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1 **Raman spectroscopic study of the sulphite bearing minerals scotlandite,**
2 **hannebachite and orschallite – implications for the desulphation of soils**

3
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9
10
11 **The structure of the naturally occurring sulphite bearing minerals**
12 **scotlandite, hannebachite and orschallite have been studied by Raman**
13 **spectroscopy. Raman bands are observed for scotlandite PbSO_3 at 935,**
14 **880, 622 and 474 cm^{-1} and are assigned to the $(\text{SO}_3)^{2-}$ $\nu_1(A_1)$, $\nu_3(E)$, $\nu_2(A_1)$**
15 **and $\nu_4(E)$ vibrational modes. For hannebachite $(\text{CaSO}_3)_2 \cdot \text{H}_2\text{O}$ these**
16 **bands are observed at 1005, 969, 655 cm^{-1} with multiple bands for the**
17 **$\nu_4(E)$ mode at 444, 492 and 520 cm^{-1} . The Raman spectrum of**
18 **hannebachite is very different from that of the compound $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$.**
19 **It is proposed, based upon Raman spectroscopy, that in the mineral**
20 **hannebachite, the sulphite anion bonds to Ca through the sulphur. The**
21 **Raman spectrum of the mineral orschallite $\text{Ca}_3[\text{SO}_4](\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ is**
22 **complex resulting from the overlap of sulphate and sulphite bands.**
23 **Raman bands at 1005 cm^{-1} and 1096 and 1215 cm^{-1} are assigned to the**
24 **$(\text{SO}_4)^{2-}$ ν_1 symmetric and ν_3 antisymmetric stretching modes. The two**
25 **Raman bands at 971 and 984 cm^{-1} are attributed to the $(\text{SO}_3)^{2-}$ $\nu_3(E)$ and**
26 **$\nu_1(A_1)$ stretching vibrations. The formation of sulphite compounds in**
27 **nature offers a potential mechanism for the removal of sulphates and**
28 **sulphites from soils.**

29
30 **KEYWORDS:** sulphite, scotlandite, hannebachite, Raman spectroscopy, gravegliaite,
31 orschallite

32

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33 INTRODUCTION

34
35 There are a number of naturally occurring sulphite minerals which are known.
36 These include scotlandite PbSO_3 ¹⁻⁴, hannebachite $(\text{CaSO}_3)_2 \cdot \text{H}_2\text{O}$ ⁵, gravegliaite
37 $\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$ ⁶ and the mixed sulphate-sulphite mineral orschallite
38 $\text{Ca}_3[\text{SO}_4](\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ ⁷. The pyramidal sulphite ion $(\text{SO}_3)^{2-}$ may bond to a metal as
39 a unidentate, bidentate or even as a bridging ligand⁸. Bonding may occur through
40 either the oxygen or the sulphur of the sulphite anion. If the latter occurs then the C_{3v}
41 symmetry of the sulphite ion will be preserved. If coordination is through the oxygen,
42 the symmetry of the anion will be reduced to C_s . In this case the doubly degenerate
43 vibrations of the free ion will split into two bands. According to Nakamoto, bonding
44 through the sulfur will shift the SO stretching bands to higher wavenumbers whilst
45 bonding through the oxygen will shift the bands to lower wavenumbers⁸.

