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Infrared spectroscopic study of natural hydrotalcites carrboydite and hydrohonessite

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Abstract

Infrared spectroscopy has proven most useful for the study of anions in the interlayer of natural hydrotalcites. A suite of naturally occurring hydrotalcites including carrboydite, hydrohonessite, reevesite, motukoreaite and takovite were analysed. Variation in the hydroxyl stretching region was observed and the band profile is a continuum of states resulting from the OH stretching of the hydroxyl and water units. Infrared spectroscopy identifies some isomorphic substitution of sulphate for carbonate through an anion exchange mechanism for the minerals carrboydite and hydrohonessite. The infrared spectra of the CO_3 and SO_4 stretching region of takovite is complex because of band overlap. For this mineral some sulphate has replaced the carbonate in the structure. In the spectra of takovites, a band is observed at 1346 cm^{-1} and is attributed to the carbonate anion hydrogen bonded to water in the interlayer. Infrared spectroscopy has proven most useful for the study of the interlayer structure of these natural hydrotalcites.

Key Words: hydrotalcite, infrared spectroscopy, Raman microscopy, molecular assembly, structured water.

1. Introduction

There exists in nature an interesting set of minerals with a layer clay-like structure based upon the hydrotalcite structure. These minerals are based upon the divalent cation Ni^{2+} replacing Mg^{2+} in a brucite structure and with some trivalent cation such as Al^{3+} or Fe^{3+} replacing some of the Mg^{2+} ions. Such replacement results in the brucite-like layers carrying a positive surface charge which may be counterbalanced by anions. The common anion is carbonate which results in the minerals hydrotalcite (Mg,Al) and takovite (Ni,Al); when the interlayer anion is sulphate the minerals are carrboydite (Ni,Al), motukoreaite (Mg,Al) honessite (Ni,Fe) and mountkeithite (Mg,Fe). The following table is a summary of these minerals based upon the work of Nickel and Wildman [1].

Divalent	Trivalent	Carbonate	Sulphate	Sulphate

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cation	cation	(8 Å)	(9 Å)	(10-11 Å)
Ni	Al	takovite		carrboydite
Mg	Al	hydrotalcite		motukoreaite
Ni	Fe	reevesite	honessite	hydrohonessite
Mg	Fe	pyroaurite		mountkeithite

Table 1 Summary of the hydrotalcites based upon divalent nickel and trivalent aluminium and ferric iron.

Interest in the study of hydrotalcites results from their potential use as catalysts [2-6]. The reason for the potential application rests with the ability to make mixed metal oxides at the atomic level, rather than at a particle level. Such mixed metal oxides are formed through the thermal decomposition of the hydrotalcite [7, 8]. Hydrotalcites may also be used as a components in new nano-materials such as nano-composites [9]. There are many other uses of hydrotalcites. Hydrotalcites are important in the removal of environmental hazards in acid mine drainage [10, 11]. Hydrotalcite formation also offer a mechanism for the disposal of radioactive wastes [12]. Hydrotalcite formation may also serve as a means of heavy metal removal from heavy metal contaminated waters [13]. Infrared spectroscopy using a number of techniques has been used to characterise a number of hydrotalcites [14]. We extend this work to a study of the natural hydrotalcites listed in Table1.

2. Experimental

2.1 Hydrotalcite samples

Hydrotalcite samples as listed in Table 1 were obtained from a number of sources. Each mineral was analysed for phase purity by X-ray diffraction and for chemical composition using the electron probe.

2.2 Infrared spectroscopy

The samples were dried to remove any adsorbed water and stored in desiccators before measurement in the FT-IR spectrometer. 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 tones 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.

