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Raman and FTIR spectroscopy of natural oxalates: Implications for the evidence of life on Mars

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Abstract **Evidence for the existence of primitive life forms such as lichens and fungi can be based upon the formation of oxalates. Oxalates are most readily detected using Raman spectroscopy. A comparative study of a suite of natural oxalates including weddellite, whewellite, moolooite, humboldtine, glushinskite, natroxalate and oxammite has been undertaken using Raman spectroscopy. 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, 1489 cm^{-1} for moolooite, 1471 cm^{-1} for glushinskite and 1456 cm^{-1} for natroxalate. Except for oxammite, the infrared and Raman spectra are mutually exclusive indicating the minerals are bidentate. Differences are also observed in the water OH stretching bands of the minerals. 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.

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The presence of oxalates is widespread in nature. These minerals form as the result of expulsion of heavy metals from fungi, lichens and plants[1—3]. The production of simple organic acids such as oxalic and citric acids has profound implications for metal speciation in biogeochemical cycles[4]. The metal complexing properties of the acids are essential to the nutrition of fungi and lichens and affect the metal stability and mobility in the environment[4]. Lichens and fungi produce the oxalates of heavy metals as a mechanism for the removal of heavy metals from the plant[5]. The presence of these oxalate crystals appears to have an effect similar to that found in cacti[6]. Among the oxalates are the two calcium oxalates known as weddelite (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. Weddelite 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[7,8]. Many other divalent oxalates exist in nature. The magnesium based oxalate is known as glushinskite[9,10]. The copper oxalate is known as moolooite[2,11] and the ferrous oxalate as humboldtine[12,13]. 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 oxammite[14].

Indeed the presence of oxalates has been evidence for the deterioration of works of art[15—17]. Carbon dating of oxalic acid enables estimates of the age of the works of art[18]. The presence of the oxalates has been used as indicators of climate change[19]. The presence of pigments in ancient works of art effected the growth of lichens on the art works[20]. 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 historian 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-organisms[20]. 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 interest[21]. Studies of the black paint have shown the presence of oxalates in the paint with serious implications for remediation[22]. The use of infrared and Raman spectroscopy for the study of oxalates originated with the necessity to study renal stones[23,24]. 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 understood[25].

Whilst there have been several studies of synthetic metal oxalates[26—32], 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 using a combination of Raman and infrared spectroscopy of a suite of common natural oxalates.

1 Experimental

(i) Minerals. Weddellite, originated from the Weddell Sea, Antarctica. Whewellite, registered sample number M5531 originated from Burg River, near Dresden, Saxony, Germany. Moolooite, originated from Murchison, Mooloo Downs Station, Western Australia. Humboldtine, sample number M13748, originated from Bohemia, Czech Republic. Glusinskite, originated from Lena coal basin, Yakutyia, Siberia, Russia. Natroxolate, sample number M46430, originated from Alluaiv Mtn., Lovozero Massif, Kola Peninsula, Russia. Oxammite, originated from Guanape Island, Peru. The samples were phase analyzed using X-ray diffraction and the compositions checked using EDX measurements.

(ii) Raman microprobe spectroscopy. The crystals of the oxaalte minerals 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 Nd-Yag laser (780 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. It should be noted that the limitations of the detector prevent the collection of data at wavenumbers above 3000 cm^{-1} Raman shift. Repeated acquisition using the highest magnification were 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.

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.

2 Results and discussion

(i) Factor group analysis. Aqueous oxalate is uncoordinated and will be of point group D_{2d}. Thus the vibrational activity is given by $G = 3A_1 + B_1 + 2B_1 + 3E$. 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 monooxalato species as will occur in the natural minerals, the symmetry species is reduced to C_{2v}. The irreducible expression is then given by $G = 6A_1 + 2A_2 + 5B_1 + 2B_2$. 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 $G = 7A_g + 3B_{1g} + 3B_{2g} + 5B_{3g} + 3A_u + 7B_{1u} + 7B_{2u} + 4B_{3u}$. 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.

