



# Vibrational spectroscopic study of the natural layered double hydroxide manasseite now defined as hydrotalcite-2H – $\text{Mg}_6\text{Al}_2(\text{OH})_{16}[\text{CO}_3]\cdot 4\text{H}_2\text{O}$



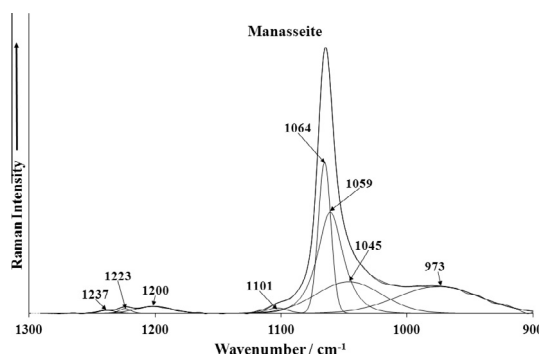
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## HIGHLIGHTS

- We have studied the so-called mineral manasseite.
- Now defined as hydrotalcite  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ .
- Hydrogen bond distances varied between 2.61 and 3.00 Å.
- Two Raman bands at 1059 and 1064  $\text{cm}^{-1}$  are observed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Raman and thermo-Raman spectroscopy have been applied to study the mineral formerly known as manasseite now simply renamed as hydrotalcite-2H  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}[\text{CO}_3]\cdot 4\text{H}_2\text{O}$ . The mineral is a member of the homonymous hydrotalcite supergroup. Hydrogen bond distances calculated using a Libowitzky-type empirical function varied between 2.61 and 3.00 Å. Stronger hydrogen bonds were formed by water units as compared to the hydroxyl units. Raman spectroscopy enabled the identification of bands attributed to the hydroxyl units. Two Raman bands at 1059 and 1064  $\text{cm}^{-1}$  are assigned to symmetric stretching modes of the carbonate anion. Thermal treatment shifts these bands to higher wavenumbers indicating a change in the strength of the carbonate bonding.

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## Introduction

Studies of anionic clays have been undertaken for a long time [1–3]. Anionic clays, hydrotalcites or layered double hydroxides (LDH) are less well-known than cationic clays such as smectites [4–6]. The structure of hydrotalcite-2H can be derived from a brucite structure ( $\text{Mg}(\text{OH})_2$ ) in which trivalent cations e.g.  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  (pyroaurite-2H) substitutes as part of the  $\text{Mg}^{2+}$ . This substitution

creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes. In hydrotalcites a broad range of compositions are possible of the type  $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2][\text{A}^{n-}]_{x/n}\cdot y\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are the di- and trivalent cations in the octahedral positions within the hydroxide layers with  $x$  normally between 0.17 and 0.33.  $\text{A}^{n-}$  is an exchangeable interlayer anion. Many variations in compositions have been reported for hydrotalcites-2H.

In recent study Mills et al. [7] have described the hydrotalcite supergroup as the grouping of several mineral groups: hydrotalcite, quintinite, fougèrite, woodwardite, glaucocerinite, wermlandite, cualstibite, hydrocalumite as well as unclassified minerals in

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a total of 43 approved minerals. In previous studies, the former hydroxalcalite-2H group minerals were described as members of manasseite groups of minerals composed by hexagonal carbonates and the trigonal carbonates known as the hydroxalcalite-3R or double layer hydroxides [8–11].

## Experimental

### Samples description and preparation

The hydroxalcalite sample studied in this work was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-028. The sample is from the Kola Peninsula, Russia. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) was applied to support the chemical characterization.

The Kola Peninsula is located in the northeastern segment of the Precambrian Baltic Shield. The region is characterized by complicated block structures, which were reactivated during several tectono-magmatic episodes. During the Devonian, numerous ultramafic, alkaline and carbonatitic intrusions were emplaced. These various ultramafic and alkaline silicate rocks found in Kovdor are considered to have been formed from several batches of a carbonated olivine melanephelinite parental magma by a mechanism involving fractional crystallization, magma mixing and/or contamination [12]. The Kovdor massif is a typical ultrabasic-alkaline complex bearing a wide compositional range of magmatic and metasomatic rocks. The Kovdor massif is an important source of industrial minerals such as magnetite, apatite, baddeleyite, phlogopite and vermiculite [13].

### Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (<http://www.microscopia.ufmg.br>).

Hydroxalcalite crystal aggregate was coated with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analysis in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and was applied to support the mineral characterization.

### Raman microprobe spectroscopy

Crystals of hydroxalcalite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10 $\times$ , 20 $\times$ , and 50 $\times$  objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2  $\text{cm}^{-1}$  and a precision of  $\pm 1 \text{ cm}^{-1}$  in the range between 200 and 4000  $\text{cm}^{-1}$ . Repeated acquisitions on the crystals using the highest magnification (50 $\times$ ) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5  $\text{cm}^{-1}$  line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

### Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525  $\text{cm}^{-1}$  range were obtained by the co-addition of 128 scans with a resolution of 4  $\text{cm}^{-1}$  and a mirror velocity of 0.6329  $\text{cm/s}$ . Spectra were co-added to improve the signal to noise ratio. The infrared spectra are given in the supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that 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 Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian 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.

## Results and discussion

### Chemical characterization

The SEM image of hydroxalcalite sample studied in this work is shown in Fig. 1. The image shows a cleavage fragment. The mineral occurs free of contamination phases. Qualitative chemical analysis shows a Mg, Al and C phase as expected for hydroxalcalite. Minor amounts of Si were also detected (Fig. 2).

### Vibrational spectroscopy

One way of looking at hydroxalcalites is to consider the molecules to be giant cations with a distribution of positive charges over the surfaces. These charges may be random or in some regular array. The positive charges must be counterbalanced by anions such as carbonate. The carbonate anions are hydrated and these hydrated anions together with water in some structured arrangements completely fill the interlayer of hydroxalcalite. The brucite-like surface will attract the anions and water molecules hydrogen bonded to the brucite-like surface. Thus, in any vibrational spectroscopic

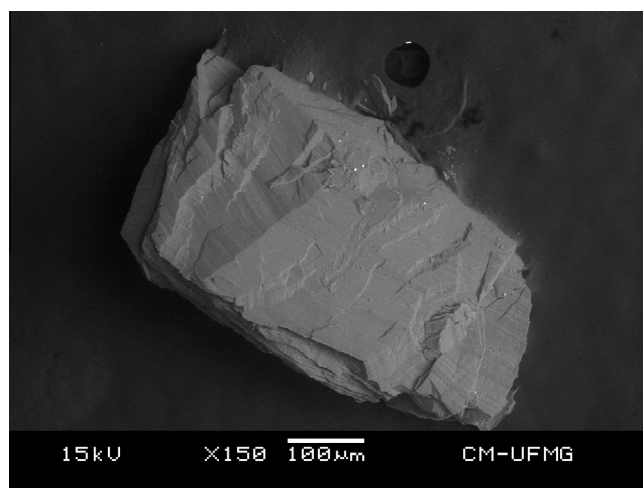


Fig. 1. Backscattered electron image (BSI) of a hydroxalcalite single crystal up to 1.0 mm in length.

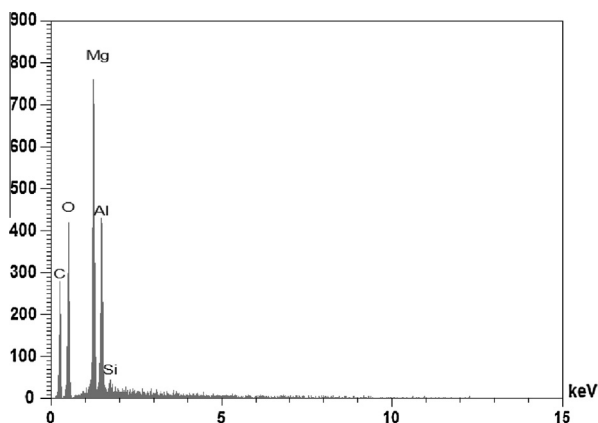


Fig. 2. EDS analysis of hydrotalcite.

