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Thermal treatment of whewellite—a thermal analysis and Raman spectroscopic study

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Abstract

Thermal transformations of natural calcium oxalate monohydrate known in mineralogy as whewellite have been undertaken using a combination of thermal analysis and Raman microscopy with the use of a thermal stage. High resolution thermogravimetry shows that three mass loss steps occur at 162, 479 and 684 °C.

Evolved gas mass spectrometry shows that water is evolved in the first step and carbon dioxide in the second and third mass loss steps. The changes in the molecular structure of whewellite can be followed by the use of the in situ Raman spectroscopy of whewellite at the elevated temperatures. The whewellite is stable up to around 161 °C, above which temperature the anhydrous calcium oxalate is formed. At 479 °C, the oxalate transforms to calcium carbonate with loss of carbon dioxide. Above 684 °C, calcium oxide is formed.

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

1. Introduction

The thermal analysis of oxalates has been studied for some considerable time [1–7]. The effect of atmosphere on the thermal analysis has been documented [8,9]. Studies on calcium oxalate mono and dihydrate have been undertaken [10,11]. One of the biggest applications of thermal analysis is in the determination of the properties of renal stones [12–16]. Thermal analysis has been successfully used to identify a range of oxalates and related minerals in the urinary tract. The preparative methodology for the synthesis of calcium oxalate minerals has been shown to effect the thermal analysis [17]. It was found that the Arrhenius parameters are significantly altered by the preparative route, initial dehydration and the environmental conditions. The temperature range for dehydration varied between 161.1 and 185.1 °C [17]. This data appears to refer to the monohydrate rather than the dihydrate. Decomposition to calcium carbonate occurred over the temperature range 459.1–495.2 °C [17]. Decomposition of the calcium carbonate occurred over a wide temperature range from 726 to 762 °C. This data appears to refer to the monohydrate only. In a study of weddellite by the authors 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 mass loss steps were found to occur at significantly lower temperatures for the dihydrate compared with the monohydrate.

The presence of oxalates often results from primitive plant growths. Their presence may offer an indicator of pre-existing life forms. The presence of oxalates has been identified on the surface of monuments and give an indication of art object breakdown [18,19]. The type of oxalate formed depends upon the host rock. The lichen will simply expel the excess heavy metal as the oxalate. The presence of oxalates has been found in the prehistoric art work 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 [20–23]. 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

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importance in the remediation of granite objects. The objective of this work is the analysis of the decomposition of whewellite using high resolution thermogravimetry coupled to evolved gas mass spectrometry complimented by in situ Raman spectroscopy at elevated temperatures.

2. Experimental

2.1. Mineral

The weddellite was obtained from the Museum Victoria. The samples were phase analyzed 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 analyzer (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 analyzed.

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 [24–26]. Spectra at elevated temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd., Waterfield, Surrey, England).

2.4. Infrared emission spectroscopy (IES)

Details of IES have been previously published [27–29]. 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. High resolution thermogravimetry coupled to a mass spectrometer

High resolution thermogravimetry of the natural whewellite is shown in Fig. 1. Three mass loss steps are observed at 162 °C (12.6%), 479 °C (19.7%) and 687 °C (31.2%). The theoretical mass loss steps are 12.3, 19.1 and 30.1%. Some difference between the experimental and theoretic results is noted; however, it must be kept in mind that the sample is a natural mineral. Studies of calcium oxalate mono and dihydrates have been undertaken for some time. Walter–Levy and Laniepce determined the thermal decomposition of calcium oxalate monohydrate in 1964. They found that the dihydrate changed to monohydrate at 120°, monohydrate to α-CaC_2O_4 at 235°, α-CaC_2O_4 to β-CaC_2O_4 at 250–370 °, β-CaC_2O_4 to γ-CaC_2O_4 at 410°, γ-CaC_2O_4 to $CaCO_3$ at 410–75°, $CaCO_3$ to CaO at 860° [30]. In a recent study, by the authors, the thermal decomposition of the natural calcium dihydrate known as weddellite mass loss steps for weddellite were found at 114, 422 and 592 °C. These temperatures are at values considerable less than the values observed for whewellite. Simons and Newkirk showed that the results of the thermal analysis depended on the way in which the experiment was undertaken [31]. Such differences in the results of the thermal analysis are often small. These observed temperature variations may be attributed to the way in which the experiment was undertaken. These variations depend upon heating rate, sample mass, and the nature and flow rate of the sweeping gas. The significance of the differences in the mass loss temperatures of weddellite and whewellite is a reflection of the bond strength of the water in the crystal. Gal et al. showed that the dehydroxylation temperature of synthetic tri, di and monohydrates was dependent upon the bonding of water [32]. The monohydrate lost water at 180 °C and the dihydrate at 150 °C. These values differ considerably for the temperature of dehydration of whewellite and weddellite.

