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Thermal treatment of weddellite—a Raman and infrared emission spectroscopic study

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Abstract

Thermal transformations of natural calcium oxalate dihydrate known in mineralogy as weddellite have been undertaken using a combination of Raman microscopy and infrared emission spectroscopy. The vibrational spectroscopic data was complimented with high resolution thermogravimetric analysis combined with evolved gas mass spectrometry. TG–MS identified three mass loss steps at 114, 422 and 592 °C. In the first mass loss step water is evolved only, in the second and third steps carbon dioxide is evolved. The combination of Raman microscopy and a thermal stage clearly identifies the changes in the molecular structure with thermal treatment. Weddellite is the phase in the temperature range up to the pre-dehydration temperature of 97 °C. At this temperature, the phase formed is whewellite (calcium oxalate monohydrate) and above 114 °C the phase is the anhydrous calcium oxalate. Above 422 °C, calcium carbonate is formed. Infrared emission spectroscopy shows that this mineral decomposes at around 650 °C. Changes in the position and intensity of the C=O and C–C stretching vibrations in the Raman spectra indicate the temperature range at which these phase changes occur.

Keywords: Oxalate; Weddellite; Glushinskite; Raman spectroscopy; Thermogravimetry

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1. Introduction

The use of chemicals such as calcium oxalate for the calibration of thermal analysis equipment is well known. Indeed such methodology has been used to study the oxidative decomposition of calcium oxalate [1,2]. The mineral calcium oxalate dihydrate found in nature is known as weddellite. Such a mineral is found in renal calculi and the thermal treatment has been utilised as a method of identification [3,4]. Other metal oxalates have been studied by thermal analysis [5,6]. These oxalates have equivalents in nature. The ferrous oxalate is known as humboldtine [7]; the copper oxalate as moolooite [8]; the magnesium oxalate as glushinskite [9]; the ammonium oxalate as oxammite [10]; the sodium oxalate as natroxalate [11]. The advent of the thermal analysis of oxalates of the above cations started in the 1960s and no doubt was related to the advances in thermal analysis technology at the time [12–17]. Some early studies attempted to analyse the naturally occurring oxalates as a result of lichen growth [18–20]. Thermal analysis has been used to study the kinetics of formation of calcium oxalate dihydrate to mimic what is occurring in renal stones [21]. The kinetics of the thermal decomposition of calcium oxalate has been determined [22].

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The application of vibrational spectroscopy to the study of oxalates has been going on for an extended period of time [23–25]. Many synthetic oxalates have been studied [26,27]. Few oxalate minerals have been studied by Raman spectroscopy [28,29]. Studies of the kinetics of the thermal decomposition of calcium oxalate monohydrate have been undertaken using variable temperature DRIFT spectroscopy [30]. In mineralogy, this mineral is known as whewellite and may also be formed as a result of plant growth. This study showed that the kinetic analysis of the dehydration process indicates that there are two reactions taking place, as well as the presence of two different equimolar water molecule environments in the crystal structure of calcium oxalate monohydrate.

The presence of oxalates has been identified on the surface of monuments and give an indication of breakdown [31,32]. The presence of oxalates has been found in the prehistoric artwork of Australian indigenous peoples. Whether the oxalates resulted from the use of plant material to ensure the primitive paintings adhered to the cave walls or whether the oxalates formed through algal/lichen growth is unknown. The presence of oxalates has been identified on the surfaces of frescoes and important art objects [33–36]. The question arises as to the removal of the oxalates without harm or destruction of the fresco. One potential method of oxalate removal and remediation of the frescoes may be through low temperature thermal treatment. Such methodology may be of importance in the remediation of granite objects. The objective of this work is the analysis of the decomposition of weddellite using Raman spectroscopy combined with a thermal stage and complimented by infrared emission spectroscopy and high resolution thermogravimetry.

2. Experimental

2.1. Mineral

The weddellite was obtained from the South Australian Museum. The samples were phase analysed using X-ray diffraction and the compositions checked using energy dispersive X-ray emission (EDX) measurements. The mineral was found to be phase pure and compositionally equivalent to calcium oxalate dihydrate.

2.2. Thermal analysis

Thermal decomposition of the natural oxalate was carried out in a TA® Instruments incorporated high resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min). Approximately 50 mg of sample was heated in an open platinum crucible at a rate of 5.0 °C/min up to 500 °C. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases were analysed.

2.3. Raman microprobe spectroscopy

The crystals weddellite were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10× and 50× objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a charge coupled device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique [37–39]. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd., Waterfield, Surrey, UK).

2.4. Infrared emission spectroscopy (IES)

Details of infrared emission spectroscopy has been previously published [40–42]. 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. Raman spectroscopy using a thermal stage

Phases changes associated with the thermal treatment of weddellite can be followed by the use of a Raman microscope in combination with a thermal stage. Such a suite of spectra are shown in Fig. 1 for weddellite. The spectra clearly show changes in the Raman spectrum between 150 and 200 °C and again between 450 and 500 °C. The C=O stretching vibration is observed for oxalate in aqueous solution at 1496 cm^{-1} and for solid potassium oxalate at 1449 cm^{-1}. The band is at 1475 cm^{-1} for weddellite in the 298 K spectrum. The observation of a single band in the 298 K spectrum suggests the equivalence of the C=O stretching vibrations. No bands are observed in the infrared spectrum at 298 K. Thus, at 298 K, the structure is centrosymmetric. Symmetry loss through thermal treatment would occur if the structure was no longer planar. Mild heating to 50 °C causes two bands to appear in the Raman spectrum at 1490 and 1464 cm^{-1}. These band positions correspond to that of the partially dehydrated weddellite which is the mineral whewellite. Thus, the bands correspond to that of calcium oxalate monohydrate [29]. The bands are observed at 1488 and 1462 cm^{-1} in the 150 °C spectrum. Thus, there is a slight red shift with thermal treatment. The band positions are in agreement with previously published data [29]. At temperatures above 150 °C, the bands are observed at 1478 and 1466 cm^{-1}. These bands correspond to the symmetric stretching modes of anhydrous calcium oxalate. At temperatures above 450 °C only a single band is observed at 1480 °C. This band corresponds to the C=O symmetric stretching mode of calcium carbonate.