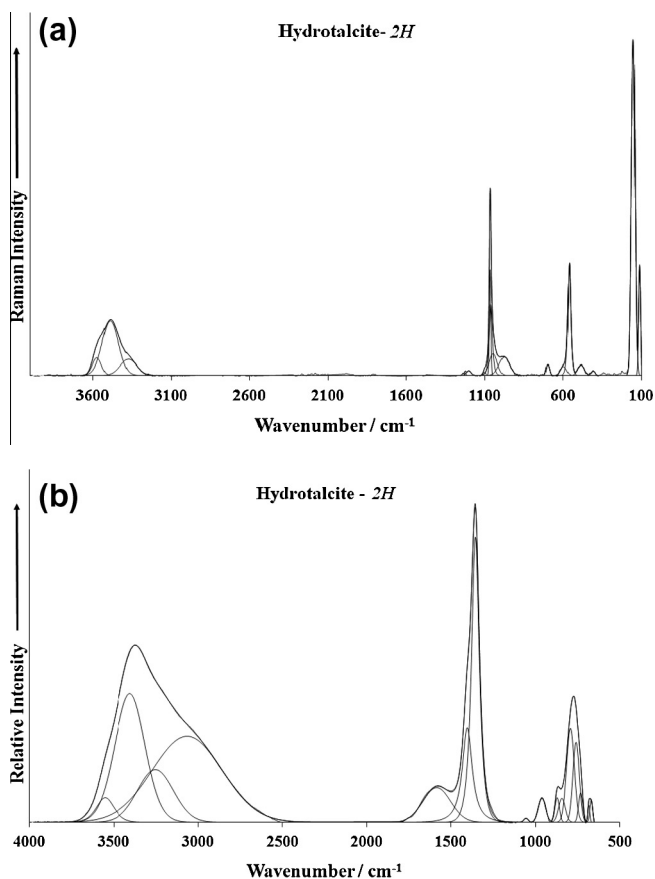


Fig. 3. (a) Raman spectrum of hydrotalcite over the 100–4000 cm<sup>-1</sup> spectral range and (b) infrared spectrum of hydrotalcite over the 500–4000 cm<sup>-1</sup> spectral range.

analysis of hydrotalcite each vibrational species will be observed. One of the difficulties of obtaining the infrared spectra of hydrotalcites is the overlap of the water hydroxyl stretching bands with those of hydroxyls bound to metal centers. The infrared absorption of water is so intense that the hydroxyl absorption bands of the metal hydroxides are difficult to detect. Water is a very poor Raman scatterer and so Raman microscopy is more useful for the measurement of the OH stretching region of the M<sub>3</sub>OH units for the study of layered double hydroxides.

The Raman spectrum of hydrotalcite-2H over the 100–4000 cm<sup>-1</sup> spectral range is displayed in Fig. 3a. This spectrum

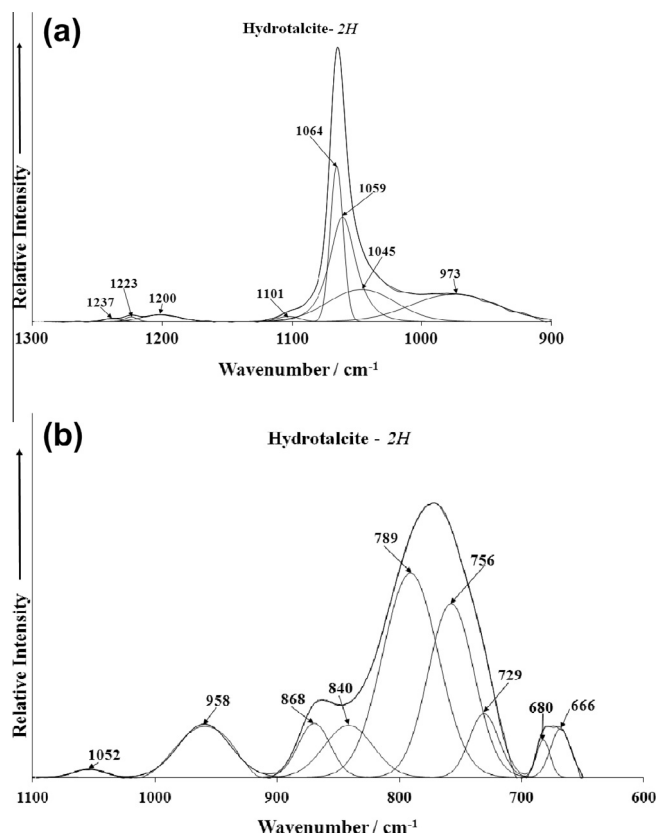


Fig. 4. (a) Raman spectrum of hydrotalcite over the 800–1400 cm<sup>-1</sup> spectral range and (b) infrared spectrum of hydrotalcite over the 500–1300 cm<sup>-1</sup> spectral range.