The following mechanism is proposed for the thermal decomposition of whewellite. It is envisaged that three mass

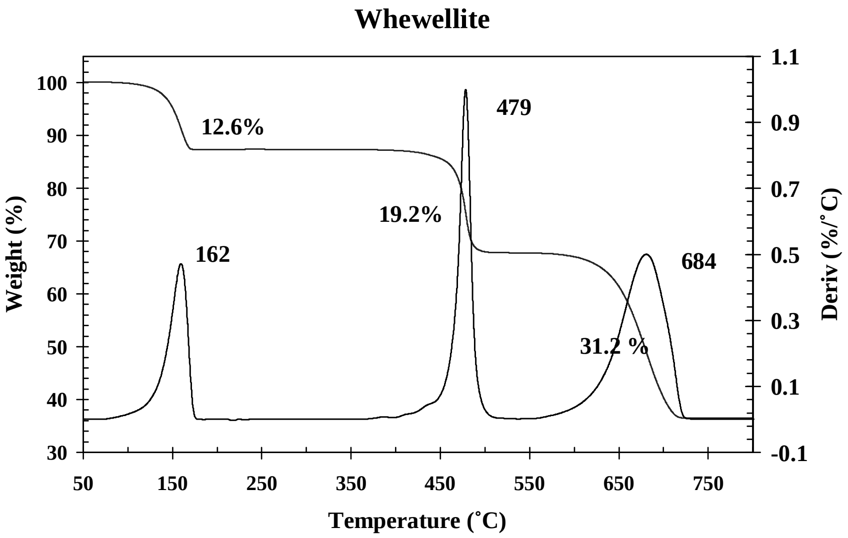

Fig. 1. High resolution thermogravimetry and differential thermogravimetry of whewellite.

loss steps are involved in the thermal decomposition of whewellite as follows:

1. $\underset{100\%}{CaC_2O_4 \cdot H_2O} \rightarrow \underset{87.7\%}{CaC_2O_4} + H_2O$
2. $\underset{87.7\%}{CaC_2O_4} \rightarrow \underset{68.5\%}{CaCO_3} + CO$
3. $\underset{68.5\%}{CaCO_3} \rightarrow \underset{38.4\%}{CaO} + CO_2$

The DTG and mass spectrometric curves for whewellite are shown in Fig. 2. The principal evolved gases are carbon dioxide and water vapour. The water vapour is evolved at 161 °C. The carbon dioxide appears to be evolved in two stages at 479 and 684 °C. Some carbon monoxide appears to be evolved at 479 °C. No water vapour is lost above 161 °C. The sum of the mass spectrometric curves of water and carbon dioxide matches the DTG curve with precision. For weddellite water vapour was evolved at 120 and 251 °C and carbon monoxide evolved at 427 and carbon dioxide at 426 and 603 °C. As for the TG mass loss results, the temperatures at which the evolved gases are observed are at significantly higher temperatures for whewellite than for weddellite.