Spectroscopic 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

3.1.1 Hydroxyl Stretching Region

The infrared spectra of the hydroxyl stretching region of the nickel containing hydrotalcites as listed in Table 1 is shown in Figure 1. The band component analyses of these hydrotalcites are reported in Table 2. Recently propositions were made for molecular assembly of the cations in hydrotalcites [15-17]. In brucite type solids, there are tripod units M_3OH with several metals such as M, M', M". In hydrotalcites such as those based upon Ni and Mg of formula $Ni_xMg_{6-}x(Alfa)_2(OH)_{16}(CO_3).4H_2O$, a number of statistical permutations of the M_3OH units are involved. These are Ni_3OH, Mg_3OH, Al_3OH and combinations such as Mg_2NiOH, Ni_2MgOH, Mg_2AlOH, Al_2MgOH, Al_2NiOH, Ni_2AlOH, and even MgNiAlOH. In the case of a pure hydrotalcite where only one divalent cation exists in the structure this number of permutations will be reduced. These types of units will be distributed according to a probability distribution according to the composition. In this model, a number of assumptions are made, namely that the molecular assembly is random and that no islands or lakes of cations are formed. Such assembly is beyond the scope of this work but needs to be thoroughly investigated. In the simplest case for carrboydite namely $Ni_6Al_2(OH)_{16}(CO_3).4H_2O$ the types of units would be Ni_3OH, Ni_2AlOH, $NiAl_2OH$ and Al_3OH. A similar situation would exist for the mineral hydrohonessite. These are $Ni_6Fe_2(OH)_{16}(CO_3).4H_2O$ hydrotalcite. In a somewhat oversimplified model, for the $Ni_6Fe_2(OH)_{16}(CO_3).4H_2O$ hydrotalcite, the most intense bands would be due to the Ni_3OH and Fe_3OH bands. In previous publications argument for molecular assembly of the divalent and trivalent cations was presented. This argument was based upon the different MOH units having different band positions. This proposal was based on synthetic hydrotalcites.

The band profiles shown in Figure 1 are broad with no distinguishable features. What this means is that the profile is based upon a continuum of states and as such no separate MOH bands can be distinguished. Further the hydroxyl stretching bands of water will overlap with these MOH hydroxyl stretching vibrations. The band profile for carrboydite may be resolved into three bands at 3600, 3360 and 3172 cm^{-1}. One possible attribution of these bands is that the first band is due to the OH stretching vibration of the NiOH and AlOH units and the next two bands are due to the symmetric and antisymmetric stretching vibrations of water. For hydrohonessite three bands are observed at 3437, 3357 and 3257 cm^{-1}. The attribution of these three bands is as for carrboydite. The two bands assigned to water are in similar positions. The band at 3437 cm^{-1} may be compared with the value of 3600 cm^{-1} for carrboydite. The difference is probably due to the FeOH units compared with AlOH units. For the mineral motukoreaite bands are observed at 3440, 3396 and 3283 cm^{-1}. Two additional bands are observed at 3659 and 3618 cm^{-1}. These latter two bands are attributed to an impurity, possibly kaolinite. The spectra obtained for reevesite in the hydroxyl stretching region were of poor signal to noise and were not used. Two samples of takovite provided infrared bands at 3368 and 3082 cm^{-1}. The spectra for these two minerals are further evidence for a continuum of states.

3.2 Water HOH bending vibrations

Often significant information can be obtained through the study of the water bending modes centred around 1620 cm^{-1}. Figure 2 displays the water bending modes for selected hydrotalcites. The water hydroxyl bending region is complex with more than one band being observed. For carrboydite two bands are observed at 1661 and 1620 cm^{-1}. A very low intensity band is also observed at 1485 cm^{-1}. This latter band may be assigned to the CO_3 antisymmetric stretching vibrations. The significance of two water bending modes rests with water being involved in the hydrotalcite structure with two different hydrogen bond strengths. The band at 1661 cm^{-1} results form water being strongly hydrogen bonded. Two possibilities exist (a) hydrogen bonding to the OH units of the hydroxyl surface and (b) hydrogen bonding to the sulphate. The second type of water is more relatively weakly hydrogen bonded and it is suggested that this type of water molecule is hydrogen bonded to the sulphate anion in the interlayer structure. For hydrohonessite, two bands are observed at 1656 and 1595 cm^{-1}. The relative intensities of the two bands are 2:1. Most of the water molecules are strongly hydrogen bonded in the hydrohonessite structure. For motukoreaite, the water bending mode is observed at 1645 cm^{-1}. The band overlaps with carbonate antisymmetric vibrations observed at 1422 and 1472 cm^{-1}. The carbonate is present as an isomorphic substitute for sulphate in the motukoreaite structure. In comparison the water bending mode for takovite is a weak shoulder on the carbonate antisymmetric stretching vibration profile. The band is observed at 1632 cm^{-1}. Thus the position of the water bending mode is a measure of the hydrogen bonding strength in the hydrotalcite structure. The order of hydrogen bonding is carrboydite, hydrohonessite, motukoreaite, takovite. What this spectroscopic evidence shows is that the hydrogen bonding of water in the interlayer is not the same for each hydrotalcite. Such a concept can be extrapolated to a measure of the stability of the hydrotalcite.

