# The Garfield and Uley nontronites – An infrared spectroscopic comparison

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**Abstract:**

FTIR and Infrared emission spectroscopy (IES) has been used to characterise the Uley (Australian) and Garfield nontronites. These clay minerals are characterised by a strong emission band at 3570 cm$^{-1}$ attributed to the FeFeOH unit. Dehydroxylation is followed by the loss of intensity of this band as a function of temperature. Dehydroxylation is also followed by the loss of intensity of the FeFeOH deformation vibration at 843 cm$^{-1}$. IES shows that the dehydroxylation occurs as a continuous process in comparison to DTA/TGA studies where the dehydroxylation occurs abruptly at 425 °C. Water in these high iron bearing smectites have been observed through the stretching mode at 3430 cm$^{-1}$ and the

bending mode at 1630 cm$^{-1}$. Different types of water are identified in the

nontronite structure by the analysis of the band profile in the 1590 to 1680 cm$^{-1}$

region.  Low frequency vibrations show that the Uley green nontronite is similar

to the Garfield nontronite. The brown Uley nontronite is closer to the Hohen-

Hagen nontronite.  The Uley nontronites may therefore be used spectroscopically

to replace other nontronites as a reference clay mineral.


*Key words:* dehydroxylation, FT-IR, infrared emission spectroscopy, montmorillonite,

                 nontronite, smectite.

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# 1. Introduction

Smectites belong to the group of clay minerals, which expand upon contact with water [1]. The presence of the water influences the physio-chemical properties for example the rheology of the clays [2]. Smectites may be either dioctahedral or trioctahedral, depending on whether the octahedral layer is filled with 2 out of 3 positions with a trivalent cation or fully filled with a divalent cation [3]. The dioctahedral smectites can be divided into two principal groups (a) aluminian smectites and (b) the iron-rich varieties including ferruginous smectites and nontronites. Two types of dioctahedral smectites exist depending on the site of the layer charges: (a) montmorillonites where the charge arises from divalent cations usually Mg replacing the $M^{3+}$ cations in the octahedral sites resulting in a diffuse layer charge, and (b) beidellites where the strongly localised charge arises from the $Al^{3+}$ substitution into the $Si^{4+}$ tetrahedral sites [1,3] In iron-rich (ferruginous) smectites and nontronites, some or all of the Al in the octahedral layer is replaced with ferric iron ($Fe^{3+}$). In the case of the ferruginous smectites the theoretical structural formula can be given by $(M^{++}_{x/2}.nH_2O)(Fe^{3+}_4)(Si_{8-x}Al_x)O_{20}(OH)_4$ [1,4]. This clay formula as written is the end member and is known as nontronite. Montmorillonites and beidellites generally have $Fe^{3+}$ <1% [5,6]. The term ferruginous smectites (or Ferrian smectites) is used for dioctahedral smectites when when $Fe^{3+}$ is >3% [1]. Ferruginous smectites have partial substitution of the aluminum by iron, whereas nontronites have total replacement.

The ideal structural formula for aluminian smectites is

$(Al_{3.15}Mg_{0.85})(Si_{8.0})O_{20}(OH)_4X_{0.85}.nH_2O$. X in the formula is a monovalent cation which counterbalances the layer charges. Structural formulae of clay minerals may be used to characterise these minerals. However non-monomineralic compositions may lead to distortion of these formulae [7]. Therefore to determine the structure a combination of chemical, diffraction and spectroscopic methods should be used. Diffraction methods provide information on the unit cell and long range ordering [8], yielding information on the average structure but not of the composition. For poorly diffracting minerals such as the nontronites, spectroscopic methods are much more useful. Methods such as infrared spectroscopy, Raman spectroscopy and nuclear magnetic resonance provide information about short range ordering and molecular structures.

Infrared spectroscopy has been used for a long period of time to study clay minerals [9-11]. In particular, infrared absorption techniques have been extensively used for the study of nontronites and other iron bearing clay minerals [see for example references 12-17]. One of the difficulties of using infrared KBr pellet absorption techniques is the possibility of exchange of the counter ions of the smectites with the potassium of the KBr discs which are made under pressure. Other absorption techniques such as self-supporting films and depsoits on windows avoid this difficulty. Both the techniques of diffuse reflectance (DRIFT) and infrared emission spectroscopy (IES) also avoid this difficulty. Infrared emission spectroscopy allows the possibility of studying the dehydroxylation and phase changes of minerals at elevated temperatures. The technique of measurement of discrete vibrational frequencies *emitted* by thermally excited molecules, known as Fourier transform Infrared Emission

Spectroscopy (FTIR ES), has not been widely used for the study of mineral structures [see for example references 18-22]. The major advantages of IES are that the samples are measured *in situ* at *elevated temperatures* and IES requires no sample treatment other than making the smectite sample of submicron particle size. Most of the smectite samples studied are of this size naturally. Further, the technique removes the difficulties of heating the sample to dehydroxylation temperatures and quenching before measurement, as IES measures the dehydroxylation process as it is actually taking place. Here in this paper we report the changes in the infrared spectrum upon thermal treatment of a series of nontronites using the FTIR ES technique.