Decomposition takes place in three steps with the loss of water in the first step, carbon monoxide and carbon dioxide 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 [10–12,33–35]. However, the evolution of CO may be brought into question as little CO is observed as a product. Previous studies have shown that H_2O, CO and CO_2 are evolved consecutively [34]. Such studies fit well with the proposed above mechanisms. The combination of thermal analysis and Raman spectroscopy has been

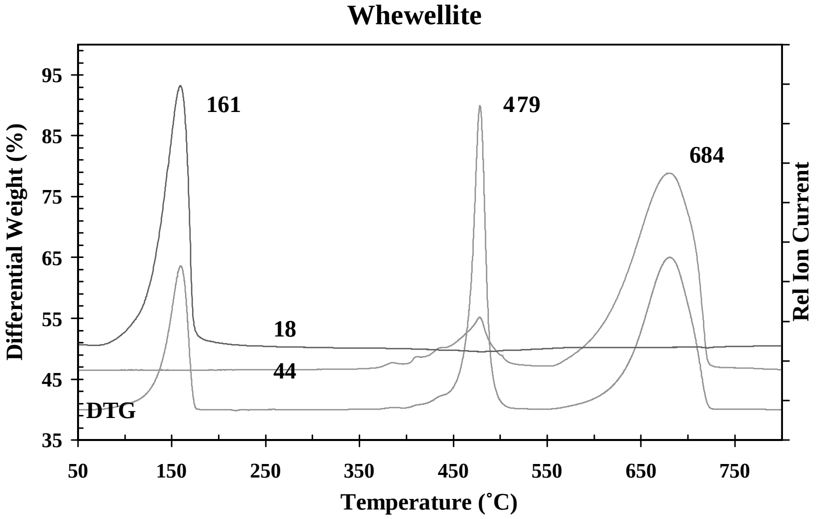

Fig. 2. Evolved gas mass spectrometry and DTG of whewellite.

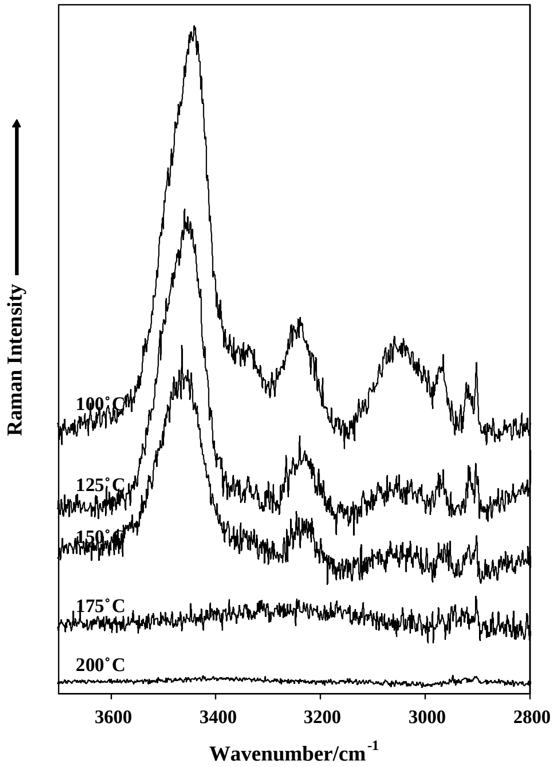

Fig. 3. In situ Raman spectra of the hydroxyl stretching region of whewellite over the 100–200 °C temperature range.