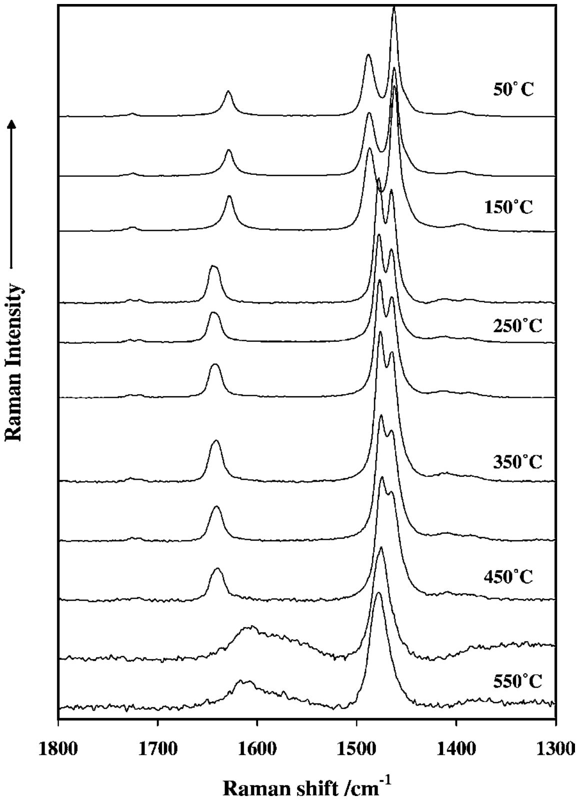

Fig. 1. Raman spectra of weddellite in the 50–550 °C temperature range.

The 298 K Raman spectrum shows a single low intensity band for weddellite at 1628 cm^{-1}. This band is attributed to the antisymmetric stretching vibration which for a planar structure should not be observed in the Raman spectrum. However, the structure is probably a distorted square antiprism [43]. This distortion results in the observation of the forbidden Raman bands. For aqueous oxalate the antisymmetric stretching (B_{2u}) mode is observed in the infrared spectrum at 1600 cm^{-1}. This band is observed at 1631 cm^{-1} in the 50 °C spectrum and at 1630 cm^{-1} for the 150 °C spectrum. This band corresponds to the C=O antisymmetric stretching mode of the calcium oxalate monohydrate. This band was reported to be at 1632 cm^{-1} which agrees well with the data reported in this work [28]. The observation of the antisymmetric stretching vibration suggests that the thermal treatment of the weddellite causes non-planarity in the structure. Thermal treatment above 150 °C shows a shift in the band positions. The two bands at 1490 and 1464 cm^{-1} shift to 1465 and 1478 cm^{-1} whilst the band at 1631 cm^{-1} shifts to 1647 cm^{-1}. The position of this band corresponds with that of anhydrous calcium oxalate [29]. Thermal analysis shows that water is lost over the 100–114 °C temperature range. Thus, the shift in the C=O stretching bands must be associated with water loss. At temperatures above 450 °C, the two bands at 1465 and 1478 cm^{-1} become a single band observed at 1478 cm^{-1}. The band at 1647 cm^{-1} disappears and is replaced with a very broad band centred at 1618 cm^{-1}. Thermal analysis shows that there is a mass loss step around 430 °C in which carbon dioxide is the evolved gas. A further weight loss step occurs around 595 °C in which further carbon dioxide is evolved. Such a temperature is above the upper temperature limit of the Raman thermal stage. It is suggested that above 450 °C, calcium carbonate is formed and above 590 °C carbon dioxide is lost and calcium oxide formed.

3.2. Infrared emission spectroscopy

The Raman data obtained by using a thermal stage is complimented by the infrared emission spectroscopy. Here in situ infrared spectra are obtained by using the hot weddellite as the emission source. Fig. 2 displays the infrared emission spectra in the 1200–1900 cm^{-1} range. The phase changes observed in the Raman spectra are also observed in the infrared emission spectra. Two bands are observed in the IE spectra at 1686 and 1633 cm^{-1} in the 75 °C spectrum. These bands show shift to higher wavenumbers with temperature increase. An additional band is observed at 1700 cm^{-1} which shows an increase in intensity over the 300–450 °C temperature range. Thermal treatment above 450 °C results in a completely different spectrum with bands observed at 1470 and 1788 cm^{-1}. This latter band shows no intensity above 550 °C and the former band intensity approaches zero at 650 °C. The Raman and infrared spectra are mutually exclusive up to 450 °C. The Raman spectra show intensity in bands in the 1470 cm^{-1} region and only very low intensity is observed in bands in this position in the IE spectra. This mutual exclusion shows that the weddellite is bidentate and planar up to 450 °C.

3.3. High resolution thermogravimetry coupled to a mass spectrometer

The Raman and IE spectra using thermal stages are supported by the evidence from high resolution thermogravimetry. The high resolution TG curve is shown in Fig. 3a and the mass spectrometric curve in Fig. 3b. The thermal decomposition of weddellite takes place in three stages at 114, 422 and 592 °C with mass loss steps of 17.5% (93.6 – 76.1), 15.4% (72.5 – 57.1) and 24.9% (55.9 – 31.0). These values compare with a theoretical mass losses of 21.6, 17.4 and 26.8%. Mass spectrometric analysis of the evolved gases shows that three gases are evolved, namely, water, carbon monoxide and carbon dioxide. Water is evolved at 96.7, 121.0 and 255.0 °C. Carbon monoxide principally comes off at 428 °C with a lesser amount at 608 °C. The carbon dioxide is emitted at 427 and 604 °C. Mass spectrometry shows that water is evolved over the 97–120 °C temperature range with a second water loss temperature range centred at 250 °C.

