Near Infrared spectroscopic study of selected hydrated hydroxylated phosphates

Ray L. Frost*

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Published as:

Copyright 2004 Elsevier

Abstract

Near infrared spectroscopy has been applied to a suite of hydrated hydroxylated phosphate minerals including cacoxenite, hureaulite, planerite, gormanite and wardite. The NIR spectra may be conveniently divided into three regions (a) the first hydroxyl fundamental (b) the water HOH overtone and (c) the region between 4000 and 4800 cm\(^{-1}\) where combination bands resulting from the bands in the mid-IR. For each of these regions, the minerals show distinctive spectra which enable their identification and characterisation. NIR spectroscopy is a less used technique which does have great application for the study of minerals, particularly minerals which have hydrogen in the structure either as hydroxyl units or as water bonded to the cation or as zeolitic water as is the case for cacoxenite. The study of minerals on planets is topical and NIR spectroscopy provides a rapid technique for the distinction and identification of minerals.

Key Words- cacoxenite, hureaulite, planerite, gormanite, strengite, variscite, combination bands, difference bands, DRIFT, mid-infrared, near-infrared, Raman.

1. Introduction

There are a considerable number of techniques that are available to the mineral scientist for obtaining molecular information. These techniques include both Raman and infrared spectroscopy. Among the infrared spectroscopic techniques, there are (a) the absorption (KBr) technique, (b) the infrared emission technique (IES), (c) the reflectance techniques including diffuse and specular reflectance, (d) attenuated total reflectance (ATR), (e) infrared microscopy and (f) photoacoustic FTIR spectroscopy (PAS). In particular the selection of the technique depends on the particular problem in hand. For example infrared emission spectroscopy is suitable for studying dehydroxylation and the thermal changes in minerals at the elevated temperatures. The pressing of a KBr pellet with minerals may alter the spectrum through absorption or exchange of the potassium into the clay structure. ATR is useful for powders but is limited by the signal to noise ratio determined by the energy throughput. PAS is a non-destructive technique useful for handling clays but is limited by the number of samples that may be handled in a

* Author to whom correspondence should be addressed (r.frost@qut.edu.au)
given period of time. Specular reflectance is not readily applicable to clay minerals as the technique normally applies to flat, shiny polished surfaces although specular infrared reflectance studies have been used to study thermally treated Li and Cs montmorillonites. The diffuse reflectance technique (DRIFT) is more applicable to powders but is limited to some extent by the Restrahlen effects where the particle size and the incident infrared wavelengths create interference effects. Such effects are minimised by mixing the mineral with KBr at the 5% level. The advantage of using the DRIFT technique is that it provides a rapid technique for analysing samples without any interference through sample preparation. The DRIFT technique avoids the possibility of ion exchange of the potassium ion and non-randomly oriented samples. The technique is particularly useful where the Restrahlen effects are minimal. These effects appear towards the low frequency region normally below 1000 cm⁻¹. Thus the DRIFT technique lends itself to the study of the hydroxyl-stretching region of kaolinites where such effects are not observed. Further such a technique is most useful in the near-IR region.