46
47 Nakamoto provides a table of wavenumbers of the band positions of sulphito
48 complexes with defined band positions⁸. Based upon infrared spectra the free
49 sulphite anion has bands at the following positions $\nu_1(A_1)$ 967 cm^{-1} , $\nu_3(E)$ 933 cm^{-1} ,
50 $\nu_2(A_1)$ 620 cm^{-1} and $\nu_4(E)$ 469 cm^{-1} . Nakamoto shows that if the sulphito group
51 bonds through the sulphur, these vibrational modes occur as follows: $\nu_1(A_1)$ 964-984
52 cm^{-1} , $\nu_3(E)$ 1057-1110 cm^{-1} , $\nu_2(A_1)$ 625-660 cm^{-1} and $\nu_4(E)$ 519-540 cm^{-1} . If the
53 sulphite bonds through the oxygen as occurs in $\text{Tl}_2[\text{Cu}(\text{SO}_3)_2]$ and $(\text{NH}_4)_9[\text{Fe}(\text{SO}_3)_6]$,
54 the bands occur at $\nu_1(A_1)$ 989/815 cm^{-1} , $\nu_3(E)$ 902, 862 and 943 cm^{-1} , $\nu_2(A_1)$ 673 and
55 638 cm^{-1} and $\nu_4(E)$ 460, 506 and 520 cm^{-1} . According to Gadsden⁹, the infrared
56 spectrum of sodium sulphite gives bands at $\nu_1(A_1)$ 1135 cm^{-1} , $\nu_3(E)$ 980 cm^{-1} , $\nu_2(A_1)$
57 635 cm^{-1} and $\nu_4(E)$ 496 cm^{-1} . For the hydrated sulphite $\text{K}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$ these
58 vibrational modes are found at 1100, 965, 620 and 480 cm^{-1} .

59
60 Minerals are excellent samples for Raman spectroscopic analysis, especially
61 where the minerals are disordered or are not well defined by X-ray diffraction.¹⁰⁻¹⁴
62 Raman spectroscopy has been used to study many related secondary minerals.¹⁵⁻²⁵
63 The aim of this paper is to present the Raman spectra of natural selected sulphites and
64 to discuss the spectra from a structural point of view.

67 **EXPERIMENTAL**

68
69 **Minerals**

70
71 The mineral hannebachite was sourced from Hannebacher Ley Volcano,
72 Germany and supplied by the Mineralogical Research Company. The compositions of
73 this mineral has been reported by Anthony *et al.* (page 277)²⁶. The mineral
74 hannebachite was reported as SO₂ 49.60%, CaO 43.42%, H₂O 6.98% which
75 corresponds to a formula of CaSO₃.H₂O. As was the scotlandite mineral which came
76 from the Leadhills, Scotland (Anthony *et al.* (page 630))²⁶. The composition of
77 scotlandite was give as SO₂ 22.30%, PbO 77.70% corresponding to a formula of
78 Pb_{1.06}S_{0.96}O₃. The mineral orschallite also originated from Hannebacher, Germany.
79 The composition has been reported by Anthony *et al.* (page 513)²⁶. The mineral
80 orschallite corresponds to the formula Ca₃(SO₃)₂(SO₄)·12H₂O.

81
82 **Raman microprobe spectroscopy**

83
84 The crystals of the sulphite minerals were placed and orientated on the stage of
85 an Olympus BHSM microscope, equipped with 10x and 50x objectives as part of a
86 Renishaw 1000 Raman microscope system. The system includes a monochromator, a
87 filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a
88 HeNe laser (633 nm) at a resolution of 2 cm⁻¹ in the range between 100 and 4000
89 cm⁻¹. Repeated acquisition using the highest magnification was accumulated to
90 improve the signal to noise ratio. Further details and the application of Raman
91 spectroscopy to the study of minerals has been published.

92
93 Spectroscopic manipulation such as baseline adjustment, smoothing and
94 normalisation were performed using the Spectralcalc software package GRAMS
95 (Galactic Industries Corporation, NH, USA). Band component analysis was
96 undertaken using the Jandel 'Peakfit' software package, which enabled the type of
97 fitting function to be selected and allows specific parameters to be fixed or varied
98 accordingly. Band fitting was done using a Gauss-Lorentz, cross-product function
99 with the minimum number of component bands used for the fitting process. The
100 Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was

101 undertaken until reproducible results were obtained with squared correlations with r^2
102 greater than 0.995.