3.3 Sulphate vibrations

The spectral region between 500 and 1500 cm^{-1} is shown in Figure 3. The results of the band component analysis reported in Table 2. Several of the spectra show complexity in this region. The reason is that both carbonate and sulphate may exist as the counter anions in the interlayer structure. The spectra of carrboydite and hydrohonessite show similarity and have simpler spectra as the dominating interlayer anion is sulphate. For carrboydite, bands are observed at 1088, 1021 and 978 cm^{-1}. The first two bands are attributed to the SO_4 antisymmetric stretching vibration and the last band to the SO_4 symmetric stretching vibration. The 978 cm^{-1} band is of low intensity. Two bands are observed at 601 and 557 cm^{-1} and are attributed to the SO_4 out-of-plane ν_4 bending modes. For hydrohonessite two bands are found at 1094 and 1060 cm^{-1} and are also attributed to the SO_4 antisymmetric stretching vibrations. A very low intensity band is observed at 972 cm^{-1} and is attributed to the sulphate symmetric stretching mode. Bish and Livingstone identified bands at 1390, 1030 and 980 cm^{-1} for both honessite and hydrohonessite [18] . The bands for hydrohonessite are broad. This again suggests that the structure is diffuse and the band centres simply represent some continuum of states. The ν_4 mode is observed at 618 cm^{-1}. For motukoreaite, the band profile is complex. Bands are observed at 1162, 1103, 1033, 1002, 909 and 874 cm^{-1}. It is likely these are mainly sulphate bands which are complicated by overlap with CO_3 stretching bands. The ν_4 mode is observed as a complex profile centred upon 663 cm^{-1}. Such complexity is due to multiple phases as has been identified by Brindley [19]. For reevesite, bands are observed at 1077, 1017 and 938 cm^{-1} and all are attributed to sulphate vibrations. The bending modes of sulphate for reevesite are observed at 650 and 606 cm^{-1}.

For the two takovites studied, the spectra are very similar with great complexity in the 700 to 1200 cm^{-1} region. Bands are observed at 1105, 1034, 990, 938, 911, 882, 820, 749 and 685 cm^{-1} for the takovite 1 sample. The infrared spectrum of the second takovite sample has bands at 1104, 1040, 981, 937, 913, 884, 831, 748 and 683 cm^{-1}. This complexity no doubt results for the overlap of the SO_4 and CO_3 stretching vibrations. This complexity is further increased because of bands in the 750 to 850 cm^{-1} range. For example carrboydite IR spectrum shows bands at 825 and 758 cm^{-1}; hydrohonessite at 771 cm^{-1}; motukoreaite at 776 and 795 cm-1; takovite at 820 and 749 cm^{-1}. These bands are attributed to water librational modes. Water librational modes are due to the ‘rocking’ vibration of water and are very sensitive to hydrogen bonding. The position of these bands at significantly high wavenumbers is also indicative of strong hydrogen bonding. Further it could be expected that M-OH deformation bands would be observed. A band is observed at around 911 cm^{-1} for the takovite mineral. One possible assignment is that this is the AlOH deformation band.

3.4 Carbonate vibrations

In the spectra of takovite, a band is observed at around 1034 cm^{-1}. It is possible that this is the CO_3 symmetric stretching vibration, even though this band is buried in the overall band profile. In the spectra of the two takovites bands are observed at 1513, 1438 and 1346 cm^{-1} and are attributed to the CO_3 antisymmetric stretching modes. The band at 1346 cm^{-1} is significant as it is assigned to the CO_3 antisymmetric stretching mode of carbonate anion hydrogen bonded to water molecule. The water hydrogens bridge to the carbonate through hydrogen bonding. The band is not present in the hydrotalcite minerals with low concentrations of carbonate present.