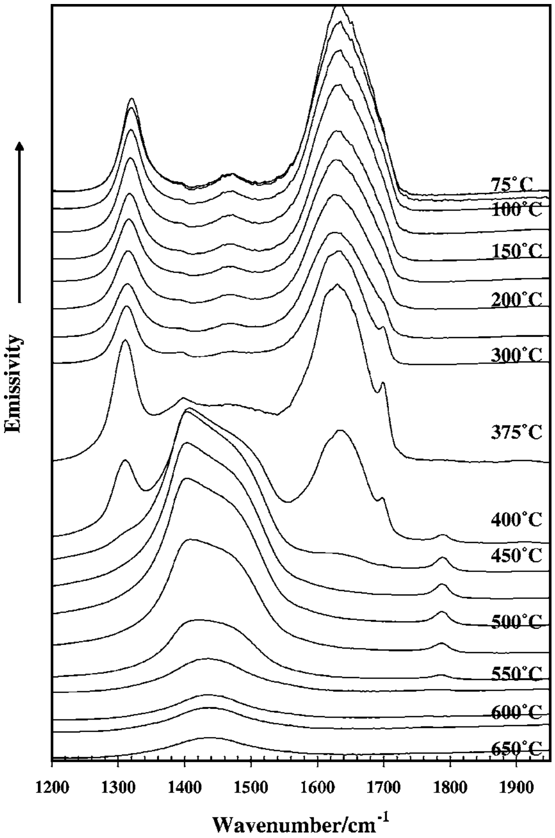

Fig. 2. Infrared emission spectra of weddellite in the 50–650 °C temperature range.

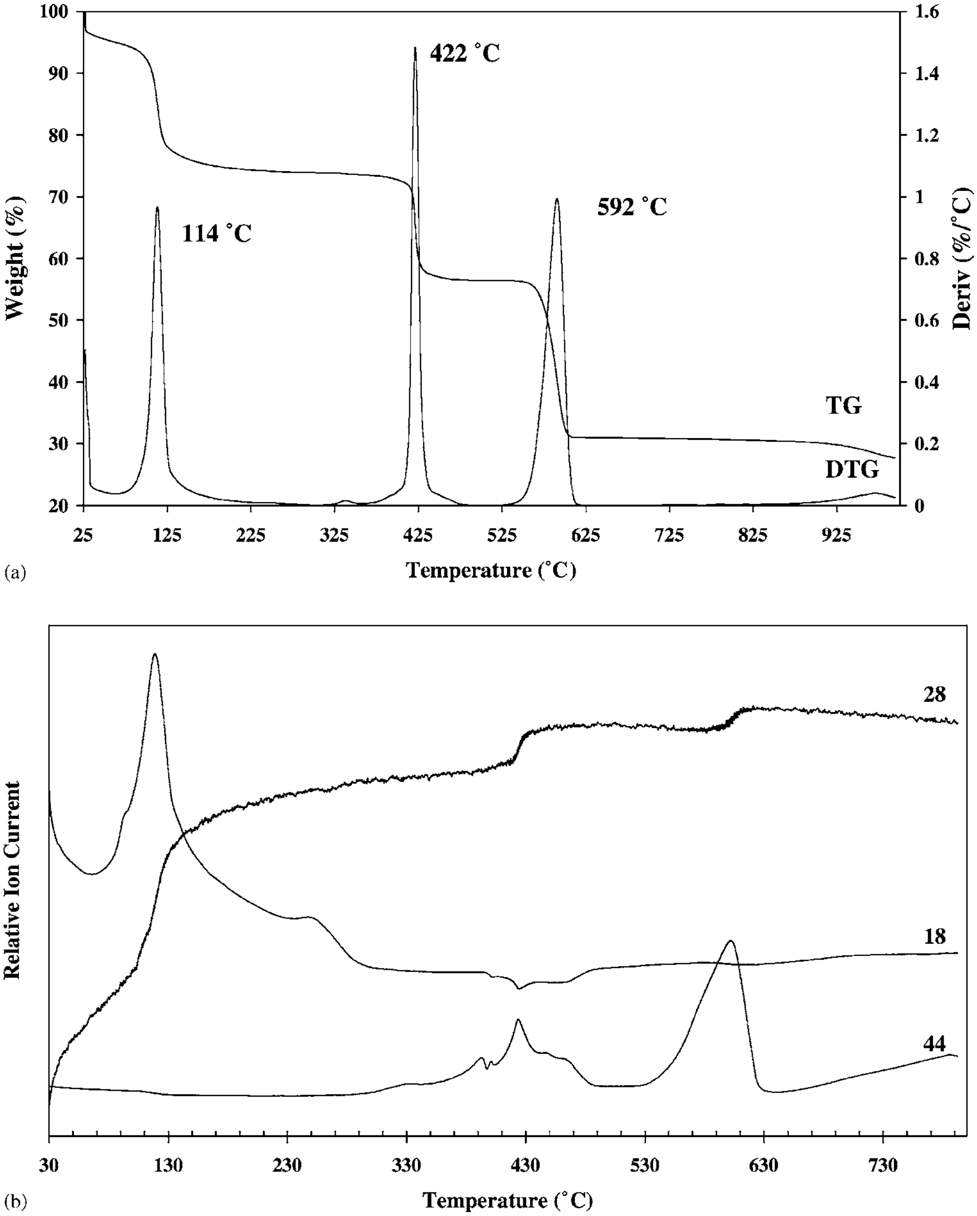

Fig. 3. (a) High resolution thermogravimetric analysis of natural weddellite. (b) Mass spectrometric analysis of weddellite.