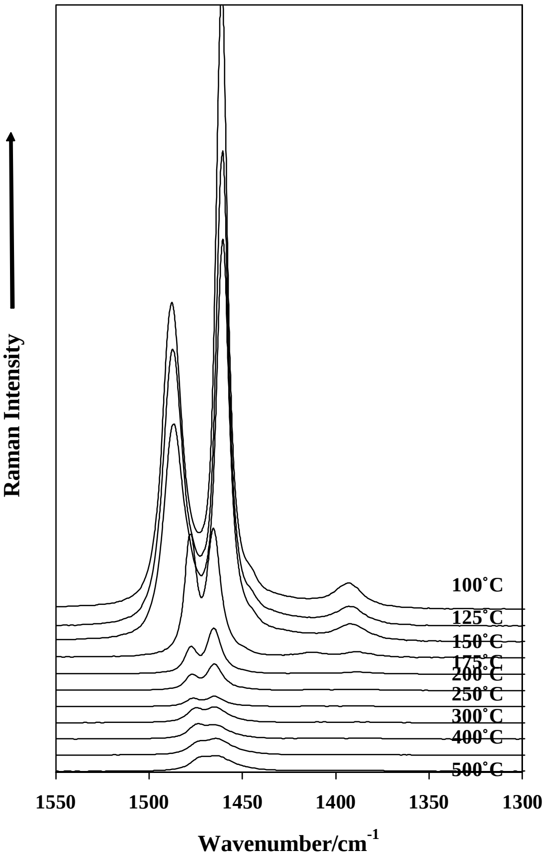

Fig. 4. In situ Raman spectra of the CO symmetric stretching region of whewellite as a function of temperature.

previously used and has shown that the thermal treatment of calcium oxalate dihydrate is calcite [36].

3.2. Raman spectroscopy using a thermal stage

The Raman spectra of the hydroxyl stretching region of thermally treated whewellite are shown in Fig. 3. Quite clearly the intensity of the bands attributed to the hydroxyl stretching modes of water is lost by 175 °C. Bands are observed for whewellite at 3484, 3427, 3344, 3253 and 3053 cm^{-1}. These bands show significant shifts in band centre at 77 K where bands are observed at 3475, 3415, 3341, 3262, 3048 and 3045 cm^{-1}. A previous study gave bands at 3486, 3426, 3342 and 3250 cm^{-1} [37]. The bands broaden considerably with thermal treatment and shift to higher wavenumbers. Such a shift indicates a weakening of the hydrogen bonding of the water in the whewellite crystal structure. In the spectrum at 100 °C, bands are observed at 3442, 3338, 3237, 3049 and 2966 cm^{-1}. The first band shifts to 3460 cm^{-1} at 150 °C before the intensity of the band is lost. The results of the Raman spectra at elevated temperatures fit well with the HRTG data. Raman spectroscopy shows no intensity remains in the OH stretching bands of water at 175 °C. The HRTG showed that a significant mass loss occurred at 161 °C and evolved gas mass spectrometry showed that water was lost at this temperature. It is interesting to compare the results of the thermal analysis and Raman spectroscopy of the natural mineral weddellite. HRTG shows that mass loss attributed to evolved water vapour occurs at 114 °C. Only two bands are observed for weddellite in the hydroxyl stretching region at 3467 and 3266 cm^{-1}. Upon thermal treatment 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} in the spectrum at 100 °C. At 150 °C, four bands are observed at 3483, 3353, 3249 and 3075 cm^{-1}. The significance of these results rests with the interpretation of the data. Mild heating of weddellite results in the formation of whewellite. In other words at relatively low temperatures, the monohydrate is formed. Thus, the Raman spectrum of the heat treated weddellite is a mix of the Raman spectra of the two minerals.

The Raman spectrum of whewellite in the 1300–1550 cm^{-1} region is shown in Fig. 4. This region is attributed to CO stretching. Two bands are observed at 1492 and 1464 cm^{-1} at 25 °C. These bands are assigned to the CO symmetric stretching vibrations. The bands shift to 1487 and 1460 cm^{-1} at 100 °C and remain constant in position up to 150 °C. Above 150 °C, a significant shift in the position of these bands is observed. The band positions are in agreement with previously published data [38]. 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 cm^{-1}. This band corresponds to the CO symmetric stretching mode of calcium carbonate. An additional band may be resolved in the spectra at 1448 cm^{-1}. A band is also observed at 1398 cm^{-1} in the 25 °C spectrum. This band shifts to 1392 cm^{-1} at 100 °C and to 1387 cm^{-1} at 200 °C. Above this temperature the band shows no intensity. The assignment of this band according to Shippey was a combination band [37]. The assignment of the band changed with dehydration. It is interesting to compare the spectrum of whewellite to weddellite. Only a single band is observed for weddellite at 1475 cm^{-1} at 25 °C. Thus, the CO stretching modes for weddellite are equivalent. No infrared band is observed in this position. This suggests the structure of weddellite is centrosymmetric. In contrast the CO stretching vibrations for whewellite are non-equivalent.