(ii) Raman spectra of the CO stretching region. The Raman spectra of the 1200—1800 cm^{-1} region is shown in Fig. 1. The results of the Raman spectroscopic analysis together with the band assignments is given in Table 1. A band is identified in all the spectra in the 1456—1473 cm^{-1} range and is assigned to the $\nu_{(C-O)}$ stretching mode. The position of this band was identified at 1449 cm^{-1} for potassium oxalate in the solid state[29]. For weddellite and humboldtine the band was observed at 1468

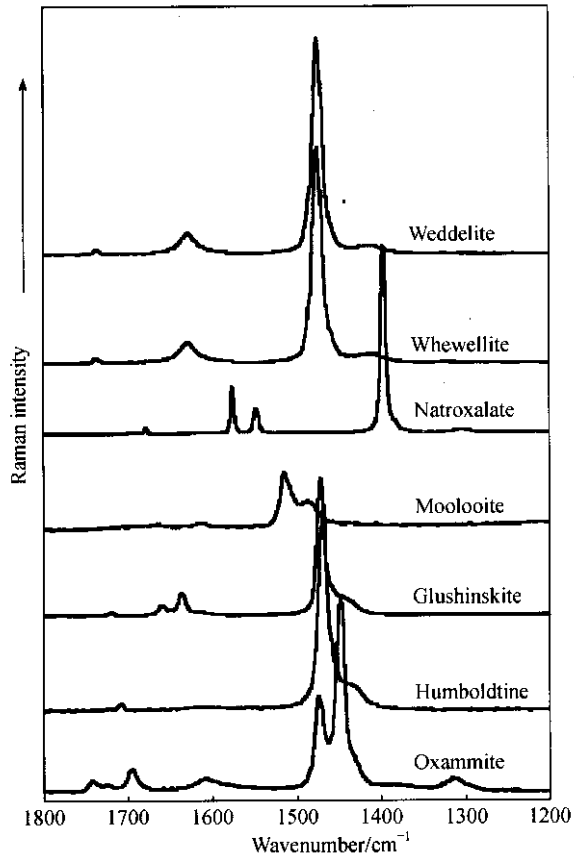

Fig. 1. Raman spetra of the 1200—1800 cm^{-1} region.

cm^{-1}. The position of the band for whewellite is the same as for weddelite. It is possible to discriminate between hydration states of calcium oxalate; the monohydrate (whewellite) featured a $\nu_{(C=O)}$ stretching band at 1493 cm^{-1} whereas the dihydrate (weddellite) had a contrasting $\nu_{(C=O)}$ stretching band at 1475 cm^{-1}. The band was observed for moolooite at 1489 cm^{-1}. Moolooite is the bis-copper(II) oxalate and the natural sample contains no water of hydration. Previous studies of the dihydrate copper(II) oxalate observed the position at 1495 cm^{-1}[29]. The Raman spectrum of the mineral glushinskite shows a band at 1471 cm^{-1}. The spectrum for natroxalate shows a band at 1456 cm^{-1}, a wavenumber position which is comparatively low compared with the other natural oxalates. Natroxalate is similar to that of moolooite in that no water of crystallisation is found for the natural mineral.

The Raman spectra of many of the minerals show additional bands on the low wavenumber side of the symmetric stretching mode. Bands are observed at 1411 cm^{-1} for weddellite and whewellite, 1433 cm^{-1} for moolooite, 1450 cm^{-1} for humboldtine and 1454 cm^{-1} for glushinskite. For oxammite a number of additional bands are observed at 1451, 1447 and 1430 cm^{-1}. It is suspected that these additional bands are also assignable to the symmetric stretching modes; but of molecular species other than the bis-oxalate complexes. Another possibility is that these bands are due to the B_{2g} mode, which is the O—C==O wag. The position of this band is identified at 1392 cm^{-1} for aqueous potassium oxalate and at 1348 cm^{-1} for potassium oxalate in the solid state[33,35]. A band