3.4. Proposed mechanism of decomposition

The proposed mechanism is as follows:

$$CaC_2O_4 \cdot 2H_2O \rightarrow CaC_2O_4 + 2H_2O \quad T = 114\,^{\circ}C$$
$$CaC_2O_4 \rightarrow CaCO_3 + CO \quad T = 422\,^{\circ}C$$
$$CaCO_3 \rightarrow CaO + CO_2 \quad T = 592\,^{\circ}C$$

Decomposition takes place in three steps with the loss of water in the first step, carbon monoxide in the second step and carbon dioxide in the third step. The mechanism is in agreement with previous studies which have been many and varied [2,4,44–47]. However, the evolution of CO may be brought into question as little CO is observed as a product (Fig. 3b, mass 28). Previous studies have shown that H_2O, CO and CO_2 are evolved consecutively [4]. Such studies fit well with the proposed above mechanisms. The thermal analysis of calcium oxalate is used as a standard for the calibration of thermal analysis equipment and for teaching purposes [48]. The combination of thermal analysis and Raman spectroscopy has been previously used and has show that the thermal treatment of calcium oxalate dihydrate is calcite [49].

3.5. Additional Raman spectroscopy using a thermal stage

Further evidence for significant changes in the structure of weddellite may be obtained by a study of the C–C stretching region. Fig. 4 shows the Raman spectra of this region as a function of temperature. The band is observed in the 895 cm^{-1} region. It is noted that the position of the C–C stretching vibration is 902 cm^{-1} for the free oxalate ion. Previous studies showed that the C–C stretching mode was observed at 896 and 904 cm^{-1} for calcium oxalate monohydrate and anhydrous calcium oxalate, respectively [29]. Upon thermal treatment the band shifts to 905 cm^{-1}. This corresponds to the C–C stretching mode of anhydrous calcium oxalate [50]. Thermal treatment above 650 °C results in no intensity in this band. An additional band is observed at 866 cm^{-1}. This band may be assigned to a O–C–O bending mode. This band shows a slight blue shift and the intensity of the band approaches zero

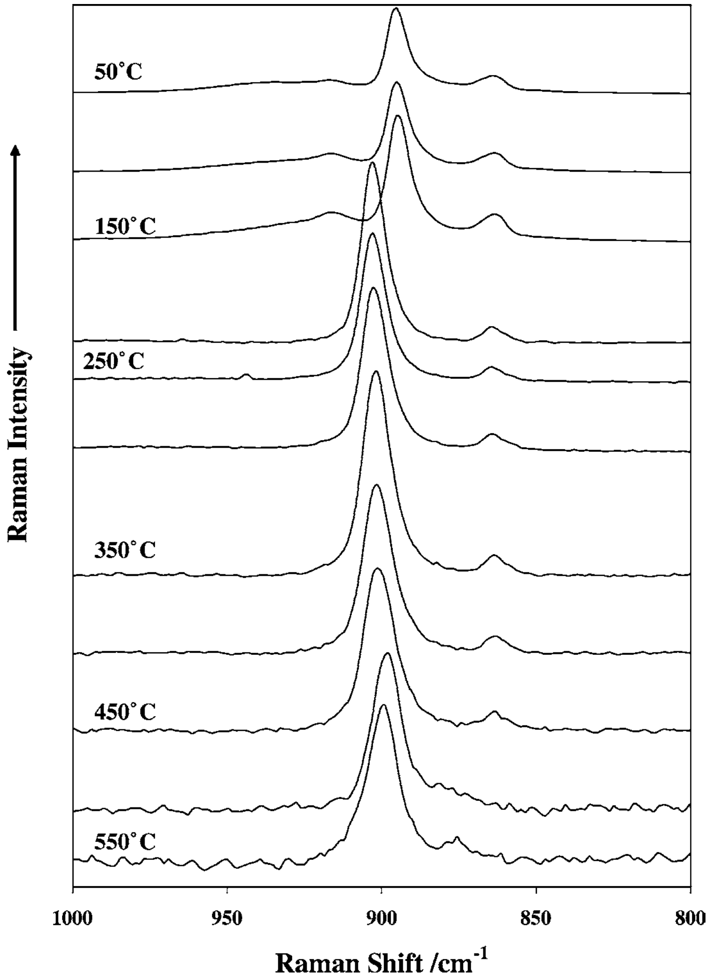

Fig. 4. Raman spectra of the 800–1000 cm^{-1} region of weddellite.

by 550 °C. In a previous study which focussed on obtaining the Raman spectra of calcium oxalate monohydrate between 134 and 210 °C, multiple C–C bands were observed indicating a mix of two phases, namely, calcium oxalate monohydrate and anhydrous calcium oxalate [28,29]. The temperature of the phase transition differs from that observed in this work by both Raman spectroscopy and by high resolution TG. The IE spectra for the 650–1000 cm^{-1} region are shown in Fig. 5. The data compliments the Raman spectra. No bands are observed around 900 cm^{-1} and a very low intensity band is observed around 867 cm^{-1}. There is a band at 788 cm^{-1} which is assigned to a O–C–O bending vibration. The intensity of this band is constant over the temperature range up to 400 °C. No change is observed in the IE spectra until 450 °C, when two bands are observed at around 784 and 761 cm^{-1}. After 500 °C, these bands are no longer observed. Two bands are observed at 872 and 711 cm^{-1} with a low intensity band at 862 cm^{-1}. The intensity of these bands