The Raman spectrum of the antisymmetric stretching region of whewellite is shown in Fig. 5. A single band is observed at 1631 cm^{-1} at 25 °C in good agreement with previously published data [37]. An additional band is observed at 1728 cm^{-1} attributed to the first overtone of the bending mode (2X ν_2). The band is observed at 1626 cm^{-1} over the 100–150 °C temperature range. Above 150 °C the band is observed at 1646 cm^{-1}. The band shows a shift to lower wavenumbers with increasing temperature. For weddellite the 298 K Raman spectrum shows a single low intensity band 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 [39]. This distortion results in the observation of the forbidden Raman bands. For aqueous oxalate the antisymmetric stretching (B_{2u}) mode is observed as an intense band in the infrared spectrum at 1600 cm^{-1}. Interestingly the band at 1724 cm^{-1} splits into two bands at 1717 and 1728 cm^{-1} at temperatures above 150 °C. The observation of the antisymmetric stretching vibration suggests that the thermal treatment of the weddellite causes non-planarity in the structure. The position of this band at 1626 cm^{-1} corresponds with that of anhydrous calcium oxalate [38].

The infrared emission spectra of thermally treated whewellite are shown in Fig. 6. The set of infrared emission spectra clearly shows the phase changes that occur with the thermal treatment of whewellite. From 100 to around 450 °C, the spectra are the infrared spectra of anhydrous calcium oxalate. The spectrum at 450 °C is the temperature

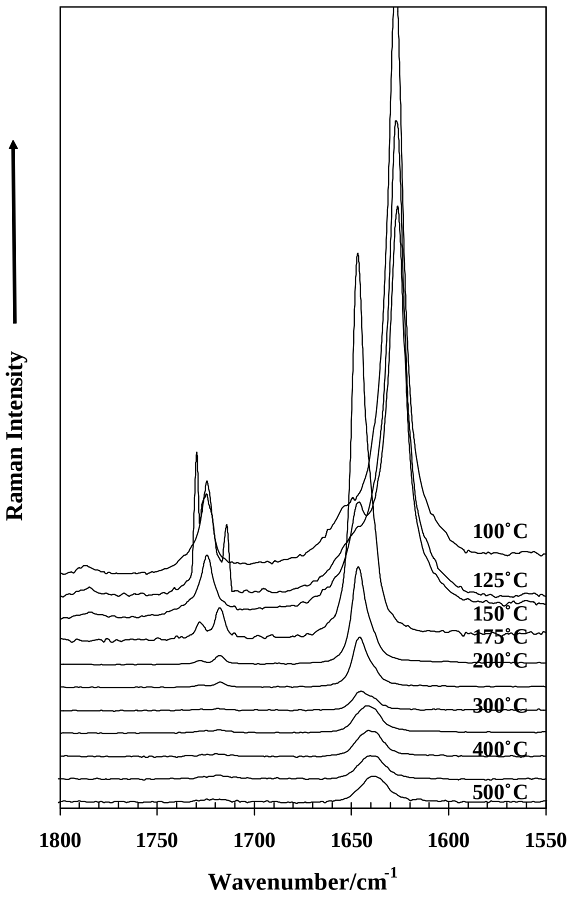

Fig. 5. In situ Raman spectra of the CO antisymmetric stretching region of whewellite as a function of temperature.