shows the position and intensity of the Raman bands across the full spectrum. It is obvious that there are large parts of the spectrum where no intensity is observed and therefore the Raman spectrum is subdivided into sections based upon the type of vibration being examined. The infrared spectrum of hydrotalcite-2H over the 500–4000 cm<sup>-1</sup> spectral range is reported in Fig. 3b. This spectrum shows the position and relative intensities of the infrared bands. Large parts of the infrared spectrum show no intensity and therefore, the infrared spectrum is subdivided into sections based upon the type of vibration being examined.

The Raman spectrum of hydrotalcite-2H over the 900–1300 cm<sup>-1</sup> spectral range is illustrated in Fig. 4a. Intense Raman bands are observed at 1059 and 1064 cm<sup>-1</sup> with broad shoulder on the low wavenumber side at 1045 cm<sup>-1</sup>. These two bands are assigned to the carbonate ν<sub>1</sub> symmetric stretching mode of the carbonate anion. In this type of layered double hydroxide there are two types of OH units, namely Al<sub>3</sub>OH and Mg<sub>3</sub>OH. It is questionable whether band fitting could resolve two bands at 2 cm<sup>-1</sup> nominal resolution. One most likely model is that the 1064 cm<sup>-1</sup> band is attributable to carbonate associated with the Al<sub>3</sub>OH unit and the 1059 cm<sup>-1</sup> band with Mg<sub>3</sub>OH unit. The Raman spectrum of magnesite (MgCO<sub>3</sub>) displays a band at 1087 cm<sup>-1</sup> (this work). Thus, the behavior of the carbonate ion in the layered double hydroxide is more like that of a perturbed carbonate ion rather than a carbonate bonded to the cation. The observation of two bands supports the concept of two types of carbonate anions. Two other bands observed at 973 and 1045 cm<sup>-1</sup> may be attributed to water librational modes. The symmetric stretching mode of smithsonite (ZnCO<sub>3</sub>) is observed at 1093 cm<sup>-1</sup> (this work). This result again suggests that the carbonate is not bonded to any of the cations and although perturbed by hydrogen bonding with water free from cations. It is possible that water acts as a donor acceptor and forms a bridging unit between the M<sub>3</sub>OH units and the carbonate anion.

The Raman spectrum (Fig. 4a) of hydrotalcite-2H shows a series of low intensity bands at 1200, 1223 and 1237  $\text{cm}^{-1}$ . The unperturbed carbonate ion is a planar triangle with point symmetry  $D_{3h}$ . Group theoretical analysis of the carbonate ion predicts four normal modes the  $\nu_1$  symmetric stretch of  $A_1'$  symmetry normally observed at 1063  $\text{cm}^{-1}$ , the anti-symmetric stretch of  $E'$  symmetry observed at 1415  $\text{cm}^{-1}$ , the  $\nu_2$  out of plane bend at 879  $\text{cm}^{-1}$  and the in-plane bend at 680  $\text{cm}^{-1}$ . For the unperturbed carbonate anion the  $\nu_1$  mode is Raman active only. For the perturbed carbonate anion, all modes are both Raman and infrared active except for the  $\nu_2$  mode, which is IR active only.