4. Conclusions

Infrared spectroscopy has proven most powerful for the characterisation of the water and anions in the interlayer of some natural hydrotalcites. The minerals carrboydite, motukoreaite, hydrohonessite and mountkeithite are all based upon the combination of water and sulphate in the hydrotalcite interlayer. Both takovite and reevesite depend upon the combination of water and carbonate anion filling the interlayer space. The proposal is made based upon Infrared spectroscopy that the hydroxyl stretching region is based upon a continuum of states with overlap of the bands due to the hydroxyl stretching vibrations. A study of the water HOH bending region shows that two water bands are present at around 1620 and 1660 cm^{-1}, indicating water molecules involved with two types of hydrogen bonding. The latter band is significant as it shows strong hydrogen bonding to the hydroxyl units. Both carbonate and sulphate are identified as the counter anions in the interlayer. In takovite, sulphate replaces the carbonate whereas with mountkeithite and reevesite and motukoreaite some carbonate replaces the sulphate. For carrboydite and hydrohonessite only low concentrations of carbonate are detected. For these natural hydrotalcites both anions are observed in the interlayer structure.

Acknowledgments

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Table 2. Infrared spectral analysis of selected hydrotalcites

Carrboydite	Hydrohonessite	Motukoreaite	Reevesite	Takovite 1	Takovite 2	Suggested assignment
		3695 3618			3692 3616	Impurity (kaolinite?)
3600 3360 3172	3437 3375 3212	3440 3395 3283	3375 3212	3368 3082	3368 3082	MOH stretching And water HOH stretching
1661 1620	1656 1595	1645	1660	1632		Water bending
		1510 1472 1422		1410 1347	1513 1439 1346	CO_3 antisymmetric stretching
1088 1021 978	1093 1060	1162 1103 1033 1002	1077 1017 938	1105 1034 990 938 911	1104 1040 981 937 913	CO_3 stretching SO_4 stretching AlOH deformation
825 758	771	909 874 795 776		882 820 749	884 831 748	Water libration
601 557	618	663	650 606	685 618	683 623	SO_4 bending

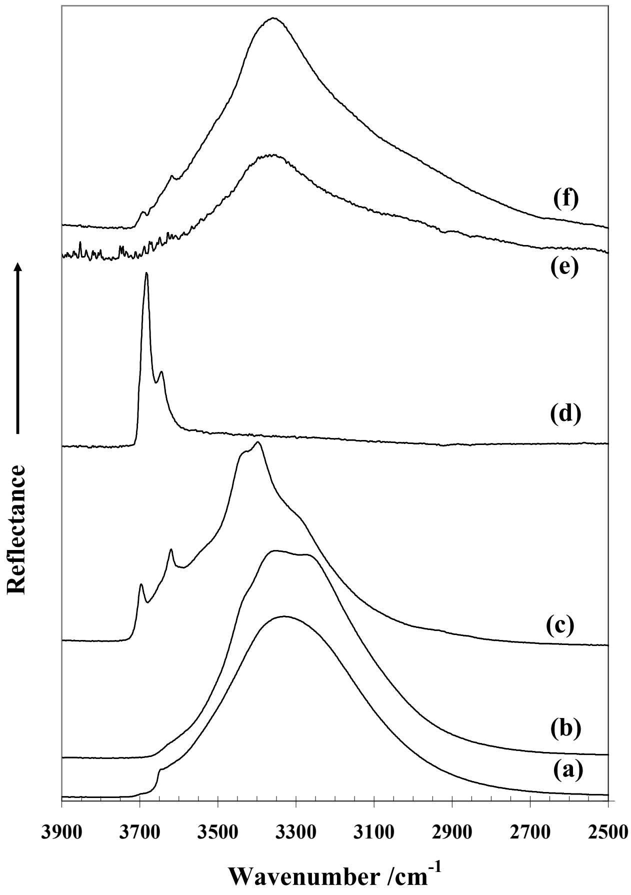

Figure 1 Infrared spectra of the hydroxyl stretching region of (a) carrboydite (b) hydrohonessite (c) motukoreaite (d) reevesite (e) takovite (f) takovite 2