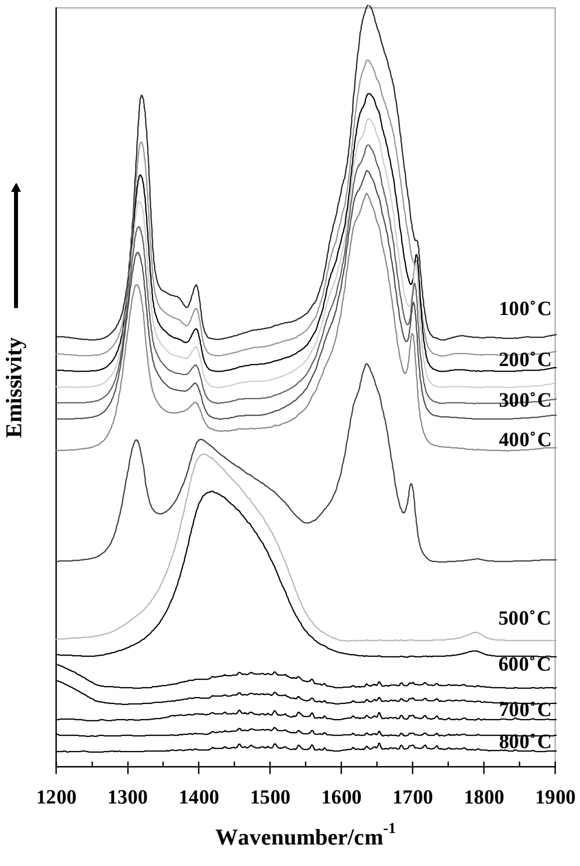

Fig. 6. Infrared emission spectroscopy of the CO stretching region of whewellite.

of the transition from calcium oxalate to calcium carbonate. The latter is represented by the broad band centred on 1413 cm^{-1}. The transition at 450 °C is in agreement with the results of the HRTG which showed a mass loss step at 479 °C. Evolved gas mass spectrometry shows that carbon dioxide is lost at this temperature. Above 600 °C, no intensity remains in the 1413 cm^{-1} band indicating that further carbon dioxide is lost and the calcium carbonate is converted to calcium oxide. HRTG showed the conversion temperature to be 684 °C. The infrared emission spectra of the CO antisymmetric stretching region centred on around 1706 cm^{-1} shows complexity. The band profile shows a shift to lower wavenumbers with thermal treatment. Four bands are observed in the CO antisymmetric stretching region at around 1587, 1621, 1652 and 1706 cm^{-1}. The intensity of the last band increases with thermal treatment. Two additional bands are observed at 1398 and 1321 cm^{-1}. No intensity remains in the bands after 450 °C. These bands have been attributed to combination bands [37]. No intensity is observed in the positions of the CO symmetric stretching modes at around 1450 cm^{-1}.

The Raman spectrum of the 850–950 cm^{-1} region is shown in Fig. 7. At 25 °C, a single Raman band is observed at 897 cm^{-1} and is assigned to the CC stretching vibration. Upon thermal treatment the band shifts to 894 cm^{-1} with additional bands observed at 916 and 861 cm^{-1}. Above 150 °C, the band is observed at 903 cm^{-1} with the additional band at 864 cm^{-1}. 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 [38]. Upon thermal treatment the CC band shifts to 905 cm^{-1}. This corresponds to the C–C stretching mode of anhydrous calcium oxalate [37].

The Raman spectrum of the low wavenumber region of whewellite is shown in Fig. 8. An intense band is observed in the 25 °C spectrum at 595 cm^{-1} with two additional bands at 521 and 503 cm^{-1}. These bands are attributed to OCO bending modes [37]. Above 150 °C, the bands shift to 596, 511 and 492 cm^{-1}, respectively. Previous studies based upon Raman spectroscopy suggested that dehydration occurred at 423 K [38]. 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. However, some discussion exists to the attribution of these bands. Previous studies have assigned the band at around 500 cm^{-1} to the bending mode of C–C–O and the MO ring and MO stretching modes [40,41]. The band at around 596 cm^{-1} is also associated with MO stretching modes [40,41].

