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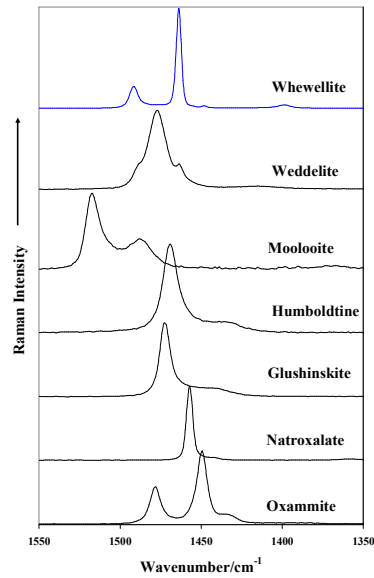
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A comparative study of natural oxalates including whewellite, weddellite, moolooite, humboldtine, glushinskite, natroxalate and oxammite has been undertaken using Raman spectroscopy at 298 and 77 K.



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Raman spectroscopic study of natural oxalates at 298 and 77 K.

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Abstract

A comparative study of a suite of natural oxalates including weddellite, whewellite, moolooite, humboldtine, glushinskite, natroxalate and oxammite has been undertaken using Raman spectroscopy at 298 and 77 K. Oxalates are found as films on host rocks as a result of heavy metal expulsion by primitive plants such as lichens and fungi. The minerals are characterised by the Raman position of the CO stretching vibration which is cation sensitive. The band is observed at 1468 cm^{-1} for weddellite, 1464 cm^{-1} for whewellite, 1489 cm^{-1} for moolooite, 1489 cm^{-1} for humboldtine, 1471 cm^{-1} for glushinskite, 1456 cm^{-1} for natroxalate and 1473 cm^{-1} for oxammite. Except for oxammite, the infrared and Raman spectra are mutually exclusive indicating the minerals are bidentate and planar. Significant differences are observed in the CC stretching region and in the OCO bending region centred upon 910 and 860 cm^{-1} respectively. The significance of this work rests with the ability of Raman spectroscopy to identify oxalates which often occur as a film on a host rock. As such Raman spectroscopy has the potential to identify the existence or pre-existence of life forms on planets such as Mars.

Keywords: oxalate, weddellite, moolooite, humboldtine, natroxalate, oxammite, glushinskite

Introduction

The study of the structure of metal oxalates has been undertaken for some considerable time.¹⁻⁶ The oxalate ion in aqueous media is in a staggered structure with D_{2d} symmetry whereas in the solid state X-ray crystallographic studies of sodium and potassium oxalates clearly show the oxalate ion is planar with D_{2h} symmetry.⁷⁻¹¹ For some oxalate salts such as ammonium the structure is D_{2d} with the angle between the COO planes lying between 22 and 28°. ¹² The aqueous oxalate anion gave spectra consistent with a staggered D_{2d} configuration with fundamental frequencies found at 1486 (A_1), 1579 (B_2), 1310 (E), 900 (A_1), 761 (E), 524 (B_2) 449 (A_1) and 301 cm^{-1} (E). ¹³ Recent work showed that nickel (II) oxalate dihydrate crystallises in a monoclinic system with four formula units in the unit cell in which planar metal oxalate layers are held together by hydrogen bonds with water molecules. ¹⁴ More recent work also showed that copper (II) oxalate dihydrate formed ribbon like polymeric chains with staggered layers. ¹⁵ It was shown that the metal oxalates had a centrosymmetric square planar structure with D_{2h} molecular symmetry. It is apparent that most metallic oxalates with two waters of hydration are planar. ¹⁶

Our interest in oxalates originates from their occurrence in nature as the products of expulsion from plants, lichens and fungi. ¹⁷⁻²² The presence of oxalates

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may be an indicator of plant life either current or in pre-existing life forms. Thus the presence of oxalates on another planet such as Mars provides an indication of existing or pre-existing life. The production of simple organic acids such as oxalic and citric acids has profound implications for metal speciation in biogeochemical cycles²³. The metal complexing properties of the acids are essential to the nutrition of fungi and lichens and affects the metal stability and mobility in the environment²³. Lichens and fungi produce the oxalates of heavy metals as a mechanism for the removal of heavy metals from the plant²⁴. A significant number of oxalates are found in nature. These oxalates depend on the host matrix on which the lichen is growing. Among the oxalates are the two calcium oxalates known as weddellite (the dihydrate) and whewellite (monohydrate). Ca-oxalate exists in two well-described modifications: as the more stable monoclinic monohydrate whewellite and the less stable tetragonal dihydrate weddellite. Weddellite serves for lichens as a water absorbing and accumulating substrate which transforms to whewellite when humidity drops. Such minerals are important in human physiology as the minerals are found in urinary tracts^{25,26}. Many other divalent oxalates exist in nature. The magnesium based oxalate is known as glushinskite^{6,27}. The copper oxalate is known as moolooite^{28,29} and the ferrous oxalate as humboldtine^{4,30}. These three oxalates are also the product of lichen growth. Two natural univalent oxalates are known. These are the oxalates of sodium and ammonium known as natroxalate and oxammite⁵.

Indeed the presence of oxalates have been evidence for the deterioration of works of art³¹⁻³³. Carbon dating of oxalic acid enables estimates of the age of the works of art³⁴. The presence of the oxalates has been used as indicators of climate change³⁵. The presence of pigments in ancient works of art effected the growth of lichens on the art works³⁶. In calcareous artifacts such as the famous Chinese terra cotta soldiers or Egyptian epigraphs they lead to a destruction of the surface by forming Ca-oxalate layers and thus to a deterioration of the historical work of art. But in places where the surface is covered by some blue colours (Egyptian and Chinese Blue, Chinese Purple) the growth of lichens is inhibited and the artifacts are well preserved. The copper ion contained in the pigments is responsible for this effect since copper is a strong poison for micro-organisms³⁶. Weddellite and whewellite very often occur together with gypsum on the surface of calcareous artifacts exposed in the Mediterranean urban environment, as main constituents of reddish patinas called in Italy 'scialbatura'. The origin of this is a matter of controversy. The observation of the interface between calcite substratum and the above mentioned secondary minerals is an important step in the explanation of alteration process of artifacts of historic and artistic interest³⁷. Studies of the black paint has shown the presence of oxalates in the paint with serious implications for remediation³⁸.