The infrared spectrum of hydrotalcite-2H (Fig. 4b) displays a low intensity band at 1052  $\text{cm}^{-1}$  which is assigned to the  $\text{CO}_3^{2-}$  symmetric stretching mode. The infrared band at 958  $\text{cm}^{-1}$  is ascribed to the water librational mode. The infrared spectrum in this region is limited because of the cut-off point of the diamond ATR cell at 550  $\text{cm}^{-1}$ . Thus, only bands above this wavenumber can be measured using this technique. The  $\nu_2$  out of plane bending mode is difficult to observe for this hydrotalcite. For  $\text{MgCO}_3$  of calcite structure  $\nu_2$  is observed as a band at 892  $\text{cm}^{-1}$ . The  $\nu_2$  bending mode varies depending upon the cation from 862 to 892  $\text{cm}^{-1}$ . This  $\nu_2$  bending mode is observed at 756, 789 and 868  $\text{cm}^{-1}$  in the infrared spectrum as a shoulder on the intense 779  $\text{cm}^{-1}$  band. This band is not observed in the Raman spectrum. Two infrared bands are observed at 666 and 680  $\text{cm}^{-1}$ . These bands may also be additional  $\nu_4$  modes ascribed to the different carbonate anions in the hydrotalcite structure.

The Raman spectra of hydrotalcite-2H in the 300–800  $\text{cm}^{-1}$  and 100–300  $\text{cm}^{-1}$  spectral range are shown in Fig. 5. The Raman spectrum in the low wavenumber region is dominated by an intense

band at 558  $\text{cm}^{-1}$  with a low intensity band at 595  $\text{cm}^{-1}$  on the high wavenumber side. The band observed at 558  $\text{cm}^{-1}$  is the second most intense band in the hydrotalcite-2H spectra and is polarized. The intensity of this band infers that it is due to a symmetric stretching vibration. One possibility is that the band originates from the carbonate-water unit. The two hydrogens of the  $\text{H}_2\text{O}$  molecule are bridged to the two oxygens of the  $(\text{CO}_3)^{2-}$  anion. The 558  $\text{cm}^{-1}$  band appears to be unique to the hydrotalcite structure. It is proposed that this band is a result of OH–O units formed as a result of the water bonding to the carbonate anion. Such a concept is supported by the infrared spectrum of the  $\nu_3$  region where splitting is observed with some 30  $\text{cm}^{-1}$  difference. This means the symmetry of the carbonate has been reduced from  $D_{3h}$  to  $C_{2v}$ . The far low wavenumber region (Fig. 5b) displays two bands at 111 and 151  $\text{cm}^{-1}$ . These bands are broad and are simply assigned to lattice vibrations.

The proposed model of carbonate anion in hydrotalcite is of  $C_{2v}$  symmetry. The  $\text{Mg}_3\text{OH}$  deformation mode is observed at 958  $\text{cm}^{-1}$  but is very weak. The  $\text{Al}_3\text{OH}$  deformation mode is probably around 1035  $\text{cm}^{-1}$  but is masked by the intense  $(\text{CO}_3)^{2-}$  stretching modes of the carbonate at 1058 and 1062  $\text{cm}^{-1}$ . Bands at 1035  $\text{cm}^{-1}$  are observed in mineral such as boehmite ( $\text{AlO}(\text{OH})$ ). The Raman spectrum of brucite shows an intense band at 442  $\text{cm}^{-1}$ . The equivalent band in the spectrum of hydrotalcite-2H is around 474  $\text{cm}^{-1}$  depending on the degree of cation substitution. This band is assigned to the  $\text{MgO}$  symmetric stretching vibration. For the formation of synthetic  $\text{Mg}_4\text{Zn}_2$  hydrotalcite-2H two bands are observed in this region at 481 and 467  $\text{cm}^{-1}$ . The band is centered on 491  $\text{cm}^{-1}$  for the synthetic  $\text{Zn}_6$  hydrotalcite. A band is also observed in brucite at 396  $\text{cm}^{-1}$ . Bands are observed at  $\sim 396$ , 362 and 302  $\text{cm}^{-1}$  in the Raman spectrum of hydrotalcite-2H. Such bands have been observed for other layered double hydroxides in these positions. These bands are attributed to the OMO bending modes. It is interesting that hydrotalcite-3R of formula  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}]$  is trigonal. Hydrotalcite-2H is also of the same formula; yet the structure is hexagonal. The Raman bands of hydrotalcite-2H and hydrotalcite-3R are in similar positions for both minerals.