## 2.    Materials and Methods

### 2.1    Nontronite Clay Minerals.

The clay minerals used are the wards Natural Science establishment: Garfield nontronite from Whitman County, Washington, USA labelled as API-H33a, or sometimes #33a [23], and Clay Mineral Society standard: the nontronite NG-1 from Hohen-Hagen, Germany [24].  This latter nontronite is no longer obtainable and there is a need for a nontronite clay to replace this standard.  The two Australian samples are from Uley Graphite Mine, Eyre Peninsula, South Australia. The calcium exchanged, < 2 μm portions, were used [25]. Samples were analysed for purity by X-ray diffraction.  Infrared spectroscopy was also used to detect low levels of other phases, particularly kaolinite and amorphous phases.  The Uley green nontronite (NAu-1) sample contained traces of kaolinite and the Uley brown nontronite (NAu-2)

contained calcite and ferrihydrite. The contaminants were at very low levels and were not detected by XRD.

The Garfield nontronite has a formula $(M^+_{1.07})[Al_{0.23}Fe_{3.71}Mg_{0.03}]$ $[Si_{7.03}Al_{0.97}]O_{20}(OH)_4$ (Manceau et al., 2000a,b). 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 Uley Green (NAu-1) nontronite 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 brown (NAu-2) nontronite has a formula of $[M^+_{0.83}]\,[Al_{0.42}Fe_{3.43}Mg_{0.04}]$ $[Si_{7.52}Al_{.06}Fe_{.42}]\,O_{20}(OH)_4$. Nontronites contain Fe predominantly in the trivalent state [26-29] The above analyses were based upon the results conducted on ignited, Ca-saturated purified fractions (nominally <0.2 μm) of each nontronite.

## 2.2   Infrared Absorption Spectroscopy.

Absorption spectra were obtained using a Perkin-Elmer Fourier transform infrared spectrometer (2000) equipped with a TGS detector.  Spectra were recorded by accumulating 1024 scans at 4 $cm^{-1}$ resolution and a mirror velocity of 0.3 cm/sec in the mid-IR.

## 2.3   Infrared Emission Spectroscopy.

FTIR emission spectroscopy was carried out on a Digilab FTS-60A spectrometer equipped with a TGS detector, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission

experiment have been published elsewhere [18]. Approximately 0.2 mg of dried nontronite was spread as a thin layer (approximately 0.2 microns) on a 6 mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating. The infrared emission cell consists of a modified atomic absorption graphite rod furnace, which is driven by a thyristor-controlled AC power supply capable of delivering up to 150 amps at 12 volts. A platinum disk acts as a hot plate to heat the smectite sample and is placed on the graphite rod. An insulated 125-$\mu$m type R thermocouple was embedded inside the platinum plate in such a way that the thermocouple junction was <0.2 mm below the surface of the platinum. Temperature control of $\pm$ 2°C at the operating temperature of the smectite sample was achieved by using a Eurotherm Model 808 proportional temperature controller, coupled to the thermocouple. The design of the IES facility is based on an off axis paraboloidal mirror with a focal length of 25 mm mounted above the heater capturing the infrared radiation and directing the radiation into the spectrometer. The assembly of the heating block, and platinum hot plate is located such that the surface of the platinum is slightly above the focal point of the off axis paraboloidal mirror. By this means the geometry is such that approximately 3 mm diameter area is sampled by the spectrometer. The spectrometer was modified by the removal of the source assembly and mounting a gold-coated mirror, which was drilled through the centre to allow the passage of the laser beam. The mirror was mounted at 45°, which enables the IR radiation to be directed into the FTIR spectrometer.

In the normal course of events, three sets of spectra are obtained: firstly the black body radiation over the temperature range selected at the various temperatures, secondly the platinum plate radiation is obtained at the same temperatures and thirdly

the spectra from the platinum plate covered with the sample.  Normally only one set of black body and platinum radiation is required. The emittance spectrum at a particular temperature was calculated by subtraction of the single beam spectrum of the platinum backplate from that of the platinum + sample, and the result ratioed to the single beam spectrum of an approximate blackbody (graphite).  This spectral manipulation is carried out after all the spectral data has been collected.  The emission spectra were collected at intervals of 50°C over the range 200 - 750 °C.   The time between scans (while the temperature was raised to the next hold point) was approximately 100 seconds.  It was considered that this was sufficient time for the heating block and the powdered sample to reach temperature equilibrium.  The spectra were acquired by coaddition of 64 scans for the whole temperature range (approximate scanning time 45 seconds), with a nominal resolution of 4 cm$^{-1}$. Good quality spectra can be obtained providing the sample thickness is not too large.  If too large a sample is used then the spectra become difficult to interpret because of the presence of combination and overtone bands. Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the Spectracalc software package (Galactic Industries Corporation, Salem, NH, USA).

*2.4    DTA/TGA.*

Differential thermal and thermogravimetric analyses of the <2 μ nontronites were obtained using a Setaram DTA/TGA instrument operating at 1.0°C per minute from ambient temperatures to 700°C.