The use of infrared and Raman spectroscopy for the study of oxalates originated with the necessity to study renal stones^{39,40}. FT Raman spectroscopy has been used to study urolithiasis disease that has been studied for many years, and the ethiopathogenesis of stone formation is not well understood⁴¹. Whilst there have been several studies of synthetic metal oxalates^{14,21,42-46}, few studies of natural oxalates have been forthcoming and no comprehensive comparison of the natural oxalates has been undertaken. Few studies of the spectroscopy of water in these minerals have been forthcoming. The objective of this work is to undertake a

comparative study of natural oxalates, occurring as films on host rocks, using Raman spectroscopy at 298 and 77 K.

EXPERIMENTAL

Minerals:

The natural minerals were obtained from Australian museums. The samples were phase analyzed using X-ray diffraction and the compositions checked using electron probe measurements.

Raman microprobe spectroscopy

The oxalate minerals exist as coatings or growths on a rock host. The crystals of the oxalate minerals were orientated as best as can be accomplished by placing the rock of sizeable proportions under the stage of an Olympus BHSM microscope 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} . It should be noted that some of the host rocks are sufficiently large that the lower part of the microscope is dismantled and removed. 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.⁴⁷⁻⁵² Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

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.

RESULTS AND DISCUSSION

Factor group analysis

Aqueous oxalate is uncoordinated and will be of point group D_{2d} .^{13,53} Thus the vibrational activity is given by $\Gamma = 3A_1 + B_1 + 2B_1 + 3E$. Thus all modes are Raman active and the $2B_1 + 3E$ modes are infrared active. All oxygens in the structure are equivalent and hence only one symmetric stretching mode should occur. Upon

coordination of the oxalate as a mono-oxalato species as will occur in the natural minerals, the symmetry species is reduced to C_{2v} . The irreducible expression is then given by $\Gamma = 6A_1 + 2A_2 + 5B_1 + 2B_2$.^{15,54} Hence all modes are both Raman and infrared active. In this situation both the symmetric and antisymmetric stretching modes will be observed. If two moles of oxalate are bonded to the cation then the molecular point group will be D_{2h} and the irreducible representation is given by $\Gamma = 7A_g + 3B_{1g} + 3B_{2g} + 5B_{3g} + 3A_u + 7B_{1u} + 7B_{2u} + 4B_{3u}$. The first four modes are Raman active (namely $7A_g + 3B_{1g} + 3B_{2g} + 5B_{3g}$) and the last four modes are infrared active (namely $3A_u + 7B_{1u} + 7B_{2u} + 4B_{3u}$). Under this symmetry, there is a centre of symmetry which means the infrared and Raman bands are exclusive.

Spectroscopy of oxalate anion

The Raman spectra at 77 K of the natural oxalates studied in this work are shown in Figures 1 to 5. Figure 1 displays the CO symmetric stretching region; Figure 2 the antisymmetric stretching region; Figure 3 the OCO bending region and Figure 4 the water OH stretching region. The results of the Raman spectroscopic analyses are reported in Table 1. The CO symmetric stretching vibration is cation and therefore mineral dependent (Figure 1). The CO 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 and is complex in the 77 K spectrum with bands observed at 1489, 1477 and 1463 cm^{-1} . The observation of a single band in the 298 K spectrum suggests the equivalence of the CO stretching vibrations and the observation of three bands in the 77K spectrum indicates a further reduction in symmetry. No bands are observed in the infrared spectrum at 298 K. Thus at 298 K, the structure is centrosymmetric. Such a symmetry loss at 77 K would occur if the structure was no longer planar. The other oxalate which shows multiple bands is oxammite. Bands are observed at 1473, 1451, 1447 and 1432 cm^{-1} in the 298 K spectrum and at 1478, 1450 and 1432 cm^{-1} in the 77 K spectrum. Previous studies have shown that the oxalate OCO planes are at some fixed angle to each other.^{12,44,55} This results in the observation of multiple bands in the CO stretching region. The infrared spectrum of oxammite also shows bands at 1466, 1447 and 1425 cm^{-1} . The observation of bands in these positions in both the infrared and Raman spectra show the structure of oxammite is no longer centrosymmetric.

The Raman spectrum of whewellite in the CO stretching region shows an intense band at 1464 cm^{-1} with a second band at 1491 cm^{-1} . These bands are observed at 1491 and 1464 cm^{-1} at 77 K. Additional bands are observed at 1448 and 1399 cm^{-1} in the 77 K spectrum. The Raman spectrum of whewellite has been published.⁴⁶ Shippey reported Raman bands at 1491, 1463 and 1397 cm^{-1} . No bands are observed in the infrared spectra round 1460 cm^{-1} and no intense bands are observed in the Raman spectra around 1600 cm^{-1} , although some low intensity bands may be observed in this region. For aqueous oxalate the antisymmetric stretching (B_{2u}) mode is observed at 1600 cm^{-1} . For weddellite and whewellite two bands are observed at 1623 and 1605 cm^{-1} . The observation that the Raman and infrared bands are mutually exclusive means that the oxalate anion is centrosymmetric.

