4]	Spokane	Hohen-Hagen	Uley brown	Uley green	Previous work [2-4]	
3596	3620	3558	3597	3572	3568		
						3560	
3434	3410	3429	3432	3414	3419	3400	V
3233	3215	3230	3232	3244	3244	3210	c
3070			3047				c
1635	1630	1630	1628	1630	1630	1625	H
1100	1090	1101	1077	1121	1110	1110	S
1022	1027	1020	1039	1033	1024	1020	S
	914						d
873	876		880	872	867		d
801	843	852		838	853	850	d
770	788	815	793	823	819	816	
		781	788	788	785 751	782	
689	695	677	693	676	676	677	
	625						t
491	519	583			594	595	t
461	478	490	487	496	493	490	
433	464	460	458		452	450	
	449			433		431	
	427	423	429		423		