103

104 RESULTS AND DISCUSSION

105

106 *Background*

107

108 S.D. Ross²⁷ lists the vibrational wavenumbers for some 17 sulphites. The
109 position of $\nu_1(A_1)$ varies from 951 cm^{-1} for BaSO_3 to 980 cm^{-1} for CaSO_3 . The
110 position of $\nu_3(E)$ always appears to be less than that of $\nu_1(A_1)$ mode except in certain
111 instances such as Na_2SO_3 where the bands are coincident. The value of ν_3 varies from
112 a minimum of 892 cm^{-1} for CdSO_3 to a maximum of 970 cm^{-1} for Na_2SO_3 . The value
113 of $\nu_2(A_1)$ varies from 619 cm^{-1} for K_2SO_3 to 640 cm^{-1} for SrSO_3 . Much greater
114 variation is observed for the ν_4 mode. 478 cm^{-1} for K_2SO_3 to 527 cm^{-1} for CdSO_3 .
115 For many divalent cation sulphites the band is split into at least two bands. There are
116 a significant number of ammoniated sulphites such as $(\text{NH}_4)_2\text{Mg}(\text{SO}_3)\cdot\text{H}_2\text{O}$ where
117 even greater variation in the sulphite band positions are observed. The calculated
118 values for the band positions of sulphite are $\nu_1(A_1)$ 972 cm^{-1} , $\nu_3(E)$ 937 cm^{-1} , $\nu_2(A_1)$
119 6234 cm^{-1} and $\nu_4(E)$ 457 cm^{-1} ²⁷.

120

121 *Raman spectroscopy of scotlandite*

122

123 Natural minerals are not necessarily the same as synthesised minerals. The
124 natural minerals may contain isomorphic substitution of both the cation and the anion,
125 resulting in greater spectral complexity. The Raman spectrum of scotlandite PbSO_3 is
126 shown in *Fig. 1*. The intense band at 935 cm^{-1} is assigned to the $(\text{SO}_3)^{2-}$ $\nu_1(A_1)$
127 stretching vibration. Ross²⁷ reports this band for (presumably) a synthesised PbSO_3
128 at 969 cm^{-1} (Table 6.32, page 177). The low intensity band at 880 cm^{-1} is attributed to
129 the $(\text{SO}_3)^{2-}$ $\nu_3(E)$ stretching vibration. Ross²⁷ reported this band at 897 cm^{-1} . It is
130 noted that for this sulphite anion the band position for the $\nu_1(A_1)$ mode occurs at a
131 higher wavenumber than the $\nu_3(E)$ mode. The low intensity band at 622 cm^{-1} is
132 ascribed to the $\nu_2(A_1)$ bending mode. In comparison the value from Ross is 625 cm^{-1}
133 which is in excellent agreement with the values reported here. The band at 474 cm^{-1}
134 is assigned to the $\nu_4(E)$ vibrational mode, in good agreement with the value of 472

135 cm^{-1} for PbSO_3 from Ross²⁷. Interestingly the band for PbSO_3 from Ross is split into
136 two bands at 472 and 483 cm^{-1} . No splitting of this band is observed in *Fig. 1*.

137

138 *Raman spectroscopy of hannebachite*

139

140 The Raman spectrum of hannebachite $(\text{CaSO}_3)_2 \cdot \text{H}_2\text{O}$ in the 100 to 1300 cm^{-1}
141 region is displayed in *Fig. 2*. The very intense sharp band at 1005 cm^{-1} is attributed
142 to the $\nu_1(A_1)$ symmetric stretching mode and the band at 969 cm^{-1} is attributed to the
143 $\nu_3(E)$ antisymmetric stretching mode. Two bands at 1094 and 1092 cm^{-1} are also
144 observed. The band at 655 cm^{-1} is assigned to the $\nu_2(A_1)$ bending mode. Three bands
145 are observed at 444, 492 and 520 cm^{-1} and are assigned to the $\nu_4(E)$ bending mode.
146 Multiple bands give an indication of the reduction in symmetry of the $(\text{SO}_3)^{2-}$ anion.
147 Ross reports the band positions of $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$ as $\nu_1(A_1)$ 972 cm^{-1} , $\nu_3(E)$ 937 cm^{-1} ,
148 $\nu_2(A_1)$ 6234 cm^{-1} and $\nu_4(E)$ 457 cm^{-1} ²⁷. The formula of the mineral hannebachite is
149 given as $2\text{CaSO}_3 \cdot \text{H}_2\text{O}$ and the spectra are very different for these two compounds. The
150 values of the band positions are in agreement with the sulphite anion coordinating
151 through the sulphur atom in the mineral hannebachite⁸.