The Raman spectrum of moolooite (Cu) shows two bands at 1514 and 1489 cm^{-1} in the 298 K spectrum which shifts to 1517 and 1490 cm^{-1} at 77 K. Moolooite is anhydrous copper(II) oxalate. This is in contrast to the published results for copper(II)

oxalate dihydrate for which the Raman spectrum showed two bands at 1526 and 1495 cm^{-1} . The reason for the differences in the band positions should be attributed to the anhydrous nature of the natural mineral moolooite. Both humboldtine and glushinskite show similar spectra with two bands observed for the CO stretching region. An intense band is observed at 1468 cm^{-1} in the 298 K spectrum for humboldtine and 1469 cm^{-1} in the 77 K spectrum. In the 298 K spectrum a broad band is observed at 1450 cm^{-1} . This band is observed at 1441 cm^{-1} at 77 K. Similarly for glushinskite an intense band is observed at 1471 cm^{-1} with a broad band at 1441 cm^{-1} . These bands are observed at 1472 and 1454 cm^{-1} in the 77 K spectrum. For natroxalate a band is observed at 1456 cm^{-1} and two bands are observed at 1457 and 1453 cm^{-1} in the 77 K spectrum. No bands were observed in these positions in the infrared spectra of moolooite, humboldtine and glushinskite.

The Raman spectra of the CO antisymmetric stretching region at 77 K are shown in Figure 2. The 298 K Raman spectrum shows a single low intensity band for weddellite at 1628 cm^{-1} . The band is observed at 1633 cm^{-1} for whewellite. This band shifts to 1633 cm^{-1} at 77 K. Low intensity bands are observed for whewellite at 77 K at 1732, 1725, 1659 and 1613 cm^{-1} . The position of these bands is in good agreement with previously published data.⁴⁶ For aqueous oxalate the antisymmetric stretching (B_{2u}) mode is observed in the infrared spectrum at 1600 cm^{-1} . For weddellite and whewellite two IR bands are observed at 1623 and 1605 cm^{-1} . In the 77 K Raman spectrum a band the band is observed at 1630 cm^{-1} with a low intensity band at 1736 cm^{-1} . A single band is observed in this region of low intensity for moolooite at 1614 cm^{-1} in the 298 K spectrum. Two bands are observed in the 77 K spectrum for moolooite at 1673 and 1614 cm^{-1} . For moolooite the infrared band is observed at 1632 cm^{-1} and is strongly asymmetric and component bands may be resolved at 1722, 1679, 1632 and 1602 cm^{-1} . No bands are observed in the infrared spectra around 1460 cm^{-1} and no intense bands are observed in the Raman spectra around 1600 cm^{-1} , although some very low intensity bands may be observed in this region. Such observations confirm the rule of mutual exclusion for the spectroscopy of these natural oxalates. Thus vibrational spectroscopy confirms the structures as planar bidentate.

For humboldtine bands are observed at 1708 and 1709 cm^{-1} in the 298 and 77 K spectra respectively. For the magnesium oxalate Raman bands are observed at 1660, 1636, 1612 cm^{-1} in the 298 K spectrum and at 1661, 1637 and 1611 cm^{-1} in the 77 K spectrum. For glushinskite infrared bands are observed at 1679, 1660, 1634 and 1603 cm^{-1} . For natroxalate three bands are observed at 1750, 1643 and 1614 cm^{-1} in the 298 K spectrum and at 1752, 1646 and 1616 cm^{-1} in the 77 K spectrum. The IR spectrum of natroxalate shows bands at 1675, 1628 and 1604 cm^{-1} . Published IR data suggests that there should be a single band at 1632 cm^{-1} .²¹ The Raman spectra of oxammite are more complex; this is due to the non-planar configuration of the OCO bonds. Raman bands are observed at 1737, 1695 and 1605 cm^{-1} in the 298 K spectrum and at 1750, 1737, 1729, 1700 and 1614 cm^{-1} in the 77 K spectrum. The reason for multiple antisymmetric stretching modes for each of the minerals is unclear; suffice to express that multiple species may be present. For example many oxalate minerals show polymerisation.^{54,56} The mineral oxammite fits well into this category. Multiple bands are observed in the infrared spectrum for both the symmetric and antisymmetric stretching modes.

The Raman spectra of the natural oxalates at 77 K show some low intensity bands which are not observable in the 298 K spectra. The bands are barely above the signal to noise. Bands are observed at 1329 cm^{-1} for weddellite, 1290 and 1370 cm^{-1} for moolooite, 1323 cm^{-1} for glushinskite, 1360 cm^{-1} for natroxalate and 1320 and 1394 cm^{-1} for oxammite. No band could be detected for humboldtine. It is considered that these bands are due to the B_{3u} OCO stretching mode. The bands are Raman forbidden but infrared active. The infrared spectra show quite intense bands centred around 1300 cm^{-1} . For weddellite and whewellite bands are observed at 1366 and 1309 cm^{-1} . For moolooite two intense bands are observed at 1317 and 1361 cm^{-1} with low intensity bands at 1352, 1311 and 1279 cm^{-1} . A band was observed at 1365 cm^{-1} and assigned to the OCO stretching mode for synthetic copper(II) oxalate dihydrate.^{54,56} Both humboldtine and glushinskite show a similar infrared pattern to moolooite with component bands at 1312 and 1357; 1314 and 1369 cm^{-1} respectively. The IR spectrum of natroxalate shows strong intensity at 1337 and 1314 cm^{-1} with low intensity bands at 1416, 1400, 1296 and 1251 cm^{-1} . The infrared spectrum of oxammite shows bands at 1288 and 1308 cm^{-1} . The reason for the multiplicity of bands cannot be attributed to a reduction in symmetry and loss of degeneracy but rather to the presence of multiple species. It is possible that not only the di-oxalate but the poly-oxalate, mono-oxalate and free oxalate are present in varying degrees of concentration.