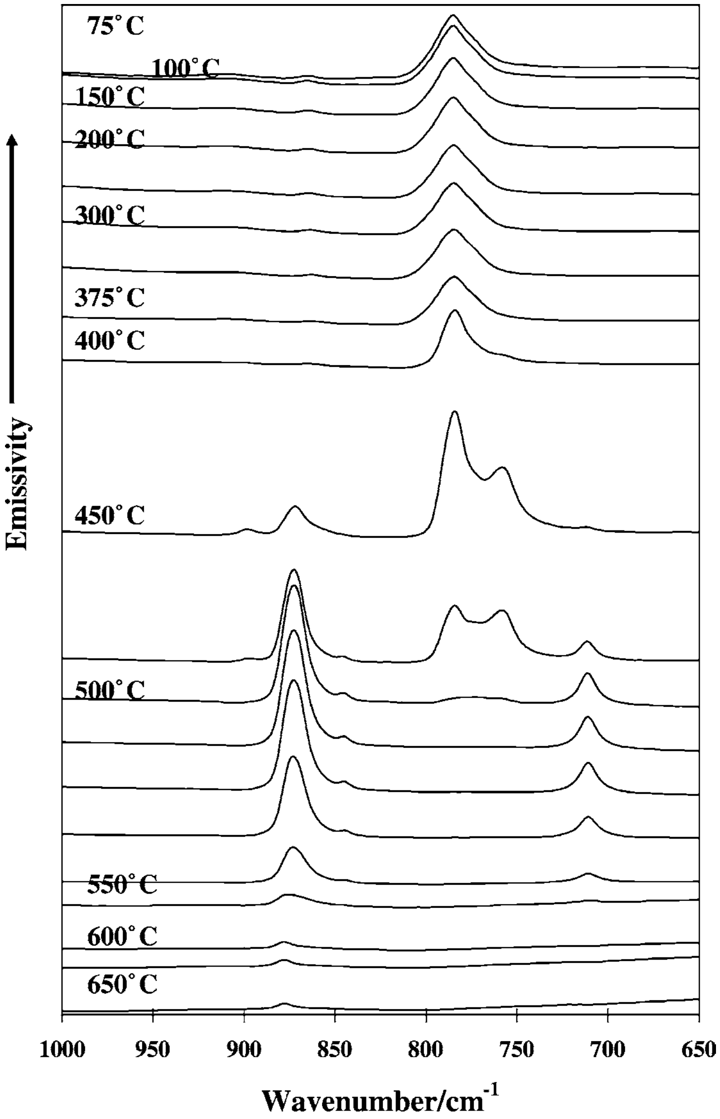

Fig. 5. Infrared emission spectra of the 200–700 cm^{-1} region of weddellite.

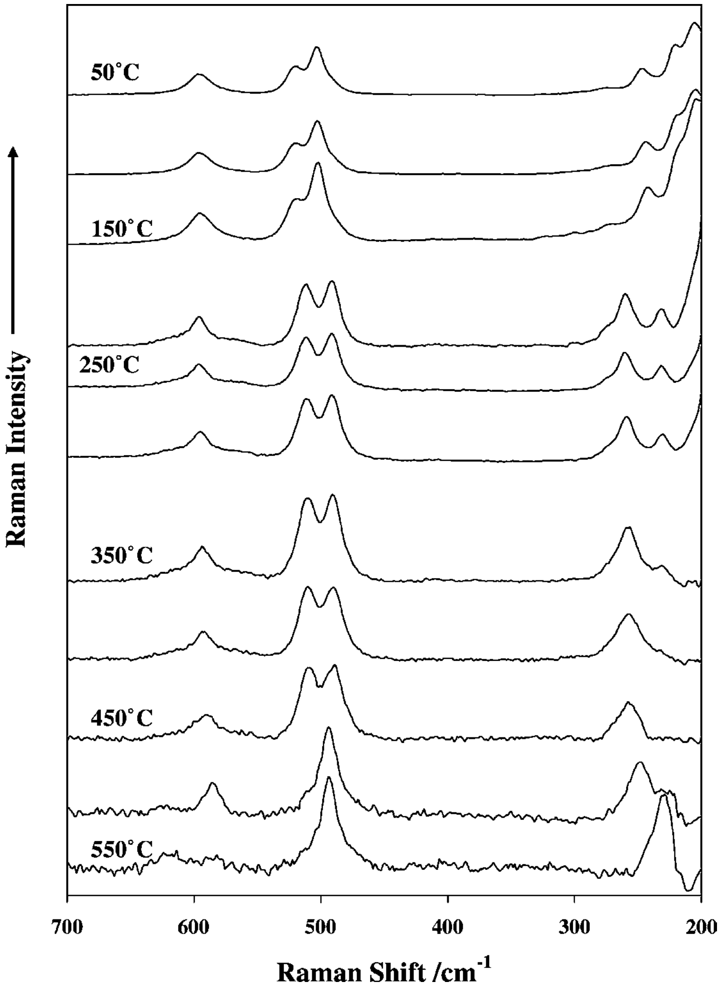

Fig. 6. Raman spectra of the 200–700 cm^{-1} region of weddellite.

decrease with temperature increase until above 650 °C no intensity remains in the bands.

The Raman spectrum of the low wavenumber region of weddellite is shown in Fig. 6. A number of intense Raman bands are observed in the 400–600 cm^{-1} region. The Raman spectrum of weddellite shows an intense band at 505 cm^{-1} with a broad band at 596 cm^{-1}. Previous studies have assigned the band at around 500 cm^{-1} to the bending mode of C–C–O and the M–O ring and M–O stretching modes [51,52]. The band at around 596 cm^{-1} is also associated with M–O stretching modes [51,52]. Importantly two bands are observed at 523 and 505 cm^{-1} with different intensities. Above 150 °C, the intensity of the two bands becomes identical. Above 450 °C, the band becomes a single band at 495 °C. The possible assignment of these bands is to O–Ca–O and C–C–O bending vibrations. Previous studies based upon Raman spectroscopy suggested that dehydration occurred at 423 K [29]. This value seems high compared with the results of this work. This study suggested that the two bands at 523 and 505 cm^{-1} were due to Breit–Wigner coupling. This work shows there is an intensity relationship between these two bands which is temperature dependent.