## 3.    Results and discussion

Two nontronites from Hohen-Hagen and Garfield have been extensively used as reference clays [15] but are becoming very difficult to obtain.  Recently, two nontronites were discovered at the Uley Graphite mine near Port Lincoln, South Australia, within heavily weathered granulite facies schist, gneiss and amphibolite of Palaeoproterozoic age [25]. Geologic evidence indicates two distinct nontronites are present: a green nontronite associated with weathered biotite schist bands, and a brown nontronite filling joints and fractures within the amphibolite composed of anorthite and highly altered alumino-ferro-hornblende [25]. Preliminary mineralogical and chemical analyses support this finding and indicate that the Uley green nontronite is similar in chemistry and structure to the Garfield nontronite, whereas the Uley brown nontronite appears to be significantly lower in aluminium and possibly contains tetrahedrally coordinated iron [25]. This makes this nontronite closer to the Hohen-Hagen nontronite.

The minerals were selected to provide a range of total $Fe^{3+}$ and Al contents. The Fe contents (ignited, $Fe_2O_3$ basis) are: Uley green 36.49; Garfield 36.4; NG-1, 37.5%; Uley brown 38.1.  The aluminium content of the Garfield nontronite 7.54 % and NG-1 nontronite 6.06 %.   The aluminium content of the Uley green nontronite and of the Uley brown sample are 8.15 % and 3.02 %. It should be noted that NG-1 and the Uley brown nontronite each contains significant amounts of ferric iron in the tetrahedral sheet.  However each of the nontronites studied here contain most of the iron as ferric iron in the octahedral sheet. Thus, based on chemical composition, the Uley smectites are members of the smectite series in which the octahedral aluminium

has been replaced by octahedral ferric iron.  It should be noted some of the Fe (≈18%) is incorporated in the tetrahedral sheets.  Nontronites contain Fe predominantly in the trivalent state. Most of the layer charge originates from the tetrahedral layer with negative 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 [27].  The two minerals are very similar in formulation, the major difference being in the iron content.

*Infrared absorption spectroscopy of the hydroxyl-stretching region.*

Figure 1 displays the infrared absorption spectra of the nontronites and the results of the band component analyses are reported in Table 1. For the Garfield nontronite bands are observed at 3575, 3424, 3251 and 3036 cm$^{-1}$ with relative intensities of 21.1, 34.9, 24.8 and 19.0 %.  Some variation in both the band position and intensities between the nontronites is observed.  Infrared absorption bands are observed for the Uley brown nontronite at 3572, 3430 and 3262 cm$^{-1}$ with relative intensities of 22.3, 39.0 and 24.9% and for the Uley green nontronite at 3567, 3426 and 3255 cm$^{-1}$ with 21.9, 50.5 and 23.5 % relative intensity. For the Hohen-Hagen nontronite, bands are observed at 3598, 3439 and 3221 cm$^{-1}$ with 12.5, 55.8 and 29.9 % relative intensity.  The infrared absorption spectra of the Uley nontronites more closely follow that of the Garfield nontronite than that of the Hohen-Hagen nontronite.

The bands at around 3560-3570 $cm^{-1}$ in the spectra of the three nontronites are assigned to the hydroxyl stretching vibration of the FeFeOH unit. The relative intensity of this band is greatly influenced by the band at ~3420 $cm^{-1}$ which is attributed to the hydroxyl stretching frequency of water from the hydrated calcium in the interlayer structure. Thus the relative intensity of the hydroxyl-stretching band of the FeFeOH unit is effected by the amount of water in the nontronites. The band at around 3240 $cm^{-1}$ may be ascribed to the overtone of the HOH water bending vibration observed at 1630 $cm^{-1}$. In the spectra of the hydroxyl-stretching region of ferruginous smectites a hydroxyl stretching frequency at around 3590 $cm^{-1}$ is observed which is attributed to the AlFeOH unit. However because of the extremely low Al content of these three nontronites, this band is not observed.

In the study of the vibrational spectra of kaolinites, the vibrations of the hydroxyl units function cooperatively as in-phase and out of phase vibrations. The question arises as to whether the FeFeOH and AlFeOH units cooperate as in-phase and out of phase vibrations. The band at 3240 $cm^{-1}$ may be interpreted as the out of phase vibration of the in phase vibration at 3400 $cm^{-1}$ rather than the overtone of the water bending vibration at 1630 $cm^{-1}$.

*3.1    Infrared emission spectroscopy of the hydroxyl-stretching region.*

The infrared emission spectra of the Garfield nontronite and the Uley green and brown nontronites are shown in Figures 2-4. A comparison of the spectral frequencies of the hydroxyl-stretching for the three nontronites is reported in Table 2.