The Raman spectra at 77 K of the low wavenumber region between 700 and 1000 cm^{-1} of the natural oxalates are shown in Figure 3. A Raman band is observed at around 900 cm^{-1} and is assigned to the $\nu(\text{C-C})$ stretching mode. The Raman spectrum of whewellite shows a single intense band at 939 cm^{-1} ; the band splits into two bands at 952 and 933 cm^{-1} at 77 K. The position of the band is in good agreement with published data.⁴⁶ The $\nu(\text{C-C})$ band for weddellite is observed at 909 cm^{-1} in the 298 K spectrum and at 947 and 912 cm^{-1} in the 77 K spectrum. Additional bands are observed at 896 and 867 cm^{-1} . It is noted that the position of the C-C stretching vibration is 902 cm^{-1} for the free oxalate ion. Thus there is a shift of some 45 cm^{-1} from the free oxalate ion position to that for the weddellite mineral. The position of the band is at 921 and 923 cm^{-1} for the 298 and 77 K spectra for moolooite. An additional band for moolooite is observed at around 830 cm^{-1} . The Raman spectrum of humboldtine shows a band at 915 cm^{-1} in the 77 K spectrum compared with a value of 913 cm^{-1} for the 298 K spectrum. A second band is observed at 857 cm^{-1} . The second band may be indicative of the non-equivalence of the C-C stretching vibrations. A similar result is observed for glushinskite. The Raman spectrum of natroxalate is interesting in that a single band is observed at 860 cm^{-1} for the 298 K spectrum which splits into two bands at 884 and 875 cm^{-1} in the 77 K spectrum. In contrast the Raman spectrum of oxammite shows three bands at 892, 856 and 815 cm^{-1} in the 298 K spectrum and at 897, 867 and 824 cm^{-1} in the 77 K spectrum. This latter band is assigned to the OCO bending modes which are strong in the infrared spectrum and of low intensity in the Raman spectrum. Two low intensity infrared bands are observed for weddellite at 884 and 957 cm^{-1} . Whewellite shows only a single band at 917 cm^{-1} . The IR spectrum of moolooite shows a very weak band at 917 cm^{-1} . Humboldtine has an infrared band at a similar position and Oxammite a band at 871 cm^{-1} . The observation is made that the C-C stretching mode is either not observed or is only weakly observed in the infrared spectra of the natural oxalates.

The low wavenumber region of the natural oxalates between 200 and 700

cm^{-1} is shown in Figure 4. A number of intense Raman bands are observed in the 400 to 600 cm^{-1} region. The Raman spectrum of whewellite displays three bands at 595, 521 and 503 cm^{-1} . The bands are observed in the same positions at 77 K. Previous studies gave equivalent bands at 592 and 517 cm^{-1} .⁴⁶ An additional low intensity band is found at 472 cm^{-1} in the 77 K spectrum of whewellite. The Raman spectrum of weddellite shows an intense band at 505 cm^{-1} with a broad band at 596 cm^{-1} . These bands are observed at 501 and 597 cm^{-1} in the 77 K spectrum. 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.^{14,15} The band at around 596 cm^{-1} is also associated with MO stretching modes.^{14,15} The spectrum for moolooite in this region is more complex. Three bands are observed at 610, 584 and 558 cm^{-1} which shift to 612, 586 and 559 cm^{-1} in the 77 K spectrum. The bands are in similar positions to that assigned to the copper(II) oxalate dihydrate.¹⁵ The differences in band position may be due to the absence of water in the natural mineral. Moolooite is anhydrous. An additional band is observed at 434 cm^{-1} in the 77 K spectrum which may be assigned to a CuO stretching vibration. Bands in these positions have been observed for other copper minerals.^{57,58}

The Raman spectrum of humboldtine is different in that a sharp band is observed at 582 cm^{-1} with a broad band centred on 518 cm^{-1} . In the 77 K spectrum the bands are observed at 586 and 506 cm^{-1} . This latter band may be resolved into two components at 529 and 504 cm^{-1} . One likely assignment of these bands is to the FeO ring and OFeO bending modes. The Raman spectrum of glushinskite displays two sharp bands at 587 and 528 cm^{-1} in the 77 K spectrum, found at 585 and 527 cm^{-1} in the 298 K spectrum. In addition a broad band is observed at 659 cm^{-1} . This band is of very low intensity and may be ascribed to the water librational mode. The Raman spectrum of natroxalate also shows sharp bands at 567 cm^{-1} in the 298 K spectrum which is resolved into two bands at 572 and 567 cm^{-1} in the 77 K spectrum. An additional band is observed at 482 cm^{-1} . The Raman spectrum is even more complex for oxammite at 77 K. Bands are observed at 507, 497, 464, 446 and 425 cm^{-1} . The band at 507 cm^{-1} may be attributed to (NH₄)O stretching vibration, whereas the bands at 497 and 464 cm^{-1} are assigned to ring deformation and O-C-O bending modes. The bands at 446 and 425 cm^{-1} are also assigned to ring deformation modes.

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 MO stretching and OMO ring bending modes may be determined. The Raman spectrum of whewellite shows low intensity bands at 249 and 222 cm^{-1} at 298 K. In the Raman spectrum of weddellite, bands are observed at 259 and 220 cm^{-1} in the 298 K spectrum which resolves into bands at 266, 252, 225 and 198 cm^{-1} in the 77 K spectrum. These bands are probably attributable to CaO ring stretching or bending modes. Raman bands are also observed for weddellite at 190 and 162 cm^{-1} in the 77 K spectrum and are best described as lattice vibrations. An intense band is observed at 209 cm^{-1} with additional low intensity bands at 231 and 300 cm^{-1} are observed for moolooite. The Raman spectrum of humboldtine shows an intense band at 249 cm^{-1} in the 77 K spectrum. The Raman spectrum of glushinskite shows a low intensity band at 317 cm^{-1} in the 77 K spectrum (310 cm^{-1} at 298 K) and more intense bands at 268, 239 and 226 cm^{-1} . No intense Raman bands were observed in the 200 to 300 cm^{-1} range for natroxalate. Two low intensity bands for natroxalate were observed at 232

and 220 cm^{-1} with lattice modes observed at 197 , 182 , 161 and 139 cm^{-1} in the 77 K spectrum. Greater complexity is observed in the Raman spectrum of oxammite at 77 K . Bands are observed at 290 , 250 , 246 , 234 , 221 , 204 , 186 and 165 cm^{-1} .