A number of intense bands are observed between 200 and 300 cm^{-1} for these natural oxalates. Raman spectroscopy does have the advantage that bands below 400 cm^{-1} are readily obtained. This is important to the study of oxalates as the M–O stretching and O–M–O ring bending modes may be determined. In the Raman spectrum of weddellite, bands are observed at 259 and 220 cm^{-1} in the 298 K spectrum. These bands are probably attributable to Ca–O ring stretching or bending modes. Low intensity bands are observed at 249, 223 and 209 cm^{-1}. The spectra in this work differs from previously published data [28,29]. In the work of Duval and Condrate, a band was observed at 209 cm^{-1} for the monohydrate and at 260 cm^{-1} for the anhydrous calcium oxalate. The position of these bands at 249, 223 and 209 cm^{-1} remains constant over the 50–150 °C temperature range. Above 150 °C, two bands are observed at 261 and 235 cm^{-1}. The intensity of the bands remains constant over the 200–350 °C temperature range. From 350 to 450 °C, the intensity of the 235 cm^{-1} band decreases. Changes are occurring in the intensity and position of these very low wavenumber bands when no changes are being observed in other higher wavenumber bands. These changes suggest that structural changes are occurring as a function of temperature on a molecular level over the complete temperature range.

To complete the vibrational spectroscopic study of the thermal treatment of weddellite, the spectra of the hydroxyl stretching region need to be studied even though the Raman spectrum of water is difficult as water is a very poor scatterer and infrared emission spectroscopy suffers from noise. Previous studies have neglected the Raman or infrared spectra of the hydroxyl stretching region during thermal treatment [28,29]. Figs. 7 and 8 show the Raman spectra and infrared emission spectra of the hydroxyl stretching region of weddellite as a function of temperature. Multiple bands are observed in the spectra. At 50 °C, bands are observed at 3493, 3444, 3351, 3261 and 3072 cm^{-1}. The bands are observed at 3505, 3454, 3351, 3244, 3074 and 3017 cm^{-1}. At 150 °C, four bands are observed at 3483, 3353, 3249 and 3075 cm^{-1}. The bands show a red shift with thermal treatment. At 200 °C, almost no intensity remains in these bands. Such an observation is in agreement with the TG–MS data which showed that a small amount of water is lost at 250 °C. X-ray crystallography shows that the two waters molecules in the lattice are independent [43]. For weddellite there are eight water molecules in the structure ($z = 8$) with space group $I4/m$, this means that there are four Raman and four infrared bands would be predicted. Also associated with the structure is zeolitic water. Thus, six Raman bands should be observed in agreement with the observed spectral results. This explains the multiplicity of bands observed in the Raman spectra of weddellite. In weddellite, the calcium co-ordination is in a distorted square antiprism and of the eight oxygen ions, six belong to four oxalic groups and two to water molecules.

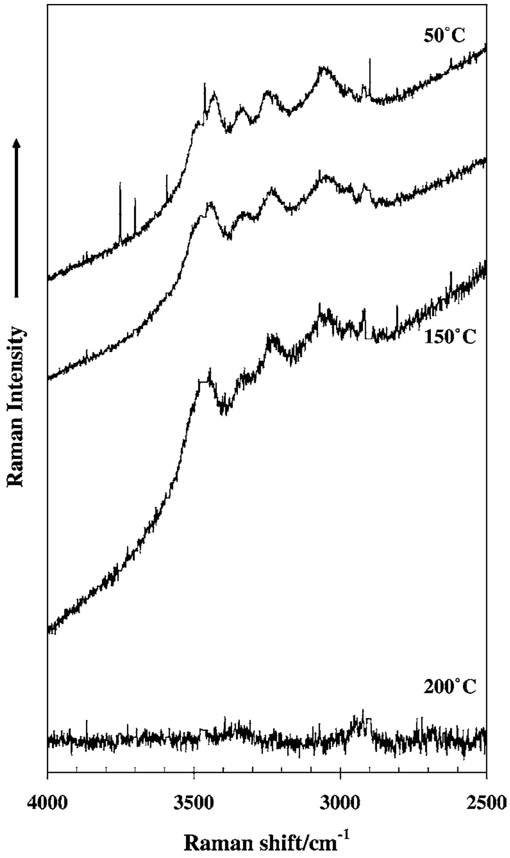

Fig. 7. Raman spectra of the hydroxyl stretching region over the 50–200 °C temperature range.

A low intensity band is observed at 2946 cm^{-1}. The presence of this band may indicate some organic impurities in the mineral sample. Multiple band in the Raman spectra show that at the molecular level more than one type of bonding of water molecules is present. The water molecules are held in the weddellite structure in different ways according to the bond strength of the OH units [53–55]. Such a conclusion was reached