The hydrated hydroxy phosphates have been studied for some considerable time [1-3]. The minerals include cacoxenite ((Fe³⁺,Al₂₅(PO₄)₁₇O₆(OH)₁₂·75H₂O) [4-6]; hureaulite ((Mn²⁺)₉(PO₄)₄[(PO₃(OH)]₂·4H₂O) [7, 8]; planerite (Al₆(PO₄)₂(PO₃OH)₂(OH)₆·4H₂O) [9-11]; gormanite ((Fe²⁺)₃Al₄(PO₄)₄(OH)₆·2H₂O) and wardite NaAl₃(PO₄)₄(OH)₄·2H₂O [12-14]. These minerals are of importance because of their presence in soils. Cacoxenite is a common accessory mineral found in oxidised magnetite, limonitic ores [15] and brecciated rock phosphate ores [16]. Less commonly cacoxenite can be found in Fe and Mn-bearing novaculites and some Fe-rich soils or in coastal plain sediments [17]. Cacoxenite is found in over 150 deposits around the world. Hureaulite is a late-stage secondary mineral formed by alteration of primary phosphates (e.g. monazite) in complex granite pegmatites and Li-pegmatites. Typically hureaulite forms by near-surface or low-temperature hydrothermal leaching, hydration and oxidation of triphylite–lithiophilite or some other Fe-Mn primary phosphate [18]. Planerite is formed in phosphate-rich aluminous deposits. Planerite is formed in phosphate-rich aluminous deposits and also forms in various slates deposits in Victoria where primary phosphate nodules have broken down. These occurrences of planerite are usually close to end-member composition. Typically planerite is microcrystalline and has an individual grain size of 2–4 µm [19]. Gormanite is found as low-temperature fracture fillings in phosphate ironstones in the Yukon, where it is the only phosphate secondary mineral. There gormanite is associated with quartz and siderite [20]. Gormanite has also been recorded from fractures in tonalite. Wardite is a low temperature component of phosphatic nodules and is rare in complex zoned pegmatites [21, 22]. Some of these minerals may form during the weathering of phosphate rocks and may form during the addition of phosphate fertilisers to acid soils.

In soils gelatinous hydrated hydroxy phosphates such as the minerals listed above may be formed in solution and precipitate from this solution [23]. Near IR spectroscopy provides a suitable method for the analysis of these types of materials [24-27]. The other use of near-IR spectroscopy is in the search for knowledge of minerals in the solar system [28-33]. Hunt et al. first applied NIR spectroscopy to the study of minerals [34, 35]. It should be recognised that Near-IR spectroscopy is known also as proton spectroscopy such that this type of spectroscopy is most useful
for measuring bonds involving hydrogen such as OH, NH, and CH etc. Thus the technique appears most suitable for the measurement of hydrated, hydroxylated phosphates as might be found in soils. Such gels in soils may contain mixed variable phosphate anions. [23] Such mixed phosphate species will depend upon the temperature and pH of the crystallisation. [36, 37] Such phenomena affect the chemistry of soils. [38] Thus it is important to understand the Near-IR spectroscopy of the minerals cacoxenite, hureaulite, planerite and gormanite since these minerals are formed in soils, slag wastes and other environmental situations. As part of a comprehensive study of the IR and Raman properties of minerals containing oxyanions, we report the Near-IR properties of the above named phases.

2. Experimental

2.1 Minerals
The minerals cacoxenite, hureaulite, planerite, gormanite and wardite were purchased from mineral supply companies and Australian museums. The minerals where practical, were analysed for phase purity by X-ray diffraction techniques and for composition by electron probe analyses.

2.2 DRIFT Spectroscopy:

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000 to 525 cm\(^{-1}\) range were obtained by the co-addition of 64 scans with a resolution of 4 cm\(^{-1}\) and a mirror velocity of 0.6329 cm/s. Near IR spectra were collected on a Nicolet Nexus FT-IR spectrometer with a Nicolet Near-IR Fibreport accessory. A white light source was used, with a quartz beam splitter and TEC NIR InGaAs detector. Spectra were obtained from 11 000 to 4000 cm\(^{-1}\) by the co-addition of 64 scans at a resolution of 8 cm\(^{-1}\). A mirror velocity of 1.2659 was used. The spectra were transformed using the Kubelka-Munk algorithm to provide spectra for comparison with absorption spectra.

The spectral manipulations of baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was carried out using the peakfit software by Jandel Scientific. Lorentz-Gauss cross product functions were used throughout and peak fitting carried out until squared correlation coefficients with \(R^2\) greater than \(>0.995\) were obtained.