Table 1 Raman spectroscopic analysis of oxalates minerals

Ca (weddellite)	Cu (moolooite)	Fe^{2+} (humboldtine)	Mg (glushinskite)	Na (natroxalate)	NH_4 (oxammite)	Infrared[41]	Band assignment
3467		3315	3391		3235		OH stretching
3266			3367		3030		
			3254				
					2995		NH stretching
					2900		
					2879		
					2161		
					1902		
1737	1673	1708	1720	1750	1737		
1628	1614	1555	1660	1643	1695	1632	$\eta_{s(C=O)}$
			1636	1614	1605		
			1612				
1475	1514						$\eta_{s(C=O)}$
1468	1489	1468	1471	1456	1473	1433	$\eta_{s(C=O)} + \eta_{(C-C)}$
					1451		
					1447		
					1430		
1411	1433	1450	1454	1358	1417	1302	$\eta_{s(C-O)} + \delta_{(O-C=O)}$
					1312		
1055	1120						
1053							
909	921	913	915		892	890	$\eta_{s(C-C)} + \delta_{(O-C=O)}$
868	831	856	861	884	866		
				875	815		
			657		642	785	$\delta_{(O-C=O)} + \eta_{(M-O)}$
596	610	582	585	567		622	water libration
	584						
505	558	518	527			519	$\eta_{(M-O)} + \eta_{(C-C)}$
			521		489	519	ring deform + $\delta_{(O-C=O)}$
				481	438	428	$\eta_{(M-O)}$ + ring deform
						419	
						377	$\delta_{(O-C=O)} + \eta_{(C-C)}$
						364	
259	290	293	310		278	291	out of plane bends
220	209	246	265		224		
			237				
			226				
188		203	221	221	210		
				156	198		
				117	181		
					160		

in this position is observed at 1358 cm^{-1} for natroxalate. Bands are observed at 1417 and 1312 cm^{-1} for oxammite, which may also be attributable to the O—C==O wag.

(iii) Infrared spectrum of the CO stretching region.

The infrared spectra of the suite of minerals is shown in Fig. 2. The results of the infrared spectral analysis are reported in Table 2. A comparison of Figs. 1 and 2 confirms the rule of mutual exclusion for the spectroscopy of these natural oxalates. 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 in Fig. 1. The exception is oxammite where bands are observed in both the Raman and infrared spectra around 1400 cm^{-1}. 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 IR spectrum of humboldtine shows a single band centred at 1615 cm^{-1}.

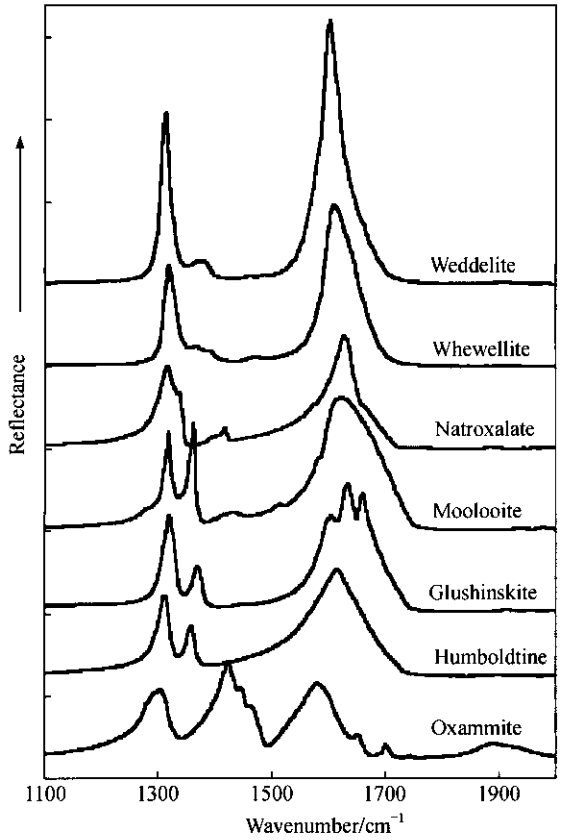

Fig. 2. Infrared spectra of the minerals.

For moolooite the 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}. For glushinskite bands are observed at 1679, 1660, 1634 and 1603 cm^{-1}. 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}[29]. 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[33,34]. 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 infrared spectra show quite intense bands centred around 1300 cm^{-1}. These bands may be assigned to B_{3u} O—C==O stretching mode. For weddelite 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 O—C=O stretching mode for synthetic copper(II) oxalate dihydrate[33,34]. 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 of 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.