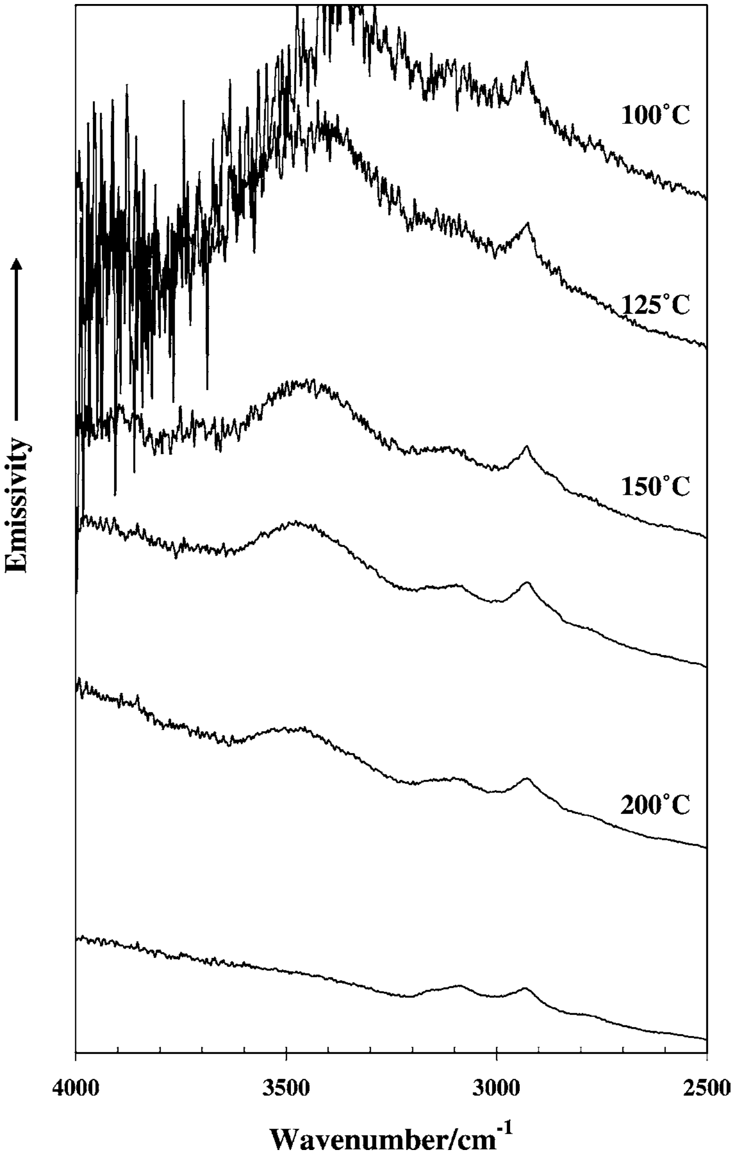

Fig. 8. Infrared emission spectra of the hydroxyl stretching region of weddellite.

by Christy et al. who used infrared spectroscopy [30]. Secondly thermal treatment may cause the conversion of weddellite to whewellite. In the IE spectra bands are observed at around 3475, 3124 and 2939 cm^{-1}. No intensity remains in the bands at 250 °C. The results of the vibrational spectroscopy of weddellite are in harmony with the thermal analysis results which show that water is lost over the 100–114 °C temperature range. The HRTG experiment takes place slowly with a small temperature ramp rate. In the vibrational spectroscopic experiment, the process occurs more rapidly.

4. Conclusions

The presence of weddellite is important in the quest for the origin of life in hazardous and harsh climatic conditions, such conditions as could be expected on planets such as Mars. Importantly this study has shown the thermal conditions above which the presence of weddellite could not be observed. Such extreme conditions are expected on a number of planets in the solar system. The identification of this mineral is important for the detection of existing or pre-existing life on planets such as Mars. A combination of Raman and infrared emission spectroscopy has been used to study the thermal decomposition of a natural sample of weddellite. The Raman spectra were obtained using a combination of Raman microscopy in combination with a thermal stage. Infrared emission spectra were obtained by collecting spectra in situ at the elevated temperatures. The spectroscopic data was complimented by high resolution thermogravimetric analysis in combination with evolved gas mass spectrometry. Both sets of spectral data show changes in the molecular structure as a function of temperature. The Raman and infrared spectra are mutually exclusive showing that structure of weddellite is bidentate and planar.

Thermal analysis shows that a weight loss step occurs over the 100–114 °C temperature range and mass spectrometry proves that this weight loss step is associated with water loss. Complexity exists in the vibrational spectra of weddellite with thermal treatment. The observation of a complex set of overlapping bands shows that more than one type of water is present and that dehydration may take place at low temperatures. The phase change at 114 °C results in the formation of anhydrous calcium oxalate which above 422 °C converts to calcium carbonate and to calcium oxide above 592 °C. These phase changes can be readily followed by Raman spectroscopy and infrared emission spectroscopy. Shifts in the band positions of the symmetric stretching modes provide details of the changes in molecular structure during these phase changes.

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References

[1] K.S. Alexander, D. Dollimore, J.G. Dunn, X. Gao, D. Patel, Thermochim. Acta 215 (1993) 171.

[2] F.M. Angeloni, Differential thermal analysis studies on the mechanism of the and oxidative decomposition of calcium oxolate monohydrate, Ph.D. thesis, Pennsylvania State University, 1966.

[3] L. Campanella, E. Cardarelli, R. Curini, G. D'ascenzo, M. Tomassetti, J. Therm. Anal. 38 (1992) 2707.

[4] F. Carrasco, Afinidad 48 (1991) 19.

[5] C.S.R. Murthy, G.N. Rao, Thermochim. Acta 55 (1982) 19.

[6] B.-R. Shen, H. Shen, Y.-X. Pan, T.-F. Chen, X.-E. Cai, Zeitschrift fuer Physikalische Chemie (Muenchen, Germany) 215 (2001) 1413.

[7] S. Caric, Bull. Soc. Fr. Mineral. Crist. 82 (1959) 50.

[8] J.E. Chisholm, G.C. Jones, O.W. Purvis, Mineral. Mag. 51 (1987) 715.

[9] M.J. Wilson, D. Jones, J.D. Russell, Mineral. Mag. 43 (1980) 837.

[10] M.M. Singh, E. Marsafy, R. Pike, Z. Szafran, in: Abstracts of Papers, Proceedings of the 222nd ACS National Meeting, CHED, Chicago, IL, USA, 26–30 August 2001.