3. Results:

For the minerals cacoxenite, gormanite, planerite, hureaulite and wardite only OH vibrations resulting from hydroxyl units or water are involved. Thus the NIR spectra will result only from these vibrations. The spectra may be conveniently divided into three regions (a) the first fundamental of the hydroxyl stretching region found in the 6000 to 7400 cm\(^{-1}\) region (b) the overtones of the water HOH stretching vibrations found in the 4600 to 5600 cm\(^{-1}\) region and (c) the OH combination region found in the 4000 to 4600 cm\(^{-1}\) region. The first fundamentals of these minerals are shown in Figure 1. The results of the spectral analysis are reported in Table 1. Even though the minerals may be classified as hydrated hydroxylated phosphate minerals,
the NIR spectra in the 6000 to 7400 cm\(^{-1}\) region are very different. Thus the individual minerals may be characterised by the NIR spectra.

The infrared spectra of the hydroxyl stretching region of the selected minerals are shown in Figure 2. The mineral cacoxenite ((Fe\(^{3+}\),Al)\(_{25}\)(PO\(_4\))\(_{17}\)O\(_6\)(OH)\(_{12}\).75H\(_2\)O) shows a broad profile in the 2500 to 3500 cm\(^{-1}\) region and such a profile is reflected in the first OH fundamental region. NIR bands may be resolved for cacoxenite at 7082, 6915, 6708 and 6650 cm\(^{-1}\). There are no well defined OH first fundamentals. It is very difficult to ascribe what bands combine to give the OH fundamentals for cacoxenite. In contrast the mineral gormanite has a well defined band at 7064 cm\(^{-1}\). A multiplicity of bands are observed in the OH stretching region of gormanite ((Fe\(^{2+}\))\(_3\)Al\(_4\)(PO\(_4\))\(_4\)(OH)\(_6\).2H\(_2\)O). In the spectra of gormanite, two sets of bands are observed. In the infrared spectra, the first set consists of three bands at 3696, 3614 and 3601 cm\(^{-1}\). The second set consists of bands at 3414, 3343, 3228 and 3027 cm\(^{-1}\). The first set of bands are assigned to MOH stretching vibrations where M is Al\(^{3+}\), Fe\(^{2+}\) or even Fe\(^{3+}\). The bands at 3614 and 3696 cm\(^{-1}\) are assigned to AlOH stretching vibrations and the band at 3601 cm\(^{-1}\) to FeOH stretching vibrations. The second set of bands is attributed to the OH stretching bands of water in the gormanite structure. In NIR spectroscopy fundamentals can occur from both Raman and infrared stretching vibrations and not only the doubling of the mid-IR stretching band. The band at 7064 cm\(^{-1}\) is likely to be the sum of two of the OH stretching vibrations.

The mineral planerite (Al\(_6\)(PO\(_4\))\(_2\)(PO\(_3\)OH)\(_2\)(OH)\(_8\).4H\(_2\)O) shows NIR bands in the OH first fundamental region at 7032, 6986, 6839, 6769, 6751 and 6544 cm\(^{-1}\). OH stretching bands are observed at 3592, 3550, 3507, 3466, 3446, 3310, 3080 and 2808 cm\(^{-1}\). The number of OH stretching vibrations simply reflects the complexity of the molecular structure of these minerals. The spectrum of planerite in the near-IR resembles the spectrum in the OH stretching region in the mid-IR region. The NIR spectrum of hureaulite shows bands at 7120, 7065, 6987, 6802 and 6679 cm\(^{-1}\). One simple interpretation is to suggest that the bands in the NIR are simply the doubling of the bands in the mid-IR. In the OH stretching region of wardite, bands are observed at 3594, 3558, 3490, 3466, 3362 and 3199 cm\(^{-1}\). NIR bands are observed at 7266, 7168, 7090, 7019, 6943 and 6793 cm\(^{-1}\).