(iv) Raman spectrum of the bending region. The Raman spectrum of the 800—1100 cm^{-1} region is shown in Fig. 3. A Raman band is observed at around 900 cm^{-1} and is assigned to the $\nu_{(C-C)}$ stretching mode. The band is observed at 909 cm^{-1} for weddelite, 921 cm^{-1} for moolooite, 913 cm^{-1} for humboldtine, 915 cm^{-1} for glushinskite, and 892 cm^{-1} for oxammite. The position for natroxalate is at 884 cm^{-1} which corresponds well with the published value of 888 cm^{-1} for solid potassium oxalate. It should be noted that there is a large shift (~40 cm^{-1}) for the C—C stretching vibration between the "free" oxalate and the oxalate in these natural oxalates. A second intense band for natroxalate is observed at 875 cm^{-1}. This implies a non-equivalence of the C—C stretching vibrations. The Raman spectra of the oxalate minerals all show a low intensity band at around 860 cm^{-1}. The band is observed at 868 cm^{-1} for weddelite, 833 cm^{-1} for moolooite, 856 cm^{-1} for humboldtine, 861 cm^{-1} for glushinskite, and 866 cm^{-1} for oxammite. The band is assigned to the O—C==O bending mode. A band is not observed in this position for potassium oxalate.

Table 2 Infrared spectroscopic analysis of oxalates minerals

Ca (weddellite)	Cu (moolooite)	Fe^{2+} (humboldtine)	Mg (glushinskite)	Na (natroxalate)	NH_4 (oxammite)	Infrared[41]	Band assignment
3593	3529	3472	3389		3195		OH stretching
3450	3347	3312	3380		3186		
3337	2971	3136	3360		3053		
3248			3305				
3089			3230				
			3126				
					2978		NH stretching
					2856		
					2840		
					2630		
					2344		
					1900		
1623	1722	1615	1679	1675	1701	1632	$\nu_{a(C=O)}$
1605	1679		1660	1628	1651		
	1632		1634	1604	1582		
	1602		1603		1527		
1500	1574	1514	1580	1538			$\nu_{a(C=O)}$
	1543	1479					
	1512						
1399	1430				1466	1433	$\nu_{s(C-O)} + \nu_{(C-C)}$
					1447		
					1425		
1366	1361	1357	1369	1416	1410	1302	$\nu_{s(C-O)} + \delta_{(O-C=O)}$
1309	1352		1322	1400	1308		
	1317	1312	1314	1337	1288		
	1311	1301	1169	1314			
	1279	1266		1296			
				1251			
917						890	$\nu_{s(C-C)} + \delta_{(O-C=O)}$
779	820	818	827	780	800	785	$_{(O-C=O)} + \nu_{(M-O)}$
762	798	766	803	771	716		
		715		756			
601			684		635	622	water libration
					617		
						519	$\nu_{(M-O)} + \nu_{(C-C)}$
						519	ring deform + $\delta_{(O-C=O)}$
						428	$\nu_{(M-O)}$ + ring deform
						419	
						377	$\delta_{(O-C=O)} + \nu_{(C-C)}$
						364	
						291	out of plane bends

(v) Infrared spectrum of the bending region. The infrared spectrum of the 500 to 1000 cm^{-1} region is shown in Fig. 4. The first observation that can be made is that the C—C stretching mode is either not observed or is only weakly observed in the infrared spectrum. Two low intensity bands are observed 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 a band at a similar position and oxammite a band at 871 cm^{-1}. An intense band is observed for weddelite at 779 cm^{-1} with a strong shoulder at 762 cm^{-1}. The infrared spectrum of whewellite shows a broad band centred upon 820 cm^{-1}. The IR spectrum of natroxalate shows two strong bands at 818 and 766 cm^{-1}. These bands are assigned to the O—C=O bending modes which are strong in the infrared spectrum and of low intensity in the Raman spectrum.