It is interesting that many papers report the spectroscopy of synthetic oxalates but fail to mention the spectroscopy of the water of crystallisation in the oxalate minerals. The Raman spectrum of the hydroxyl stretching region for the natural oxalates is shown in Figure 5. Firstly moolooite and natroxalate do not have any water of crystallisation and consequently no Raman spectrum of the OH stretching region is found. The Raman spectra of weddellite and whewellite are different in the OH stretching region. Two bands are observed for weddellite at 3467 and 3266 cm^{-1} in the 298 K spectrum whereas 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 . Bands are observed at 3475 , 3415 , 3341 , 3262 , 3048 and 3045 cm^{-1} . Previous study gave bands at 3486 , 3426 , 3342 and 3250 cm^{-1} .⁴⁶ The values are in reasonable agreement with this study. The Raman spectrum of weddellite shows a complex spectrum at 77 K with bands observed at 3450 and 3232 cm^{-1} . The Raman spectrum of humboldtine at 77 K shows an intense band at 3298 cm^{-1} with a broad low intensity band at 2902 cm^{-1} . The Raman spectrum at 298 K of the hydroxyl stretching region of glushinskite shows a sharp intense band at 3367 cm^{-1} with low intensity bands at 3391 and 3254 cm^{-1} . The spectrum of glushinskite shows an intense band at 3361 cm^{-1} with low intensity bands at 3379 , 3294 and 2902 cm^{-1} . The Raman spectrum of oxammite in the hydroxyl stretching region shows complexity with the overlap of the OH and NH stretching vibrations. Two bands are observed in the 298 K spectrum at 3235 and 3030 cm^{-1} and are assigned to the OH vibrations. These bands are resolved into bands at 3228 , 3167 , 3041 and 3017 cm^{-1} in the 77 K spectrum. Bands in the 298 K spectrum are observed at 2995 , 2900 and 2879 cm^{-1} and are attributed to the NH vibrational modes. These bands are resolved into component bands at 3001 , 2939 , 2903 and 2869 cm^{-1} in the 77 K spectrum.

Conclusions

A suite of natural oxalate minerals have been characterised by Raman spectroscopy at 77 K . Each oxalate mineral has its own characteristic spectrum with the minerals weddellite and whewellite showing strong similarities in their spectrum except for the water OH stretching region and in the very low wavenumber region. Both natroxalate and moolooite are characterised by the lack of water OH stretching vibrations. The positions of the symmetric and antisymmetric stretching vibrations are characteristic of the particular oxalate and it is suggested that the position of the bands depends on the size and polarity of the cation. The MO stretching and OMO bending vibrations are also characteristic of the natural oxalate.

If life existed on Mars at some time in the past or even exists in the present time, low plant life forms such as fungi and lichens may have left evidence of their existence. Such organisms may be found in very hostile environments^{22,59,60}. Lichens and fungi can control their heavy metal intake through expulsion as metal salts such as oxalates and similar acids. The presence of these oxalates can be used as a marker for the pre-existence of life. Thus the study of the common natural oxalates is of great importance. Included in the natural oxalates are the minerals whewellite and the

dihydrate weddellite. These two minerals are amongst the most common of the natural oxalates. The minerals on planets such as Mars may be explored by robotic devices which carry portable Raman spectrometers with perhaps fibre optics to collect spectral data. The interpretation of the spectra of natural oxalates is important in these types of studies.

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Ca weddellite		Ca whewellite		Cu moolooite		Fe ²⁺ humboldtite		Mg glushinskite		Na natroxalate		NH ₄ oxammite		Infrared	Band assignments
298 K	77 K	298 K	77 K	298 K	77 K	298 K	77 K	298 K	77 K	298 K	77 K	298 K	77 K	published	
3467	3450	3484	3475	3486	3467	3315	3298	3391	3379			3235	3228		OH stretching
3266	3232	3427	3415	3426		2902	2902	3367	3361			3030	3167		
		3344	3341	3342				3254	3294				3041		
		3253	3262	3250				2902	2902				3017		
		3053	3048	3250											
		3045	3045	3250											
		2972	2922	2919								2995	3001		NH stretching
		2918	2903	2919								2900	2939		
		2903	1892									2879	2903		
												2161	2184		
												1902	1917		
1737	1736	1732	1725	1728		1708	1709	1720	1719	1750	1752	1737	1750		
													1737		
													1729		
													1700		
1628	1630	1633	1659	1650		1555		1660	1661	1643	1646	1695	1614	1632	v _a (C=O)
			1632	1630				1636	1637	1614	1616	1605	1573		
			1613					1612	1611						
1475	1489	1492	1491	1491											
		1464	1464	1463											
		1463													
1468			1448			1468	1469	1471	1472	1456	1457	1473	1478	1433	v _s (C-O) + v(C-C)
						1441	1441	1454	1454	1456	1453	1451	1450		
												1447	1432		
1411	1417	1399	1397	1397		1450		1454	1454	1358	1325	1417	1417	1302	v _s (C-O)

1055 1053	1055 1054											1369 1288 1170	1120								1312	1319		+ $\delta(\text{O}-\text{C}=\text{O})$	
909	947 912	939	952 933	939	921	923	913	915	915	915	986 917	892	897	890										$\nu_s(\text{C}-\text{O})$ + $\delta(\text{O}-\text{C}=\text{O})$	
868	896 885	897 888 865	897 884 861	895 885 864	831	830	856	857	861	860	884 875	866 815	867 824												
			799 665	779				657		659		642	641	785											$\delta(\text{O}-\text{C}=\text{O})$ + $\nu(\text{M}-\text{O})$
596	597 521	595 521	595 521 503	592 517	610 584	612 586	582	586	585	587	567			622											Water libratio n
505	501	503	472	499 470	558	559	518	506	527	528			507	519											$\nu(\text{M}-\text{O})$ + $\nu(\text{C}-\text{C})$
									521			489	497 464												Ring deform + $\delta(\text{O}-\text{C}=\text{O})$
			342 304 293	422 340	434						481	438	446 425	428 419											$\nu(\text{M}-\text{O})$ + ring deform
														377 364											$\delta(\text{O}-\text{C}=\text{O})$ + $\nu(\text{C}-\text{C})$
259	266 252	249 222	254 224	268 250 224	290	300	293		310	317		278	290 251 246 234	291											Out of plane bends