The spectra show the presence of water vapour. This is observed by the superimposition of the high frequency in the 1400 to 1700 and 3300 to 3900 $cm^{-1}$ region. This water vapour is a result of the loss of the hydration water and is more pronounced in the low temperature IES spectra at 200 and 250 °C. Bands observed in the 2950 $cm^{-1}$ region are due to the presence of organics. Three hydroxyl-stretching frequencies for the Garfield nontronite are observed in the 200 °C spectrum at 3692, 3574, and 3478 $cm^{-1}$. The latter two bands may correspond with the two Raman bands observed at 3574 and 3436 $cm^{-1}$. However it is probable that these are two different vibrational modes. The Uley brown nontronite shows three bands at 3727, 3574, and 3416 $cm^{-1}$ in the 200 °C spectrum. For Uley green nontronite three bands are observed at 3690, 3585, and 3458 $cm^{-1}$. All three nontronites have a common emission band at 3574 $cm^{-1}$, which is assigned to the FeFeOH hydroxyl-stretching vibration. The IES band at around 3700 $cm^{-1}$ is also common to the nontronites and is attributed to FeAlOH stretching vibrations. Another possibility for bands in this position is the attribution to SiOH stretching vibrations. It is not uncommon to observe SiOH vibrations in the 3700 to 3750 $cm^{-1}$ region [18]. At the lower temperatures for emission spectroscopy (200 and 250 °C), bands are also observed at the 3440 and 3200 $cm^{-1}$ positions. The spectra from and above 300 °C, do not show bands in these positions.

The intensity of the 3560 $cm^{-1}$ band decreases as a function of temperature and mimics the dehydroxylation of nontronites as determined by thermal analysis techniques. Dehydroxylation takes place between 400 and 450 °C, when no intensity remains in the hydroxyl-stretching bands. Figure 5 displays the variation of relative intensity of the three nontronites as a function of temperature. The loss of intensity of

the Uley green and Garfield nontronites as a function of temperature are similar. It would appear that the loss of intensity is continuous rather than stepped as with a TGA pattern. The TGA pattern for the three nontronites over the same temperature range is shown in Figure 6. Little difference can be observed in the TGA patterns for these three nontronites. A very small perceptible weight change may be observed for the Uley brown nontronite at around 250 °C. It is thought that this weight change is due to the presence of an impurity of ferrihydrite. The reason why there is a difference between the intensity-temperature graphs and the TGA curves may be attributed to the way in which the experiment is carried out. The IES experiment is a step process in which the temperature is ramped to the next temperature and then there is a time arrest before collecting the spectral data. The TGA experiment is a continuous experiment with a constant increase in temperature with time.

Figure 7 reports the DTA patterns of the dehydroxylation of the nontronites over the 200 to 600 °C temperature range. The DTA patterns are in good harmony with both the TGA and the decrease in intensity patterns. The DTA patterns show a second endotherm at around 580 °C. This endotherm is not related to the dehydroxylation of the nontronites since no intensity remains in the infrared spectrum of the hydroxyl stretching bands at this temperature. It is suggested that this endotherm is related to a phase change of the dehydroxylated nontronites.

*3.2    Infrared spectroscopy of the Low frequency region.*

The results of the absorption spectra of the low frequency region are reported in Table 2. Bands in this region may be attributed to (a) SiO stretching vibrations.

These vibrations are in the 900 to 1100 cm$^{-1}$ region and are ascribed to FeSiO and SiO

units [14,27] (b) The 815-860 cm$^{-1}$ region [27]. These bands are attributed to the

hydroxyl-deformation of the FeFeOH unit. (c) Bands in the 520 to 600 cm$^{-1}$ region.

These bands are attributed to FeFeOH hydroxyl translational modes. (d) Bands

observed around 430 and 490 cm$^{-1}$ are attributed to the SiOFe lattice flexing

vibrations. Bands which are observed at 780 and ~816 cm$^{-1}$ are attributable to traces

of quartz impurities. Table 2 shows a comparison of the infrared absorption and low

frequency bands of nontronite. Figures 3-5 show the low frequency region of the

three nontronites and the results of the band component analysis are shown in Table 4.

The lower detection limit in the IES spectra is 450 cm$^{-1}$. As a consequence bands

measured in the absorption spectra are not observed in the IES spectra. The

conclusion may be drawn that the spectra of the low frequency region are very

similar. Further the IES spectra show strong resemblance to the absorption spectra.

The analyses show bands are observed in similar positions for each of the nontronites.

The Uley nontronite shows a broad band at around 1450 cm$^{-1}$. This band is attributed

to the presence of fine particles of calcite. The band starts to disappear at 400 °C and

no intensity remains at 600 °C.


Of particular importance in the IES spectra, is the observation of bands in the

770 to 870 cm$^{-1}$ region. This spectral region shows the hydroxyl deformation region

and the assignment of bands in this region characterises the chemistry and formulation

of the nontronites. The Garfield nontronite shows bands at 870, 844, 817 and 778

cm$^{-1}$. The 870 cm$^{-1}$ band is assigned to the hydroxyl deformation of the AlFeOH unit.