(vi) Raman spectrum of the deformation modes of oxalate. The Raman spectrum of the low wavenumber region is shown in Fig. 5. Raman bands are observed for weddelite and whewellite at 596 and 505 cm^{-1}. Natroxalate has Raman bands at 567 and 481 cm^{-1}. The band at 596 cm^{-1} is broad and of low intensity, and is attributed to water librational modes. The band at 505 cm^{-1} for the calcium oxalates and at 481 cm^{-1} for the sodium oxalate may be attributed to the symmetric O—C=O bending mode.

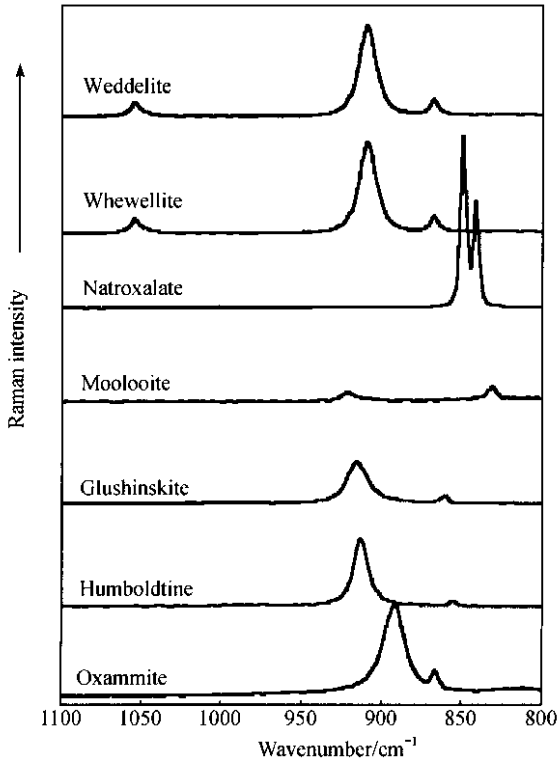

Fig. 3. Raman spectra of the 800—1100 cm^{-1} region.

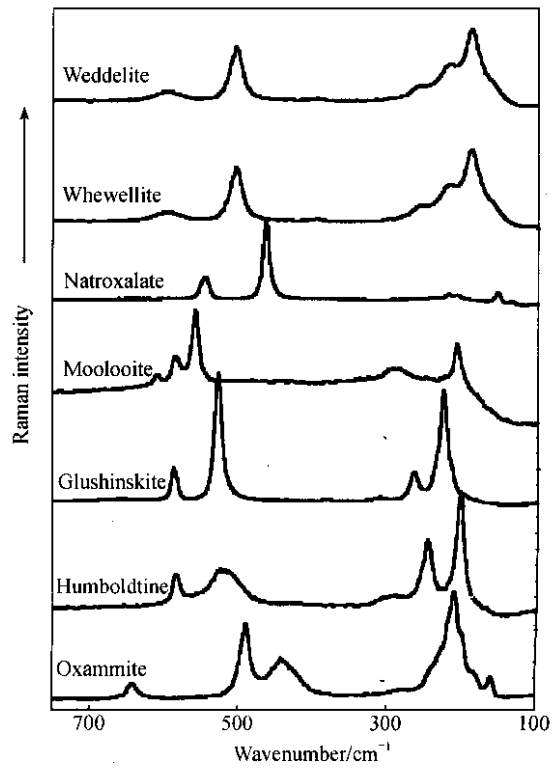

Fig. 5. Raman spectrum of the low wavenumber region.