152

153 *Raman spectroscopy of orschallite*

154

155 The Raman spectrum of orschallite in the 900 to 1400 cm^{-1} region is shown in
156 *Fig. 3*. Compared with the Raman spectrum of hannebachite, the spectrum of
157 orschallite is complex. The Raman spectroscopy of the aqueous sulphate tetrahedral
158 oxyanion yields the ν_1 vibration at 981 cm^{-1} , the ν_2 mode at 451 cm^{-1} , the ν_3 mode at
159 1104 cm^{-1} and the ν_4 mode at 613 cm^{-1} . The Raman band at 1005 cm^{-1} with a
160 component band at 1011 cm^{-1} is assigned to the $(\text{SO}_4)^{2-}$ ν_1 symmetric stretching mode.
161 A comparison of the spectra of hannebachite and orschallite shows the presence of
162 peaks in the 1050 to 1250 cm^{-1} region of orschallite, which are absent in the spectra of
163 hannebachite. Two bands are observed in the Raman spectrum of orschallite at 1096
164 and 1215 cm^{-1} . The bands are of low intensity and are assigned to the $(\text{SO}_4)^{2-}$ ν_3
165 antisymmetric stretching mode. The two bands at 971 and 984 cm^{-1} are attributed to
166 the $(\text{SO}_3)^{2-}$ $\nu_3(E)$ and $\nu_1(A_1)$ stretching vibrations. The Raman spectrum of orschallite
167 in the 100 to 800 cm^{-1} region is shown in *Fig. 4*. The band at 651 cm^{-1} is attributed to

168 the $(\text{SO}_3)^{2-}$ $\nu_2(A_1)$ bending mode. This band may be coincident with or overlap the
169 with the the $(\text{SO}_4)^{2-}$ ν_4 mode which would be expected at around 613 cm^{-1} . The
170 spectral region between 400 and 550 cm^{-1} shows great complexity which no doubt
171 results from the overlap of the $(\text{SO}_4)^{2-}$ ν_2 mode at 451 cm^{-1} and the $(\text{SO}_3)^{2-}$ $\nu_4(E)$
172 bending mode. Further it is likely that coupling occurs between these vibrations. Four
173 bands are observed at 441 , 492 , 521 and 532 cm^{-1} . One possible assignment is that the
174 first two bands are due to the $(\text{SO}_3)^{2-}$ $\nu_4(E)$ bending modes and the latter two bands
175 are due to the $(\text{SO}_4)^{2-}$ ν_2 bending mode.

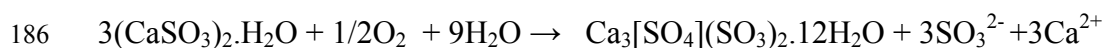
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177 The Raman spectrum of orschallite in the 3000 to 3800 cm^{-1} region is shown
178 in Fig. 5. The Raman spectrum of water in minerals is often of low intensity due to
179 the very poor scattering cross section of water. The Raman band at 3383 cm^{-1} is
180 assigned to the water stretching mode. This band was not observed in the Raman
181 spectrum of hannebachite. A Raman band at 1628 cm^{-1} was also observed in the
182 spectrum of orschallite and is assigned to the water bending mode.

183

184 *Possible Relationship between hannebachite and orschallite*

185



187

188 There is a possible relationship between the minerals hannebachite and
189 orschallite as per the above equation. Such an equation has implications for the
190 removal of sulphate from soils.

191

192 *Implications for the desulphation of soils*

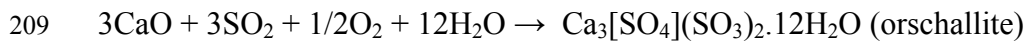
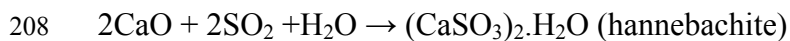
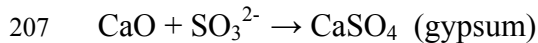
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194 The remediation of acid sulphate soils is of fundamental importance in Australia²⁸⁻³⁰.
195 Various technologies are available such as bioremediation^{28,31}. Another possibility is
196 to add various chemicals to the soils including basic compounds such as quicklime
197 and hydrated lime. Such chemicals may react with the SO_2 of the atmosphere or with
198 SO_2 generated in soils. However it must be understood that by chemical reactions, the
199 problem is simply not being transferred from one point to another. For example the

200 sulphate may be removed but through the formation of gypsum , the soil becomes
201 contaminated with this mineral.