The two bands at 844 and 817 cm$^{-1}$ are attributed to the FeFeOH hydroxyl

deformation. It is not known why two hydroxyl bands are observed for the FeFeOH

unit. One possibility is that some form of cis-trans isomerisation of this unit exists. This band has disappeared by 350 °C. This observation fits well the decrease in intensity of the hydroxyl stretching vibration at 3570 cm$^{-1}$. Here the IES spectra showed a continuous decease in intensity. The band at 778 cm$^{-1}$ is attributed to the MgFeOH deformation. The IES spectra of the Uley green nontronite shows bands at 870, 844, 819 and 777 cm$^{-1}$. The attribution of the bands is the same for all the nontronites. However the spectra clearly show intensity differences for the 844 and 819 cm$^{-1}$ bands. The Uley brown nontronite IES spectra clearly show bands at 870, 840, 820 and 785 cm$^{-1}$. Significantly for the Uley brown nontronite, the band at 785 cm$^{-1}$ shows increased intensity compared with the other nontronites. This band is attributed to the MgFeOH unit hydroxyl deformation. The increased intensity of this band reflects the higher Mg content in the octahedral position. The Hohen-Hagen nontronite spectra show bands at 870, 842, 820 and 788 cm$^{-1}$. This nontronite also shows intensity in the band at 785 cm$^{-1}$ [28]. The reason why this band occurs at such low frequencies is that the FeMg pairs sharing OH are preferentially along 010 plane with the OH vector extending in the 100 towards the dioctahedral vacancy. The band is present in both the Garfield and Uley green nontronites but is of very low intensity. A band is observed in all the spectra at ~680 cm$^{-1}$ and is attributed to the bending vibration of the SiOFe unit.

The role of water in smectites often controls their physio-chemical behaviour for example clay rheology. Infrared spectroscopy is one of the best methods for determining the presence of water through the observation of the water HOH bending mode at 1630 cm$^{-1}$. Thermal analysis shows that water can be difficult to remove from smectites and water coordinating to the interlayer cation may not come off until

~330 °C. Infrared absorption spectroscopy shows a broad band centred on 1630 cm$^{-1}$ with a component at ~1675 cm$^{-1}$. Two different types of water are identified by the presence of these two bands namely hydrogen bonded water and water coordinated to the interlayer cations. Table 5 reports the analysis of the water bending vibration in the infrared emission spectra for the nontronites as a function of temperature. For each of the nontronites three water bending vibrations are identified: a high frequency band at around 1680 cm$^{-1}$ attributed to water coordinated to the interlayer cation, a normal frequency band at ~1650 cm$^{-1}$ attributed to interlayer water and the low frequency band at 1595 cm$^{-1}$ assigned to non-hydrogen bonded water. The IES spectra show the presence of water up to 400 °C. This water may arise from the water in the hydration sphere of the interlayer cation and the water could also come from the dehydroxylation of the nontronite itself. The frequencies of the water bending modes move to higher wavenumbers with increasing temperature.


4.      **Conclusions**


No difference was observed between the absorption and emission spectra of the nontronites. The nontronites are characterised by three bands in the hydroxyl-stretching region with the band at 3570 cm$^{-1}$ assigned to the hydroxyl stretching vibration of the FeFeOH unit. Dehydroxylation of nontronites has been determined using both DTA/TGA methods and infrared emission spectroscopy. Infrared emission spectroscopy shows that the dehydroxylation is a temperature-continuous process with the significant loss of intensity of the hydroxyl stretching vibrations in the 400 to 500°C temperature range.

Importantly the technique of infrared emission spectroscopy enables the spectra of the nontronites at elevated temperatures to be determined. Further the IES spectra of the Uley green nontronite are identical to that of the Garfield nontronite. The Uley brown nontronite appears to be intermediate between the Garfield and Hohen-Hagen nontronites in terms of spectroscopy. Thus it is concluded that the Uley nontronites are worthwhile nontronite clay minerals, which might replace both the Garfield and Hohen-Hagen nontronites, which are no longer available, at least from a vibrational spectroscopy point of view.

**Acknowledgments**

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| Nontronites | Infrared Absorbance | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ |
|---|---|---|---|---|---|
| | Suggested Assignments | Hydroxyl stretch of FeFeOH unit | OH stretch of water | First overtone of the HOH bend of water | Possible difference band |
| Hohen-Hagen | Band Centre/cm$^{-1}$<br>Relative Intensity/% | 3598<br>12.5 | 3439<br>55.8 | 3221<br>29.8 | 2935<br>1.7 |
| Garfield | Band Centre/cm$^{-1}$<br>Relative Intensity/% | 3575<br>21.1 | 3424<br>34.9 | 3251<br>24.9 | 3036<br>19.0 |
| Uley brown | Band Centre/cm$^{-1}$<br>Relative Intensity/% | 3572<br>21.9 | 3430<br>50.5 | 3262<br>23.5 | 3043<br>4.0 |
| Uley green | Band Centre/cm$^{-1}$<br>Relative Intensity/% | 3566<br>22.3 | 3426<br>39.0 | 3256<br>24.9 | 2998<br>13.7 |