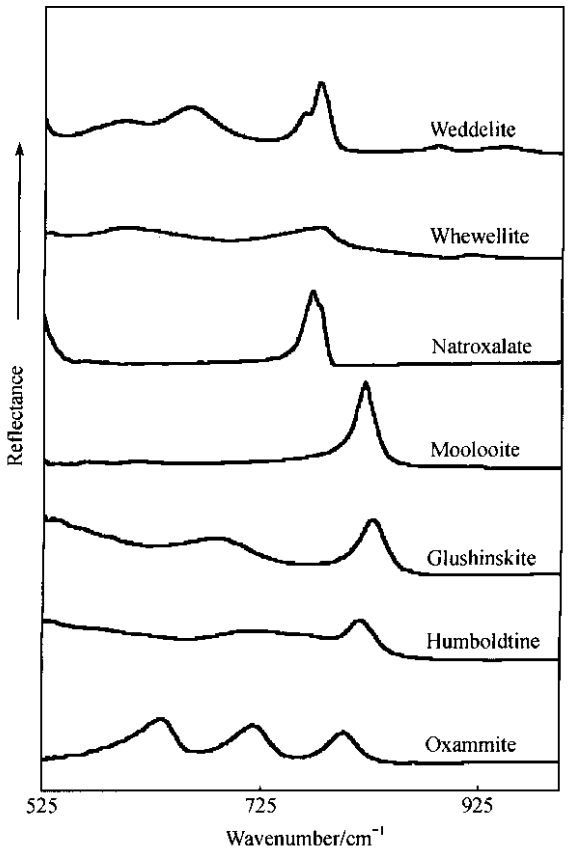

Fig. 4. Infrared spectrum of the 500—1000 cm^{-1} region.

For humboldtine the bands are observed at 582 and 518 cm^{-1}. The Raman spectrum of moolooite shows more complexity with bands observed at 610, 584 and 558 cm^{-1}. Such complexity was observed in the Raman spectrum of a synthetic copper(Ⅱ) oxalate dihydrate[35]. In this work, Raman bands were observed at 616, 591, 563 and 498 cm^{-1}. Raman bands were observed at 642, 489 and 438 cm^{-1} for oxammite.

Fig. 5 also shows some quite intense bands in the 100—300 cm^{-1} range. Both weddelite and whewellite show bands at 259, 220, 188 and 162 cm^{-1}. One possible assignment is that the bands are due to CaO stretching and bending vibrations. The intensities of the bands for natroxalate are weak. For moolooite bands are observed at 209 and 290 cm^{-1}. These bands may be assigned to the CuO stretching and bending modes respectively. The position of the bands differs slightly from that published for the copper(Ⅱ) oxalate dihydrate[35]. Intense bands are observed for both glushinskite and humboldtine at 310, 265, 237 and 226 cm^{-1}, and 293, 246 and 203 cm^{-1} respectively. The Raman spectrum of oxammite is quite complex with multiple bands observed at 278, 224, 210, 198, 181 and 160 cm^{-1}.

(ⅶ) Raman spectrum of the OH stretching region.

It is interesting that many papers report the spectroscopy of 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 Fig. 6. 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 weddelite and whewellite are different in the OH stretching region. Two bands are observed for weddelite at 3467 and 3266 cm^{-1} whereas bands are observed for whewellite at 3462, 3359, 3248 and 3067 cm^{-1}. The Raman spectrum 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 raman spectrum of oxammite in this region shows complexity with the overlap of the OH and NH stretching vibrations. Two bands are observed at 3235 and 3030 cm^{-1} and are assigned to the OH vibrations. Bands are observed at 2995, 2900 and 2879 cm^{-1} and are attributed to the NH vibrational modes.

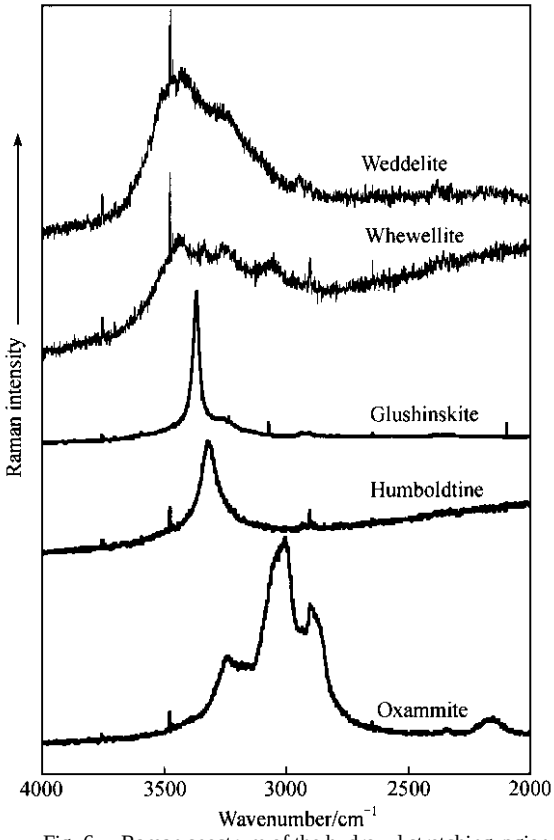

Fig. 6. Raman spectrum of the hydroxyl stretching region.