202

203 A soil containing sulphate or sulphite ions may be remediated by the addition
204 of CaO or Ca(OH)₂. The reaction of these chemicals with either sulphite, sulphate or
205 sulphur dioxide will result in the formation of several compounds. The following
206 reactions are envisaged:



210 Other reactions based upon the use of Ca(OH)₂ could also be employed. It is possible
211 that a range of sulphites can be formed including the naturally occurring sulphites
212 hannebachite and orschallite.

213

214 **CONCLUSIONS**

215

216 Raman spectroscopy has been used to study the sulphite bearing minerals
217 scotlandite, hannebachite and orschallite. Raman bands are identified and related to
218 the structure of the minerals. Such a study has not been previously undertaken. Based
219 upon Raman spectra of many sulphite chemicals, it is proposed that hannebachite
220 bonds to the calcium through the sulphur i.e. a sulphito complex is formed. It is
221 probable a similar bonding occurs in the mineral orschallite, even though the mineral
222 contains both sulphate and sulphite ions.

223

224 The formation of sulphites may result from two possible applications: firstly
225 the reaction of greenhouse gases with alkaline minerals such as quick and slaked lime
226 and secondly the use of such materials for the desulphation of soils. It is possible to
227 theorise about a wide range of reactions such of which involve the formation of
228 sulphite minerals such as scotlandite, hannebachite and orschallite.

229

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231

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236

237

238 **REFERENCES**

- 239 1. Green, DI. *Min. Mag.* 1989; **53**: 653.
 240 2. Paar, WH, Braithwaite, RSW, Chen, TT, Keller, P. *Min. Mag.* 1984; **48**: 283.
 241 3. Pertlik, F, Zemann, J. *TMPM, Tsch. Min. Petr. Mitt.* 1985; **34**: 289.
 242 4. Sarp, H, Burri, G. *Schweizerische Min. Petr. Mitt.* 1984; **64**: 317.
 243 5. Hentschel, G, Tillmanns, E, Hofmeister, W. *Neues Jahr. Min., Monat.* 1985:
 244 241.
 245 6. Basso, R, Lucchetti, G, Palenzona, A. *Zeit. Krist.* 1991; **197**: 97.
 246 7. Weidenthaler, C, Tillmanns, E, Hentschel, G. *Min. Petr.* 1993; **48**: 167.
 247 8. Nakamoto, K *Infrared Spectra of Inorganic and Coordination Compounds.*
 248 *2nd ed*, Wiley London 1970.
 249 9. Gadsden, JA *Infrared spectra of minerals and related compounds*;
 250 Butterworths: London, 1975.
 251 10. Frost, RL, Cejka, J, Ayoko, G. *J. Raman Spectrosc.* 2008; **39**: 495.
 252 11. Frost, RL, Cejka, J, Ayoko, GA, Dickfos, MJ. *J. Raman Spectrosc.* 2008; **39**:
 253 374.
 254 12. Frost, RL, Dickfos, MJ, Cejka, J. *J. Raman Spectrosc.* 2008; **39**: 582.
 255 13. Frost, RL, Hales, MC, Wain, DL. *J. Raman Spectrosc.* 2008; **39**: 108.
 256 14. Frost, RL, Keeffe, EC. *J. Raman Spectrosc.* 2008; **in press**.
 257 15. Palmer, SJ, Frost, RL, Ayoko, G, Nguyen, T. *J. Raman Spectrosc.* 2008; **39**:
 258 395.
 259 16. Frost, RL, Bouzaid, JM. *J. Raman Spectrosc.* 2007; **38**: 873.
 260 17. Frost, RL, Bouzaid, JM, Martens, WN, Reddy, BJ. *J. Raman Spectrosc.* 2007;
 261 **38**: 135.
 262 18. Frost, RL, Cejka, J. *J. Raman Spectrosc.* 2007; **38**: 1488.
 263 19. Frost, RL, Cejka, J, Ayoko, GA, Weier, ML. *J. Raman Spectrosc.* 2007; **38**:
 264 1311.
 265 20. Frost, RL, Cejka, J, Weier, ML. *J. Raman Spectrosc.* 2007; **38**: 460.
 266 21. Frost, RL, Cejka, J, Weier, ML, Martens, WN, Ayoko, GA. *J. Raman*
 267 *Spectrosc.* 2007; **38**: 398.
 268 22. Frost, RL, Dickfos, MJ. *J. Raman Spectrosc.* 2007; **38**: 1516.
 269 23. Frost, RL, Palmer, SJ, Bouzaid, JM, Reddy, BJ. *J. Raman Spectrosc.* 2007;
 270 **38**: 68.
 271 24. Frost, RL, Pinto, C. *J. Raman Spectrosc.* 2007; **38**: 841.
 272 25. Frost, RL, Weier, ML, Williams, PA, Leverett, P, Klopogge, JT. *J. Raman*
 273 *Spectrosc.* 2007; **38**: 574.
 274 26. Anthony, JW, Bideaux, RA, Bladh, KW, Nichols, MC *Handbook of*
 275 *Mineralogy*; Mineral Data Publishing: Tuscon, Arizona, USA, 2000; Vol. 4.
 276 27. Ross, SD *Inorganic Infrared and Raman spectra*; McGraw-Hill: London,
 277 1972.
 278 28. Costa, MC, Duarte, JC. *Water, Air, & Soil Pollution* 2005; **165**: 325.
 279 29. Smith, CD, Martens, MA, McElnea, AE. *Aust. Inst. Min. Met.* 2003; **3/2003**:
 280 469.
 281 30. Powell, B, Martens, M. *Mar. Pollut. Bull.*, 2005; **51**: 149.
 282 31. Haakansson, T, Suer, P, Mattiasson, B, Allard, B. *Inter. J. Envir. Sc. Tech.*
 283 2008; **5**: 267.
 284
 285