The water overtone region of these minerals is shown in Figures 3 and 4. Figure 3 displays the spectra of hureaulite, planerite and cacoxenite; Figure 4 that of wardite and gormanite. The intensity of the last two minerals is on a much lower scale than for the first three making the comparison on the one graph difficult. The reason for this is not known as all the selected minerals have water in the structure. Cacoxenite has water in channels in the structure. The NIR spectrum of hureaulite shows two bands at 5166 and 5000 cm\(^{-1}\). This spectrum is typical of a ‘water’ type spectrum for minerals. The spectrum of cacoxenite is similar with three bands observed at 5196, 5087 and 4907 cm\(^{-1}\). The spectrum of planerite in this region is more complex with intense bands observed at 5066, 4957 and 4853 cm\(^{-1}\). The spectrum of planerite in this region suggests that the behaviour of water in planerite is different. For gormanite two bands were observed at 5240 and 4841 cm\(^{-1}\) but were of very low intensity. A similar situation is found for wardite with the most intense bands observed at 5180 and 4867 cm\(^{-1}\).
The NIR spectra of these phosphate minerals in the 4000 to 4800 cm\(^{-1}\) region are shown in Figure 5. This region is the spectral region of the combination bands involving for example OH stretching and OH deformation vibrations. Cacoxenite shows no intensity for bands in this spectral region. Gormanite spectrum shows three major peaks at 4602, 4544 and 4172 cm\(^{-1}\). For planerite a set of bands at 4633, 4551, 4476 and 4439 cm\(^{-1}\) are observed. The NIR spectrum of hureaulite in this region shows low intensity bands at 4561, 4528 and 4409 cm\(^{-1}\). It is not known why the bands for hureaulite and gormanite show no intensity in this region. The conclusion that may be reached is that the bands in the mid-IR do not combine to give bands in the NIR. The NIR spectrum of wardite in this region is intense with bands observed at 4564, 4597, 4541, 4445 and 4345 cm\(^{-1}\).

4. Conclusions

Among the very wide range of techniques available to scientists studying minerals, one of the perhaps least used techniques is that of NIR spectroscopy. NIR spectroscopy has wide application for the study of minerals on planets, interstellar dust and the like. Yet in the laboratory NIR spectroscopy is not used to characterise minerals. This work has shown the application of NIR spectroscopy to the study of a suite of hydrated hydroxylated phosphate minerals of differing crystal structure. NIR spectroscopy shows distinctive spectra which enable their identification and characterisation.

Acknowledgements

The financial and infra-structure support of the Queensland University of Technology Inorganic Materials Research Program of the School of Physical and Chemical Sciences is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding.

References

[7]. P. B. Moore and T. Araki, American Mineralogist 58 (1973) 302.
[8]. J. Murdoch, American Mineralogist 28 (1943) 19.
Table 1 Results of the NIR spectral analysis of selected hydrated hydroxylated phosphate minerals