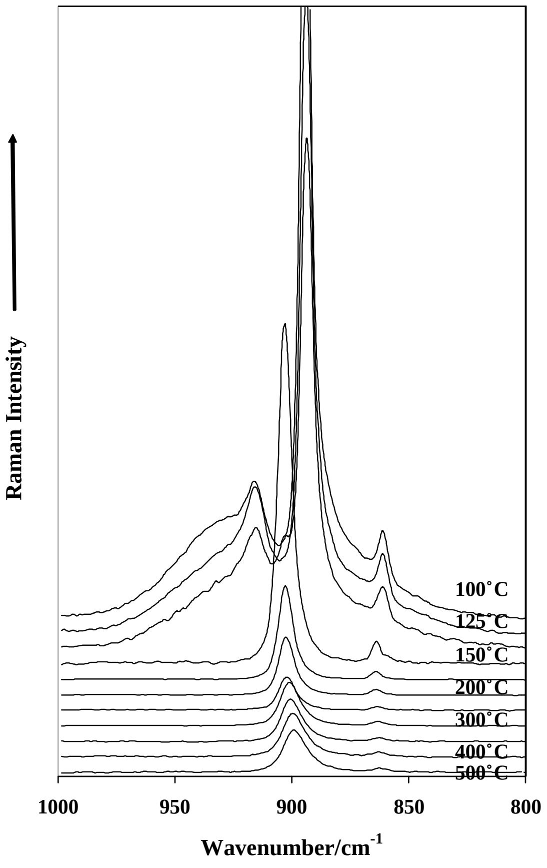

Fig. 7. In situ Raman spectra of the CC stretching region of whewellite.

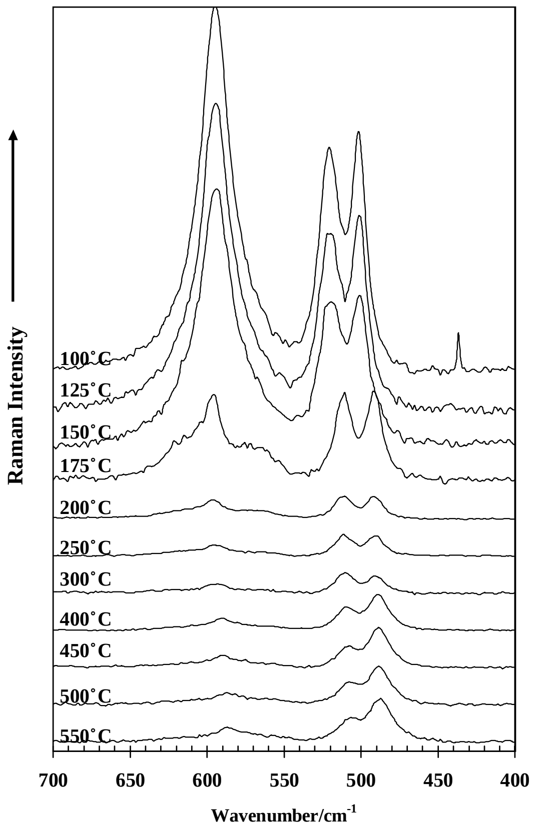

Fig. 8. In situ Raman spectra of the low wavenumber region of whewellite.

4. Conclusions

The existence of oxalates in nature can be observed as a result of the expulsion of heavy metals from primitive plant forms. The presence of whewellite 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 whewellite 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 in situ Raman spectroscopy and thermal analytical techniques has been used to study the thermal decomposition of a natural whewellite. The Raman spectra were obtained using a combination of Raman microscopy in combination with a thermal stage. The spectroscopic data was complimented by high resolution thermogravimetric analysis in combination with evolved gas mass spectrometry. Raman spectral data show changes in the molecular structure as a function of temperature.

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