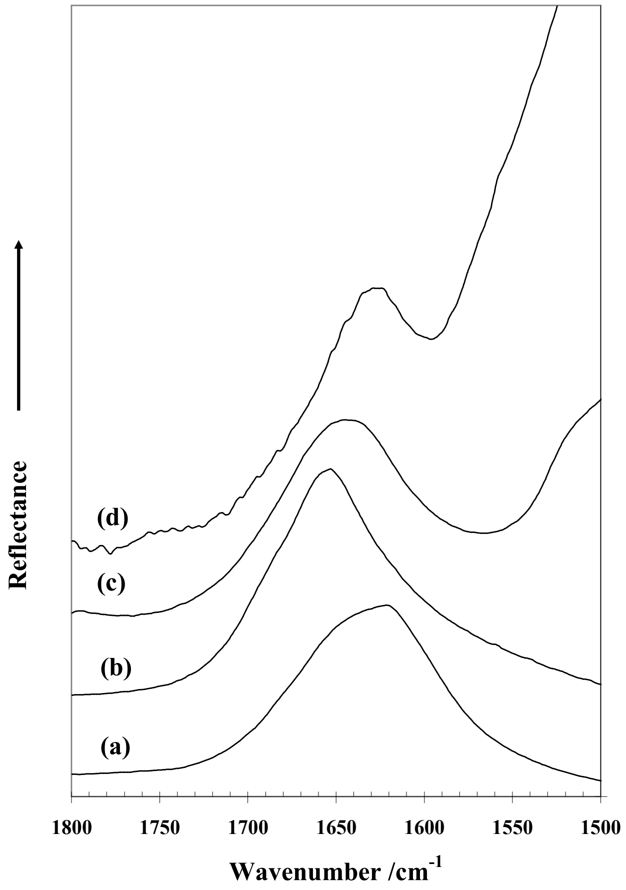

Figure 2 Infrared spectra of the water bending region of (a) carrboydite (b) hydrohonessite (c) motukoreaite (d) takovite 2

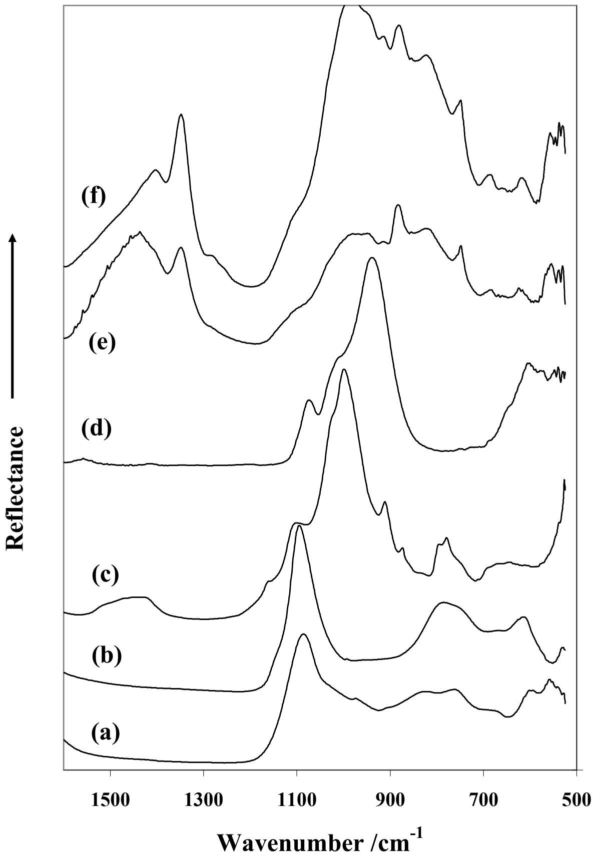

Figure 3 Infrared spectra of the 500 to 1500 cm^{-1} region of (a) carrboydite (b) hydrohonessite (c) motukoreaite (d) reevesite (e) takovite (f) takovite 2