The patterns of the OH stretching vibrations observed in the Raman spectra are reflected in the infrared spectra (Fig. 7). The spectra of weddelite and whewellite are different. The infrared spectrum of weddelite shows OH stretching vibrations at 3593, 3450, 3337, 3248 and 3089 cm^{-1}. The infrared spectra of whewellite shows a broad pattern. No spectrum is observed for natroxalate and a low intensity broad band is observed for moolooite and in all probability represents adsorbed water. The infrared spectrum of glushinskite and humboldtine show intense bands at 3389 and 3472 cm^{-1} respectively. Low intensity bands are observed for glushinskite at 3380, 3360, 3305, 3230 and 3126 cm^{-1}. Low intensity bands are observed for humboldtine at 3312 and 3136 cm^{-1}. In the case of oxammite infrared bands are observed at 3195, 3186 and 3053 cm^{-1} and are attributed to the water OH stretching vibrations. The infrared bands observed at 2978, 2856, 2840, 2630 and 2344 cm^{-1} are assigned to NH stretching vibrations. It is probable that the large number of bands observed in the NH stretching region is ascribed to the non-planar nature of oxammite[36]. It has been suggested that the oxalate is twisted around the C—C bond by some 28° [37].

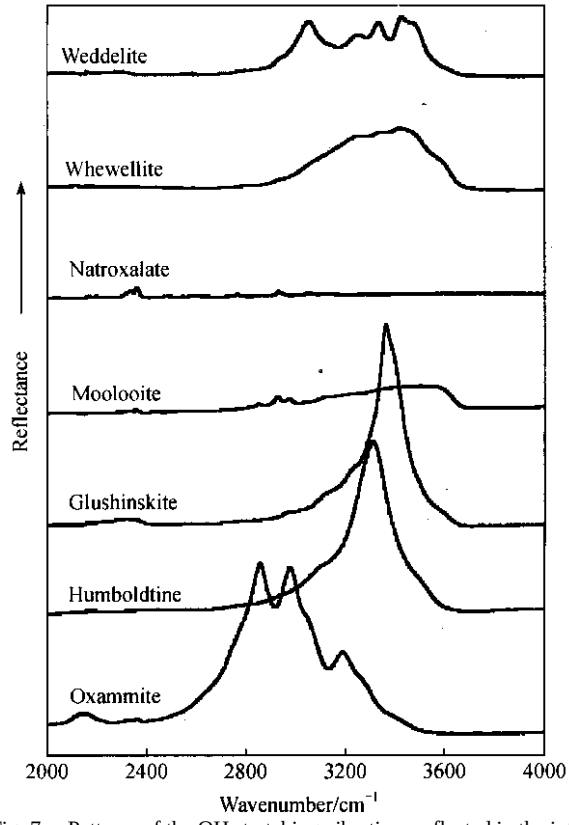

Fig. 7. Patterns of the OH stretching vibrations reflected in the infrared spectra.

3 Conclusions

A suite of natural oxalate minerals have been characterised by both Raman and infrared spectroscopy. 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 spectra of the natural oxalates are different. There are a number of reasons for this difference as follows: oxalates may have different structures for example oxammite has a chair-like formation whereas several oxalates are centro-symmetric and planar; the natural oxalates for example moolooite may form polymers with repeat oxalate units; the oxalates may also be a mixture of more than one mineral, for example oxammite may be a mixture of the dihydrate, the anhydrous chemical and a polymer.

If life existed on Mars at some time in the past or even exists in the present time, low life forms such as fungi and lichens may exist. Such organisms may be found in very hostile environments[38—41]. Lichens and fungi can control their heavy metal intake through expulsion of metal salts such as oxalates. 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. The minerals on planets such as Mars may be explored by robotic devices which carry portable spectrometers with possible 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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