**Table 1 Infrared absorption bands of the hydroxyl-stretching region of nontronite**

**Table 2 Infrared absorption and emission bands of nontronite**

| Infrared absorption spectroscopy | | | | Infrared emission spectroscopy (200 °C) | | | | Suggested Assignments |
|---|---|---|---|---|---|---|---|---|
| Garfield Nontronite | Uley Green | Uley Brown | Hohenhagen, Germany 32.2% Fe | Garfield Nontronite | Uley Green | Uley Brown | Hohenhagen, Germany 32.2% Fe | |
| 3575 | 3572 | 3572 | 3598 | 3573 | 3585 | 3574 | 3597 | FeFeOH stretch |
| | | | | 3478 | 3463 | 3460 | 3432 | OH stretch of water |
| 3424 | 3426 | 3430 | 3439 | | 3430 | 3416 | | OH stretch of water |
| 3251 | 3255 | 3262 | 3221 | | | | 3232 | First overtone of HOH bending |
| 3036 | 3036 | 3036 | 3036 | | | 3067 | 3047 | Combination band |
| 1670 1630 | 1670 1630 | 1670 1630 | 1670 1630 | 1647 1580 | 1650 1590 | 1680 1642 1580 | 1628 | HOH bending |
| | | | | 1206 | 1226 | | | |
| 1132 | 1131 | 1131 | | 1136 | 1165 | 1131 | | SiO stretch |
| 1093 | 1093 | 1093 | 1092 | 1070 | 1105 | 1104 | 1077 | SiO stretch |
| 1032 | 1333 | 1333 | 1032 | | 1003 | 1037 | 1039 | FeSiO stretch |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 973 | 972 | 972 | 972 | 974 | 928 | 970 | | SiO stretch |
| 879 | 880 | 880 | 879 | 893 | | 894 | 880 | AlFeOH deformation |
| | | | | 841 | | 841 | | FeFeOH deformation |
| 778 | 777 | 777 | 795 | 804 | 812 | 815 | 793 | Quartz impurity |
| 755 | 755 | 755 | | | | | 788 | MgFeOH deformation |
| 680 | 680 | 680 | 680 | 671 | 673 | 676 | 693 | |
| 656 | 655 | 655 | | | | | | |
| 588 | 568 | 568 | | 580 | 593 | 590 | | FeOSi bend |
| 547 | 547 | 547 | | 478 | 481 | 494 | 487 | SiOFe bend |
| 450 | 450 | 450 | 463 | | | | 458 | SiOSi bend (463 is quartz impurity) |
| 429 | 428 | 428 | 429 | | | | | SiOFe bend Octahedral Fe |

**Table 3 Bands of the hydroxyl-stretching region of the infrared emission spectra of Garfield nontronite, Uley brown nontronite, Uley green nontronite as a function of temperature.**

| Nontronites | | Temp/ $^0$C | 200 | 250 | 300 | 350 | 400 | 450 | 500 |
|---|---|---|---|---|---|---|---|---|---|
| Garfield | Band Centre/cm$^{-1}$ | $\nu_1$ | 3692 | 3699 | 3687 | 3684 | 3697 | 3706 | 3709 |
| | Relative Intensity/% | | 6.7 | 23.7 | 22.0 | 21.2 | 9.4 | 8.7 | 9.5 |
| | Band Centre/cm$^{-1}$ | $\nu_2$ | 3574 | 3572 | 3572 | 3570 | 3567 | 3584 | 3612 |
| | Relative Intensity/% | | 38.2 | 29.4 | 34.0 | 33.0 | 31.6 | 25.4 | 18.2 |
| | Band Centre/cm$^{-1}$ | $\nu_3$ | 3478 | 3512 | 3523 | 3518 | 3452 | 3427 | 3440 |
| | Relative Intensity/% | | 35.7 | 16.3 | 19.7 | 18.8 | 47.8 | 47.9 | 45.0 |
| | Band Centre/cm$^{-1}$ | $\nu_4$ | | 3389 | 3433 | 3418 | | | |
| | Relative Intensity/% | | | 19.0 | 13.9 | 19.7 | | | |
| Uley brown | Band Centre/cm$^{-1}$ | $\nu_1$ | 3727 | 3714 | 3735 | 3710 | 3708 | | |
| | Relative Intensity/% | | 26.2 | 4.8 | 24.9 | 17.8 | 13.7 | | |
| | Band Centre/cm$^{-1}$ | $\nu_2$ | 3574 | 3576 | 3576 | 3578 | 3580 | | |
| | Relative Intensity/% | | 49.1 | 86.6 | 72.0 | 73.6 | 66.8 | | |
| | Band Centre/cm$^{-1}$ | $\nu_3$ | 3460 | 3450 | | | 3430 | | |
| | Relative Intensity/% | | 2.0 | 2.0 | | | 9.4 | | |
| | Band Centre/cm$^{-1}$ | $\nu_4$ | 3416 | 3390 | | | | | |
| | Relative Intensity/% | | 19.0 | 6.2 | | | | | |
| Uley green | Band Centre/cm$^{-1}$ | $\nu_1$ | 3690 | 3692 | 3645 | 3671 | 3676 | | |
| | Relative Intensity/% | | 29.0 | 36.8 | 57.8 | 14.4 | 16.0 | | |
| | Band Centre/cm$^{-1}$ | $\nu_2$ | 3585 | 3574 | 3571 | 3575 | 3572 | | |
| | Relative Intensity/% | | 48.2 | 46.7 | 35.6 | 49.4 | 49.5 | | |
| | Band Centre/cm$^{-1}$ | $\nu_3$ | 3458 | 3466 | 3468 | 3473 | 3455 | | |
| | Relative Intensity/% | | 43.8 | 16.5 | 6.6 | 27.3 | 25.4 | | |
| | Band Centre/cm$^{-1}$ | $\nu_4$ | | | | 3351 | 3347 | | |
| | Relative Intensity/% | | | | | 8.9 | 9.0 | | |