[11] A.P. Khomyakov, Zapiski Vserossiiskogo Mineralogicheskogo Obshchestva 125 (1996) 126.

[12] W.W. Wendlandt, T.D. George, K.V. Krishnamurty, J. Inorg. Nucl. Chem. 21 (1961) 69.

[13] H.G. Mcadie, Anal. Chem. 35 (1963) 1840.

[14] H.H. Horowitz, G. Metzger, Anal. Chem. 35 (1963) 1464.

[15] D. Dollimore, D.L. Griffiths, D. Nicholson, J. Chem. Soc. (1963) 2617.

[16] D.E. Dollimor, D.N. Nicholso, J. Inorg. Nucl. Chem. 25 (1963) 739.

[17] V.V. Subba Rao, R.V.G. Rao, A.B. Biswas, J. Inorg. Nucl. Chem. 27 (1965) 2525.

[18] B.D. Mitchell, A.C. Birnie, J.K. Syers, Analyst (London) 91 (1966) 783.

[19] K.P. Pribylov, D.S. Fazlullina, Zh. Neorg. Khim. 14 (1969) 660.

[20] H.A. Papazian, P.J. Pizzolato, J.A. Patrick, J. Am. Ceram. Soc. 54 (1971) 250.

[21] L. Lepage, R. Tawashi, J. Pharm. Sci. 71 (1982) 1059.

[22] R. Lozano, J. Roman, F. De Jesus, A. Jerez, M. Gaitan, E. Ramos, Thermochim. Acta 143 (1989) 93.

[23] E.C. Gruen, R.A. Plane, Inorg. Chem. 6 (1967) 1123.

[24] J. Gupta, Indian J. Phys. 10 (1936) 199.

[25] G.M. Begun, W.H. Fletcher, Spectrochim. Acta 19 (1963) 1343.

[26] N.A. Chumaevskii, O.U. Sharopov, Zh. Neorg. Khim. 33 (1988) 1914.

[27] R.J.H. Clark, S. Firth, Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. 58A (2002) 1731.

[28] D. Duval, R.A. Condrate, Phys. Status Solidi B: Basic Res. 132 (1985) 83.

[29] D. Duval, R.A. Condrate Sr., Appl. Spectrosc. 42 (1988) 701.

[30] A.A. Christy, E. Nodland, A.K. Burnham, O.M. Kvalheim, B. Dahl, Appl. Spectrosc. 48 (1994) 561.

[31] B. Prieto, M.R.D. Seaward, H.G.M. Edwards, T. Rivas, B. Silva, Biospectroscopy 5 (1999) 53.

[32] J.M. Holder, D.D. Wynn-Williams, F.R. Perez, H.G.M. Edwards, New Phytologist 145 (2000) 271.

[33] H.G.M. Edwards, N.C. Russell, M.R.D. Seward, Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. 53A (1997) 99.

[34] H.G.M. Edwards, N.C. Russell, M.R.D. Seaward, D. Slarke, Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. 51A (1995) 2091.

[35] H.G.M. Edwards, D.W. Farwell, M.R.D. Seaward, Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. 47A (1991) 1531.

[36] H.G.M. Edwards, K.A.E. Edwards, D.W. Farwell, I.R. Lewis, M.R.D. Seaward, J. Raman Spectrosc. 25 (1994) 99.

[37] R.L. Frost, J.T. Kloprogge, J. Raman Spectrosc. 31 (2000) 415.

[38] R.L. Frost, J. Kristof, E. Horvath, J.T. Kloprogge, J. Colloid Interface Sci. 226 (2000) 318.

[39] R.L. Frost, J. Kristof, J.T. Kloprogge, in: C.S.F. Gomes (Ed.), Proceedings of the First Latin-American Clay Conference, vol. 1, Associacao Portueguesa de Argilas (APA), Funchal, Madeira, Portugal, 17–22 September 2000, 292 pp.

[40] R.L. Frost, Z. Ding, J.T. Kloprogge, W.N. Martens, Thermochim. Acta 390 (2002) 133.

[41] R.L. Frost, Z. Ding, W.N. Martens, T.E. Johnson, Thermochim. Acta 398 (2003) 167.

[42] R.L. Frost, J. Kristof, E. Horvath, J.T. Kloprogge, J. Raman Spectrosc. 32 (2001) 873.

[43] V. Tazzoli, C. Domenehetti, Am. Mineralogist 65 (1980) 327.

[44] J.C. Chang, A study of the thermal decomposition of calcium oxolate, Ph.D. thesis, University of Akron, Akron, OH, USA, 1976.

[45] S. Gurrieri, G. Siracusa, R. Cali, J. Therm. Anal. 6 (1974) 293.

[46] J. Mu, D.D. Perlmutter, Thermochim. Acta 49 (1981) 207.

[47] Y. Zhang, M. Luo, Zhonghua Yixue Zazhi (Beijing, China) 65 (1985) 474.

[48] A.M.M. Gadalla, Thermochim. Acta 74 (1984) 255.

[49] H. Chang, P.J. Huang, Anal. Chem. 69 (1997) 1485.

[50] T.A. Shippey, J. Mol. Struct. 63 (1980) 157.

[51] H.G.M. Edwards, D.W. Farwell, S.J. Rose, D.N. Smith, J. Mol. Struct. 249 (1991) 233.

[52] R.I. Bickley, H.G.M. Edwards, S.J. Rose, J. Mol. Struct. 243 (1991) 341.

[53] J.F. Wood, Proc. Univ. Durham Philos. Soc. 7 (1926) 111.

[54] R. Marignan, Bull. Soc. Chim. Fr. (1948) 350.

[55] S.B. Hendricks, Z. Kristallogr. 91 (1935) 48.