220	225 198	203 193		209	209	231 209	246	249	265 237 226	268 239 226		232	224	221 204	Lattice modes
188 162	190 179			194 141 94 77	183	203	204 178	221	197 178	221 156 117	220 197 182 161 139	210 198 181 160	186 165	Lattice modes	

Table 1 Spectroscopic analysis of natural oxalates at 298 and 77 K

LIST OF FIGURES

- Figure 1** Raman spectra of the CO symmetric stretching region of weddellite, moolooite, humboldtine, glushinskite, natroxalate and oxammite at 77 K.
- Figure 2** Raman spectra of the CO anti-symmetric stretching region of weddellite, moolooite, humboldtine, glushinskite, natroxalate and oxammite at 77 K.
- Figure 3** Raman spectra of the CC stretching region of weddellite, moolooite, humboldtine, glushinskite, natroxalate and oxammite at 77 K.
- Figure 4** Raman spectra of the low wavenumber region of weddellite, moolooite, humboldtine, glushinskite, natroxalate and oxammite at 77 K.
- Figure 5** Raman spectra of the OH stretching region of weddellite, humboldtine, glushinskite and oxammite at 77 K.

LIST OF TABLES

- Table 1** Spectroscopic analysis of natural oxalates at 298 and 77 K

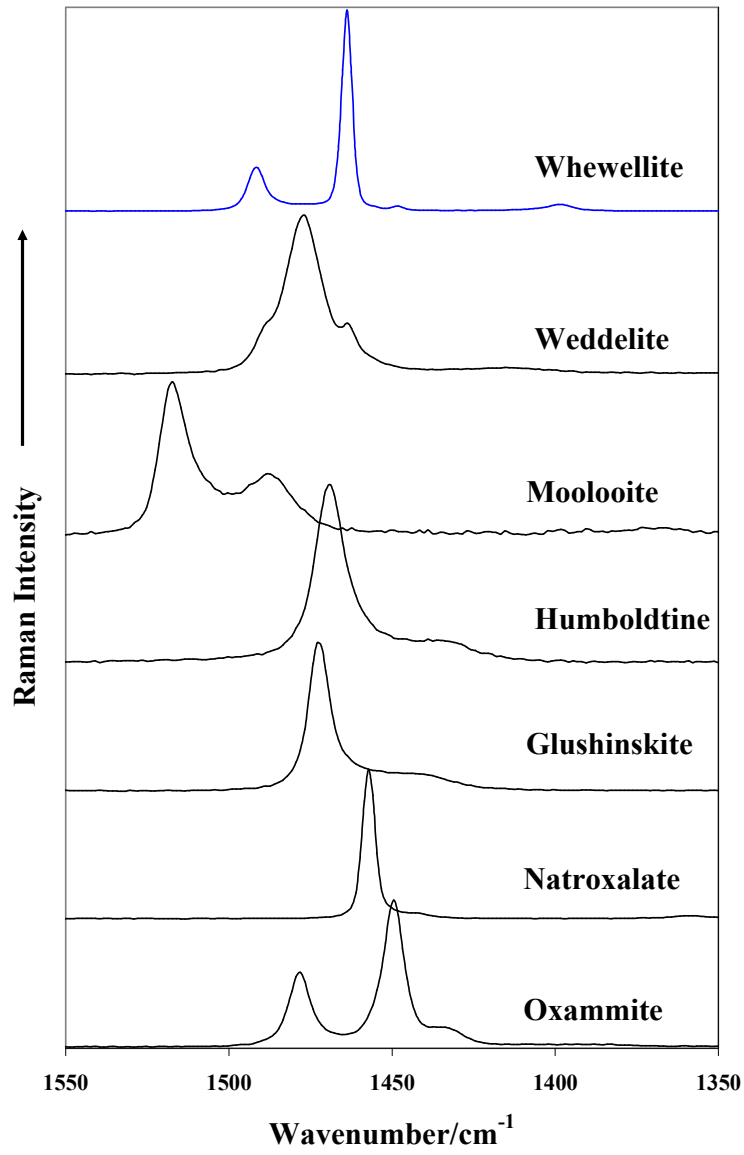


Figure 1

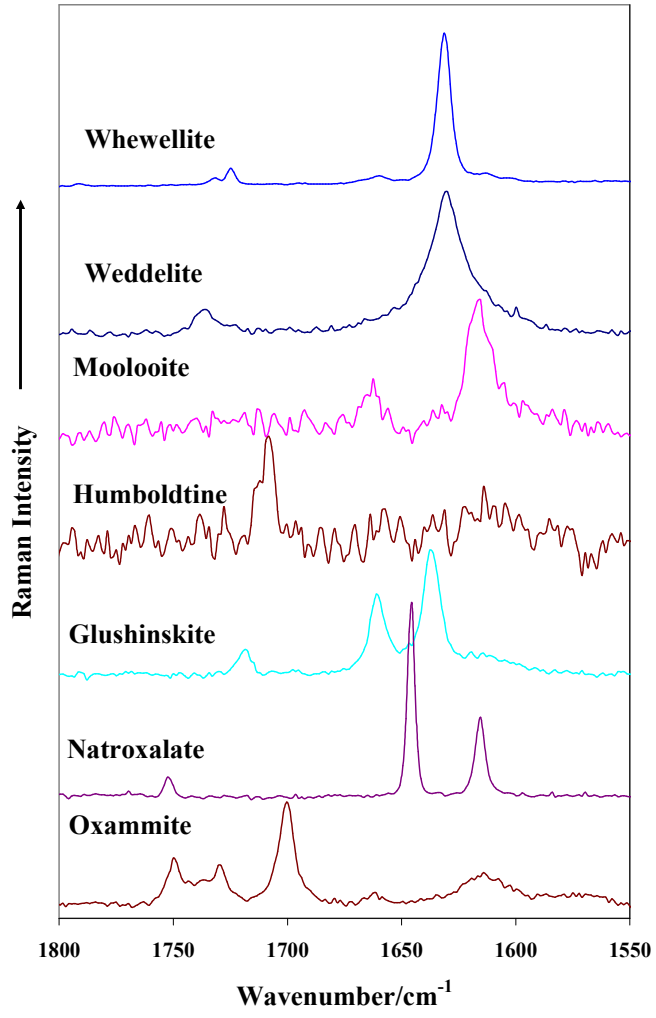


Figure 2

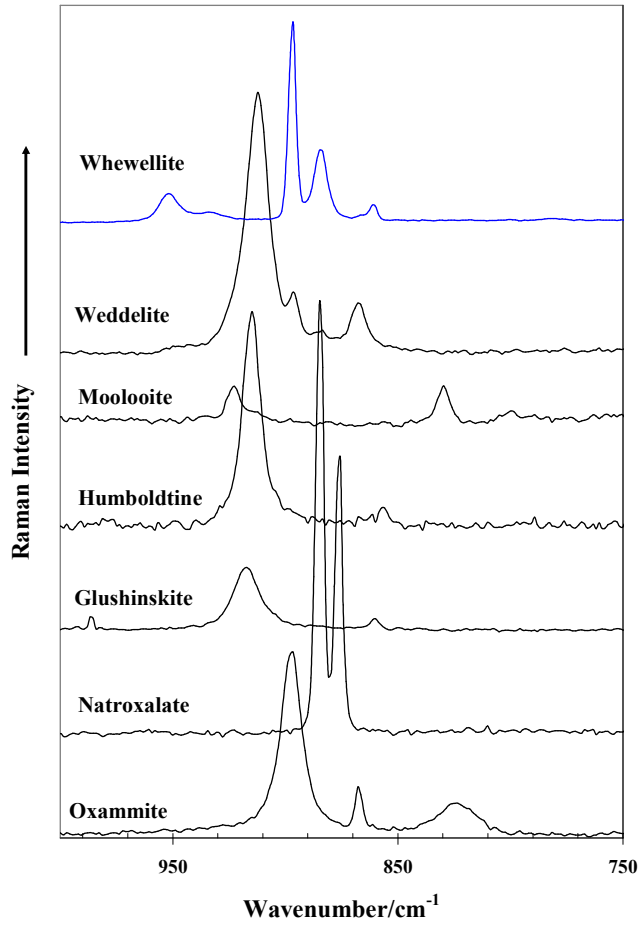


Figure 3

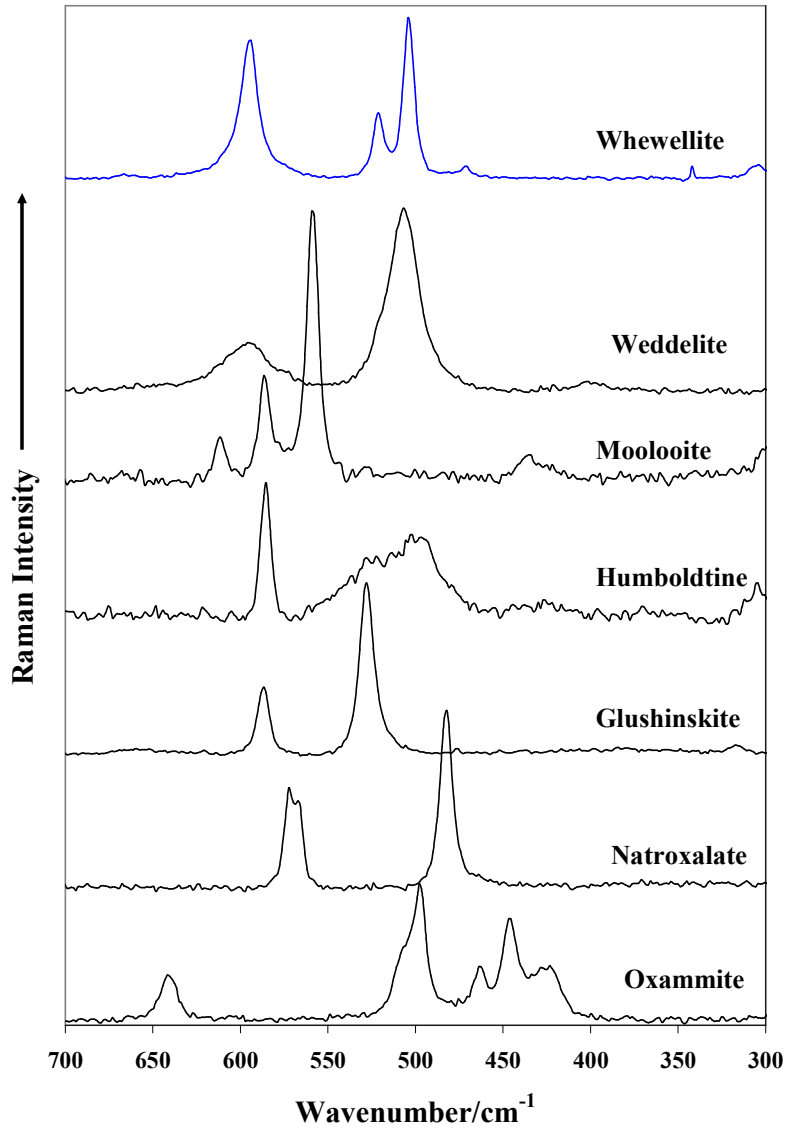


Figure 4

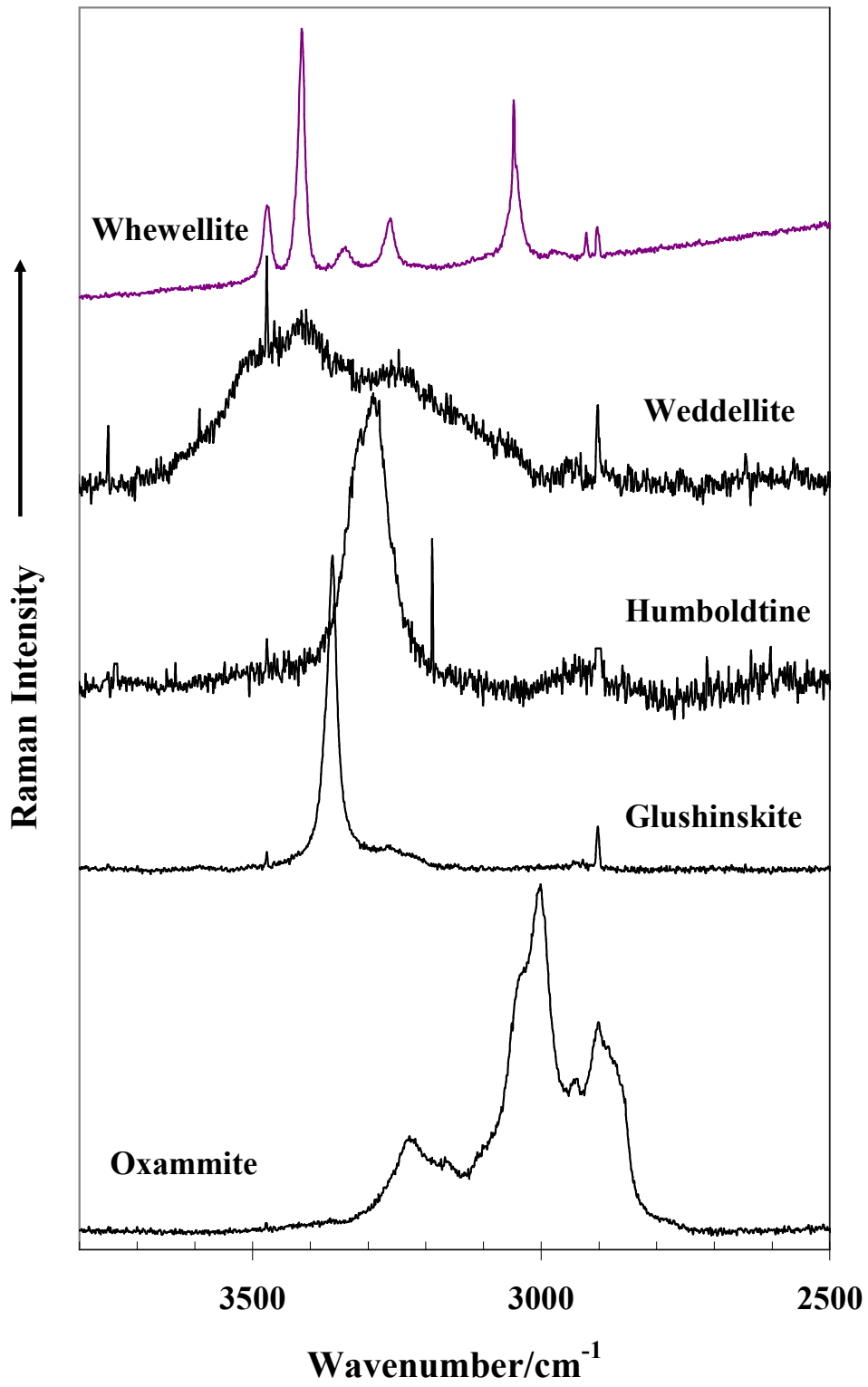


Figure 5

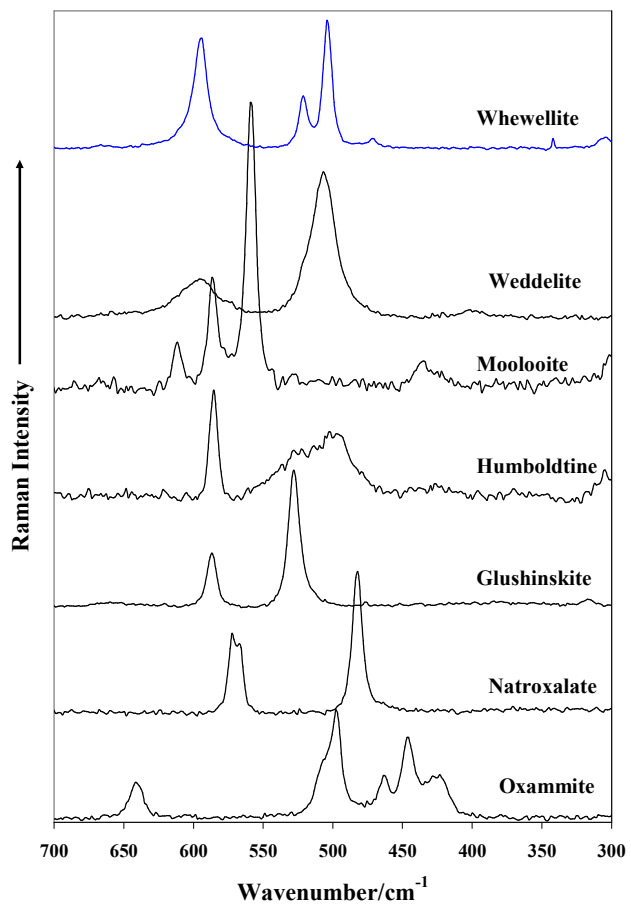


Figure 4 Repeated