**Table 4 Table of the low frequency region of the infrared emission spectra of Garfield nontronite and Uley brown and green nontronites.**

| Nontronite | Temp/°C | 200 | 250 | 300 | 350 | 400 | 450 | 500 | 550 | 600 | 650 | 700 | 750 | 800 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Garfield | $\nu_1$ | 1206 | 1216 | 1219 | 1217 | 1217 | 1218 | 1216 | 1210 | 1205 | 1201 | 1192 | 1193 | 1199 |
| | $\nu_2$ | 1136 | 1143 | 1146 | 1148 | 1151 | 1154 | 1154 | 1149 | 1142 | 1135 | 1117 | 1107 | 1109 |
| | $\nu_3$ | 1070 | 1071 | 1073 | 1074 | 1074 | 1075 | 1075 | 1069 | 1059 | 1050 | 1036 | 1021 | 1018 |
| | $\nu_4$ | 974 | 973 | 972 | 971 | 972 | 971 | 970 | 961 | 952 | 946 | 938 | 939 | 939 |
| | $\nu_5$ | 893 | 897 | 896 | 892 | 888 | 882 | 881 | 869 | 858 | 855 | 871 | 873 | 876 |
| | $\nu_6$ | 841 | 841 | 841 | 841 | 841 | | | | | | | | |
| | $\nu_7$ | 804 | 806 | 806 | 812 | 817 | 817 | 813 | 807 | 802 | 799 | 806 | 805 | 805 |
| | $\nu_8$ | 671 | 671 | 670 | 670 | 671 | 672 | 672 | 671 | 671 | 671 | 670 | 671 | 670 |
| | $\nu_9$ | 597 | 597 | 596 | 597 | 599 | 601 | 599 | 587 | 587 | 572 | 587 | 585 | 599 |
| | $\nu_{10}$ | 580 | 580 | 580 | 580 | 580 | 578 | 570 | 541 | 538 | | | | |
| | $\nu_{11}$ | 555 | 553 | 554 | 554 | 553 | 537 | 528 | 515 | 514 | 528 | 529 | 527 | 524 |
| | $\nu_{12}$ | 518 | 515 | 519 | 520 | 514 | 504 | 503 | 500 | 501 | 505 | 506 | 506 | 508 |
| | $\nu_{13}$ | 478 | 478 | 479 | 483 | 487 | 489 | 491 | 492 | 494 | | | | |
| Uley Brown | $\nu_1$ | 1131 | 1131 | 1131 | 1131 | 1133 | 1134 | 1134 | 1146 | 1147 | 1161 | 1172 | 1174 | 1178 |
| | $\nu_2$ | 1104 | 1104 | 1103 | 1103 | 1102 | 1102 | 1102 | 1094 | 1097 | 1095 | 1101 | 1100 | 1101 |
| | $\nu_3$ | 1037 | 1036 | 1036 | 1036 | 1039 | 1039 | 1040 | 1060 | 1050 | 1027 | 1028 | 1027 | 1028 |
| | $\nu_4$ | 970 | 969 | 968 | 968 | 968 | 967 | 967 | 967 | 964 | 942 | 942 | 941 | 942 |
| | $\nu_5$ | 894 | 901 | 902 | 904 | 901 | 900 | 899 | 888 | 890 | | | | |
| | $\nu_6$ | 841 | | | | 849 | 852 | 853 | 864 | 859 | 869 | 869 | 869 | 869 |
| | $\nu_7$ | 815 | 829 | 832 | 830 | | | | | | 791 | 784 | 782 | 776 |
| | $\nu_8$ | 676 | 674 | 674 | 675 | 675 | 675 | 675 | 675 | 675 | 675 | 675 | 674 | 673 |
| | $\nu_9$ | 605 | 598 | 598 | 599 | 600 | 601 | 601 | 602 | 602 | 603 | 602 | 602 | 602 |
| | $\nu_{10}$ | 590 | | | | | | | | | 540 | 544 | 541 | 544 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\nu_{11}$ | 545 | 543 | 540 | 538 | 535 | 531 | 533 | 533 | 528 | 522 | 525 | 526 | 525 |
| | $\nu_{12}$ | 513 | 504 | 504 | 510 | 517 | 516 | 517 | 517 | 517 | | | | |
| | $\nu_{13}$ | 494 | | | | | | | | | | | | |
| Uley Green | $\nu_1$ | 1227 | 1225 | 1224 | 1221 | 1220 | 1220 | 1220 | 1220 | 1221 | 1221 | 1221 | 1221 | 1221 |
| | $\nu_2$ | 1165 | 1164 | 1167 | 1166 | 1167 | 1167 | 1167 | 1167 | 1167 | 1167 | 1167 | 1167 | 1167 |
| | $\nu_3$ | 1105 | 1104 | 1106 | 1107 | 1107 | 1107 | 1107 | 1107 | 1107 | 1107 | 1107 | 1107 | 1107 |
| | $\nu_4$ | 1003 | 1007 | 1006 | 1005 | 1005 | 1005 | 1006 | 1006 | 1005 | 1005 | 1005 | 1005 | 1005 |
| | $\nu_5$ | 928 | 929 | 931 | 931 | 931 | 931 | 930 | 930 | 930 | 930 | 930 | 930 | 930 |
| | $\nu_6$ | | | | | | | | 895 | 895 | 895 | 895 | 895 | 895 |
| | $\nu_7$ | 815 | 813 | 811 | 813 | 814 | 814 | 814 | 805 | 805 | 805 | 805 | 805 | 805 |
| | $\nu_8$ | 673 | 673 | 673 | 674 | 674 | 674 | 674 | 675 | 675 | 675 | 675 | 675 | 675 |
| | $\nu_3$ | 593 | 593 | 591 | 579 | 572 | 572 | 572 | 572 | 572 | 572 | 572 | 572 | 572 |
| | $\nu_9$ | 481 | 481 | 478 | 479 | 479 | 479 | 479 | 479 | 479 | 479 | 479 | 479 | 479 |