<table>
<thead>
<tr>
<th>Cacoxenite</th>
<th>Gormanite</th>
<th>Planerite</th>
<th>Hureaulite</th>
<th>Wardite</th>
<th>Suggested Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band Centre (cm$^{-1}$) / Intensity (%)</td>
<td>Band Centre (cm$^{-1}$) / Intensity (%)</td>
<td>Band Centre (cm$^{-1}$) / Intensity (%)</td>
<td>Band Centre (cm$^{-1}$) / Intensity (%)</td>
<td>Band Centre (cm$^{-1}$) / Intensity (%)</td>
<td></td>
</tr>
<tr>
<td>7082 / 3.12</td>
<td>7032 / 0.42</td>
<td>7120 / 2.19</td>
<td>7266 / 4.68</td>
<td>First fundamental overtone</td>
<td></td>
</tr>
<tr>
<td>6915 / 13.15</td>
<td>6896 / 3.09</td>
<td>7065 / 0.36</td>
<td>7168 / 2.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6708 / 2.40</td>
<td>6839 / 0.41</td>
<td>6987 / 12.31</td>
<td>7090 / 2.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6650 / 15.92</td>
<td>6769 / 14.22</td>
<td>6802 / 10.02</td>
<td>7019 / 8.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6751 / 0.62</td>
<td>6679 / 16.66</td>
<td>6943 / 11.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6544 / 6.32</td>
<td></td>
<td>6793 / 8.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5601 / 0.22</td>
<td>5762 / 0.57</td>
<td>5676 / 1.12</td>
<td>5870 / 0.29</td>
<td>Water OH overtones</td>
<td></td>
</tr>
<tr>
<td>5251 / 2.02</td>
<td>5509 / 0.24</td>
<td>5166 / 31.70</td>
<td>5592 / 0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5196 / 15.77</td>
<td>5225 / 1.26</td>
<td>5000 / 24.03</td>
<td>5510 / 0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5087 / 23.40</td>
<td>5152 / 2.12</td>
<td></td>
<td>5364 / 0.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4907 / 23.82</td>
<td>5066 / 26.08</td>
<td></td>
<td>5180 / 1.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4957 / 19.46</td>
<td></td>
<td>5167 / 0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4853 / 7.59</td>
<td></td>
<td>4876 / 2.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4787 / 1.67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4594 / 0.17</td>
<td>4633 / 5.57</td>
<td>4561 / 0.74</td>
<td>4645 / 4.41</td>
<td>OH combination bands</td>
<td></td>
</tr>
<tr>
<td>4716 / 2.60</td>
<td>4551 / 4.62</td>
<td>4528 / 0.35</td>
<td>4597 / 5.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4602 / 28.45</td>
<td>4476 / 2.56</td>
<td>4409 / 0.52</td>
<td>4541 / 8.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4544 / 10.27</td>
<td>4439 / 3.05</td>
<td></td>
<td>4445 / 9.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4516 / 9.07</td>
<td></td>
<td></td>
<td>4345 / 14.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4172 / 31.54</td>
<td></td>
<td></td>
<td>4216 / 6.22</td>
<td>OH combination bands</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4174 / 7.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3529 / 2.55</td>
<td>3592 / 0.15</td>
<td>3565 / 2.00</td>
<td>3594 / 1.14</td>
<td>OH stretching vibrations</td>
<td></td>
</tr>
<tr>
<td>3417 / 11.45</td>
<td>3550 / 2.18</td>
<td>3432 / 11.55</td>
<td>3558 / 2.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3269 / 23.76</td>
<td>3507 / 2.88</td>
<td>3263 / 24.89</td>
<td>3490 / 3.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3089 / 31.14</td>
<td>3466 / 0.72</td>
<td>3041 / 27.56</td>
<td>3466 / 3.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2833 / 9.42</td>
<td>3446 / 6.58</td>
<td></td>
<td>3362 / 2.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3310 / 27.61</td>
<td></td>
<td>3199 / 3.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3027 / 14.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2691 / 3.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2464 / 0.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

OH stretching vibrations
List of Figures

Figure 1 NIR spectra of cacoxenite, gormanite, planerite, hureaulite and wardite in the first OH fundamental region.

Figure 2 Infrared spectra of the OH stretching region of cacoxenite, gormanite, planerite, hureaulite and wardite in the OH stretching region.

Figure 3 NIR spectra of cacoxenite, planerite, and hureaulite in the 4600 to 5600 cm$^{-1}$ region.

Figure 4 NIR spectra of gormanite and wardite in the 4600 to 5600 cm$^{-1}$ region.

Figure 5 NIR spectra of cacoxenite, gormanite, planerite, hureaulite and wardite in the OH combination region.

List of Tables

Table 1 Results of the NIR spectral analysis of selected hydrated hydroxylated phosphate minerals
Figure 1

Wavenumber /cm$^{-1}$

- Wardite
- Hureaulite
- Planerite
- Gormanite
- Cacoxenite
Figure 2

Wavenumber / cm\(^{-1}\)

- Wardite
- Hureaulite
- Planerite
- Gormanite
- Cacoxenite

Relative Intensity
Figure 3

- Hureaulite
- Planerite
- Cacoxenite

Kubelka-Munk

Wavenumber /cm$^{-1}$
Figure 4

Kubelka-Munk

Wardite

Gormanite

Wavenumber /cm$^{-1}$
Figure 5

![Graph showing wavenumber distribution for different minerals](image-url)

- Wardite
- Hureaulite
- Planerite
- Gormanite
- Cacoxenite

Wavenumber / cm⁻¹