The Raman spectrum of hydrotalcite-2H in the 3200–3700  $\text{cm}^{-1}$  spectral range is reported in Fig. 6a. Three Raman bands may be resolved in this broad spectral profile at 3371, 3487 and 3573  $\text{cm}^{-1}$ . The infrared spectrum of hydrotalcite-2H in the 3200 to 3700  $\text{cm}^{-1}$  spectral range is reported in Fig. 6b. Again the spectral profile is broad and four bands may be resolved at 3061, 3249, 3401 and 3549  $\text{cm}^{-1}$ . The spectral profile is broad and it is unlikely that there will be any unique solution for any band component analysis of the infrared and Raman profiles. However it is useful to determine the bands in the spectral profiles [14,15]. This technique enables a study of the bands and their possible assignments.

The bands are broad and the width varies from 70 to 328  $\text{cm}^{-1}$ . The first band at 3589  $\text{cm}^{-1}$  with a band width approximately 50% less than the other bands may be attributed to the OH stretching from the brucite-like surface [16–25]. Previous studies have identified bands in these positions to the OH stretching vibrations [16–25].

An empirical relationship has been developed for the variation of hydrogen bond distances and infrared spectroscopic wavenumbers [26]. Studies have shown a strong correlation between OH stretching frequencies and both O...O bond distances and H...O hydrogen bond distances [27–30]. Libowitzky [26] showed that a regression function can be employed relating the hydroxyl stretching frequencies with regression coefficients better than 0.96 using infrared spectroscopy [26]. The function is described as:

$\nu_1 = (3592 - 304) \times 109^{\frac{d(\text{O}-\text{O})}{0.1321}} \text{cm}^{-1}$ . Thus OH–O hydrogen bond distances may be calculated using the Libowitzky empirical function [26]. The infrared bands listed above hence provide estimates

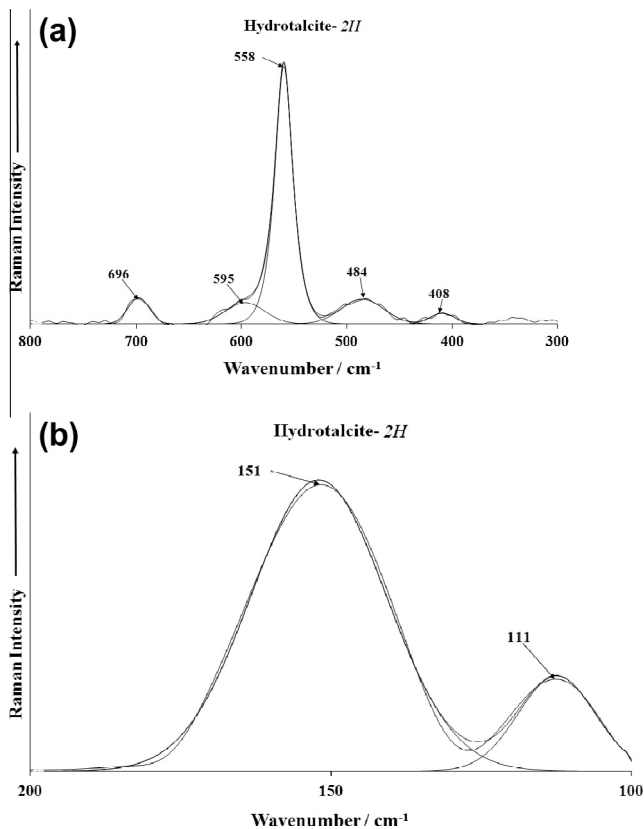


Fig. 5. (a) Raman spectrum of hydrotalcite over the 300–800  $\text{cm}^{-1}$  spectral range and (b) Raman spectrum of hydrotalcite over the 100–300  $\text{cm}^{-1}$  spectral range.