**Table 5 Bands of the water-bending region of the infrared absorption spectra of nontronites from (a) Hohen-Hagen (b) Garfield (c) Uley brown (d) Uley green**

| Nontronites | | Temperature/$^0$C | 200 | 250 | 300 | 350 | 400 |
|---|---|---|---|---|---|---|---|
| Garfield | Band Centre/cm$^{-1}$ Relative Intensity/% | $\nu_1$/cm$^{-1}$ % | | 1666 45 | 1680 25 | 1690 13 | 1690 10 |
| | Band Centre/cm$^{-1}$ Relative Intensity/% | $\nu_2$ | 1647 75 | | 1647 10 | 1652 21 | 1650 20 |
| | Band Centre/cm$^{-1}$ Relative Intensity/% | $\nu_3$ | 1595 25 | 1595 55 | 1590 65 | 1575 66 | 1570 70 |
| Uley brown | Band Centre/cm$^{-1}$ Relative Intensity/% | $\nu_1$ | 1680 5 | 1684 12 | 1680 27 | 1690 7 | 1690 5 |
| | Band Centre/cm$^{-1}$ Relative Intensity/% | $\nu_2$ | 1653 43 | 1643 51 | 1640 18 | 1638 45 | 1637 28 |
| | Band Centre/cm$^{-1}$ Relative Intensity/% | $\nu_3$ | 1610 7 | | | | |
| | Band Centre/cm$^{-1}$ Relative Intensity/% | $\nu_4$ | 1560 32 | 1567 18 | 1570 55 | 1565 41 | 1560 51 |
| Uley green | Band Centre/cm$^{-1}$ Relative Intensity/% | $\nu_1$ | | | | 1674 26 | |
| | Band Centre/cm$^{-1}$ Relative Intensity/% | $\nu_2$ | 1650 72 | 1653 79 | 1659 53 | 1632 11 | |
| | Band Centre/cm$^{-1}$ Relative Intensity/% | $\nu_3$ | 1585 15 | 1570 21 | 1570 39 | 1567 6 | |

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Figure 1 Infrared absorption spectra of the hydroxyl-stretching region of (a) Garfield (b) Uley green and (c) Uley brown nontronites.

Figure 2 Infrared emission spectra of Garfield nontronite from 200 to 800 °C at 50 °C intervals.

Figure 3 Infrared emission spectra of Uley green nontronite from 200 to 800 °C at 50 °C intervals.

Figure 4 Infrared emission spectra of Uley brown nontronite from 200 to 800 °C at 50 °C intervals.

Figure 5 Variation in the relative intensity of the 3570 cm$^{-1}$ band as a function of temperature for (a) Garfield (b) Uley green (c) Uley brown nontronites.

Figure 6 Thermogravimetric patterns for (a) Garfield (b) Uley green (c) Uley brown nontronites.

Figure 7 DTA patterns for (a) Garfield (b) Uley green (c) Uley brown nontronites.

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Table 2 Infrared absorption and emission bands of nontronite

Table 3 Table of the hydroxyl-stretching region of the infrared emission spectra of Garfield nontronite, Uley brown nontronite, Uley green nontronite as a function of temperature.

Table 4 Bands of the low frequency region of the infrared emission spectra of Garfield nontronite and Uley brown and green nontronites, as a function of temperature.

Table 5 Bands of the water-bending region of the infrared absorption spectra of nontronites from (a) Hohen-Hagen (b) Garfield (c) Uley brown (d) Uley green