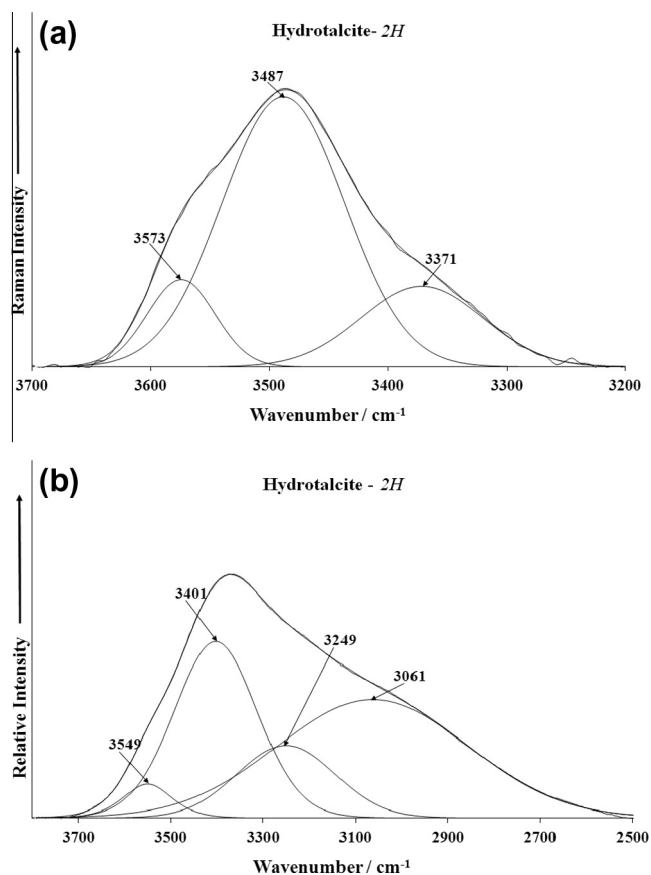


Fig. 6. (a) Raman spectrum of hydrotalcite over the 2600–4000 cm<sup>-1</sup> spectral range and (b) infrared spectrum of hydrotalcite over the 2600–4000 cm<sup>-1</sup> spectral range.

of hydrogen bond distances of 3.00, 2.843, 2.78, 2.71, 2.65 and 2.61 Å. The significance of these results rests with their interpretation. The hydrogen bond distances may be divided into two groups (a) those above 2.70 Å and those below 2.70 Å. Such a division is entirely arbitrary but serves to differentiate bonds which may be regarded as stronger hydrogen bonds (group b) as opposed to weaker hydrogen bonds as with group a. The stronger hydrogen bonds are formed with the bonding involving the water molecules.

## Conclusions

Insight into the unique structure of hydrotalcite-2H has been obtained using a combination of Raman and infrared spectroscopy. The hydroxyl-stretching units of Al<sub>3</sub>OH, Mg<sub>3</sub>OH, and Zn<sub>3</sub>OH are identified by unique band positions. Water plays a unique role in the stabilization of the hydrotalcite-2H structure. The position and intensity of the Raman bands in the hydroxyl-stretching region indicates that the water is highly structured. The position of the bands in the hydroxyl deformation region of the infrared spectrum supports the concept of structured water between the hydrotalcite layers. Four types of water are identified (a) water hydrogen bonded to the interlayer carbonate ion (b) interlamellar water (c) water hydrogen bonded to the hydroxyl units (d) water which bridges the carbonate anion and the M<sub>3</sub>OH surface. The position of the suite of bands associated with the carbonate ion indicates the carbonate ion is perturbed and not bonded to the metal centers but is strongly hydrogen bonded to the interlayer water. An intense

band at around 558 cm<sup>-1</sup> is observed and it is proposed that this band is due to the librational mode of water hydrogen bonded to the metal hydroxyl surface.

In this work, the Raman spectra of the interlayer anions of carbonate of a natural mineral (hydrotalcite-2H) have been collected. The splitting of the  $\nu_3$ ,  $\nu_4$  and  $\nu_2$  modes indicates symmetry lowering. The symmetry lowering must be taken into account through the bonding of carbonate anion to both water and the brucite-like hydroxyl surface. Water plays an essential role in the hydrotalcite-2H structure as may be evidenced by the position of the water bending modes. The water is strongly hydrogen bonded to both the anions and the hydroxyl surface. Raman spectroscopy has the advantage that water molecules are not observed as water is a very poor Raman scatterer. Water is however easily measured with infrared spectroscopy. The combination of the two techniques enables the bands ascribed to hydroxyl units and to water molecules to be distinguished. Thus the cation OH stretching vibrations are more readily observed with Raman spectroscopy.

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