286 **List of Figs**

287

288 *Fig. 1* Raman spectra of scotlandite in the 100 to 1300 cm^{-1} region.

289 *Fig. 2* Raman spectra of hannebachite in the 100 to 1300 cm^{-1} region.

290 *Fig. 3* Raman spectra of orschallite in the 900 to 1400 cm^{-1} region.

291 *Fig. 4* Raman spectra of orschallite in the 100 to 800 cm^{-1} region.

292 *Fig. 5* Raman spectra of orschallite in the 3000 to 3800 cm^{-1} region.

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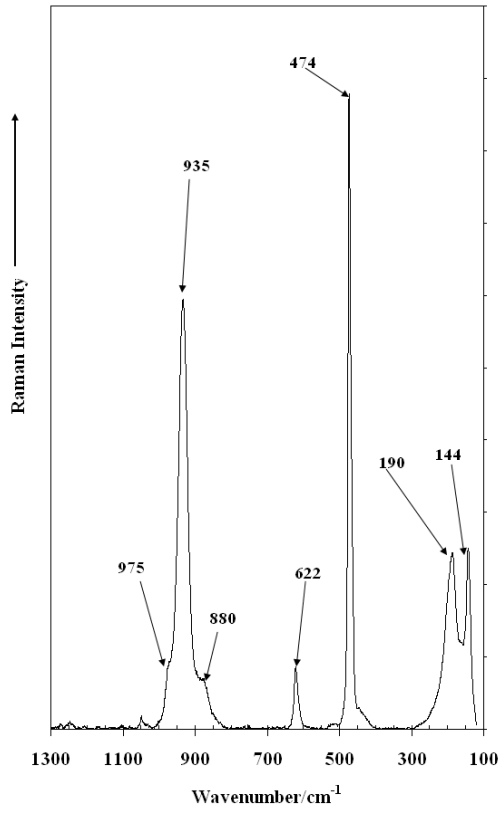
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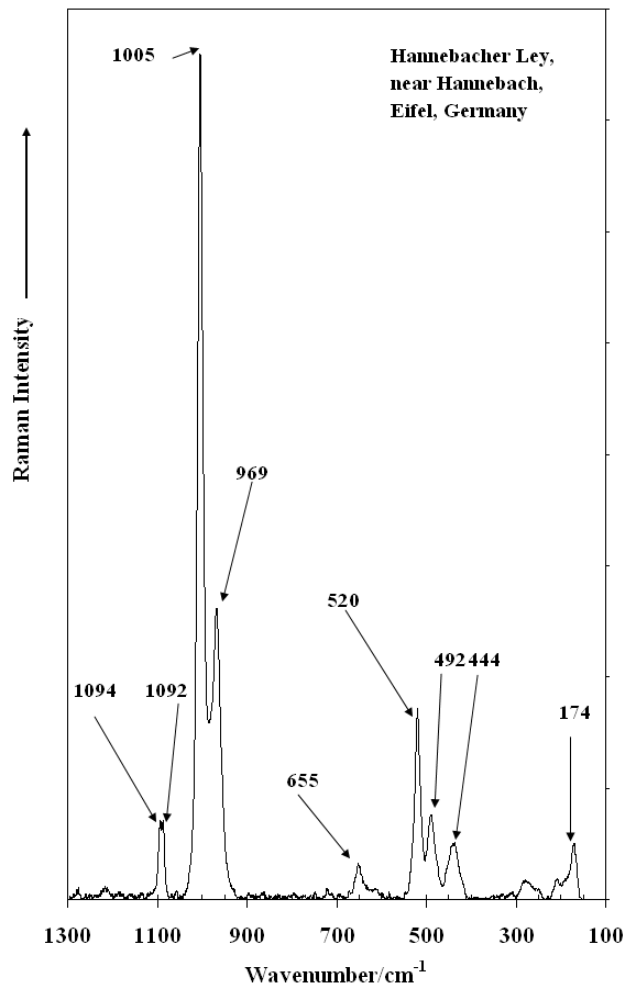


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Fig. 1 scotlandite

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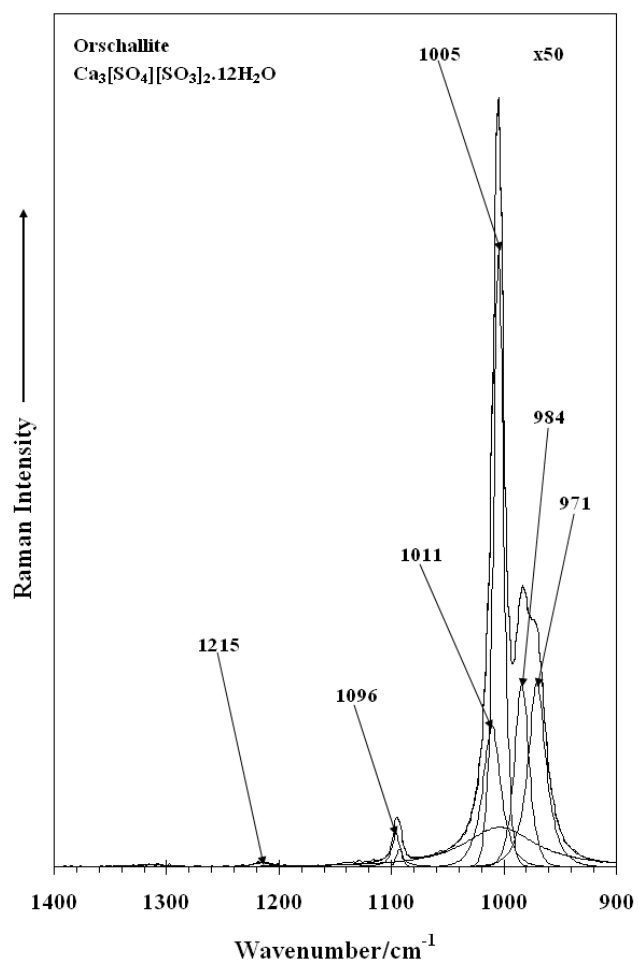
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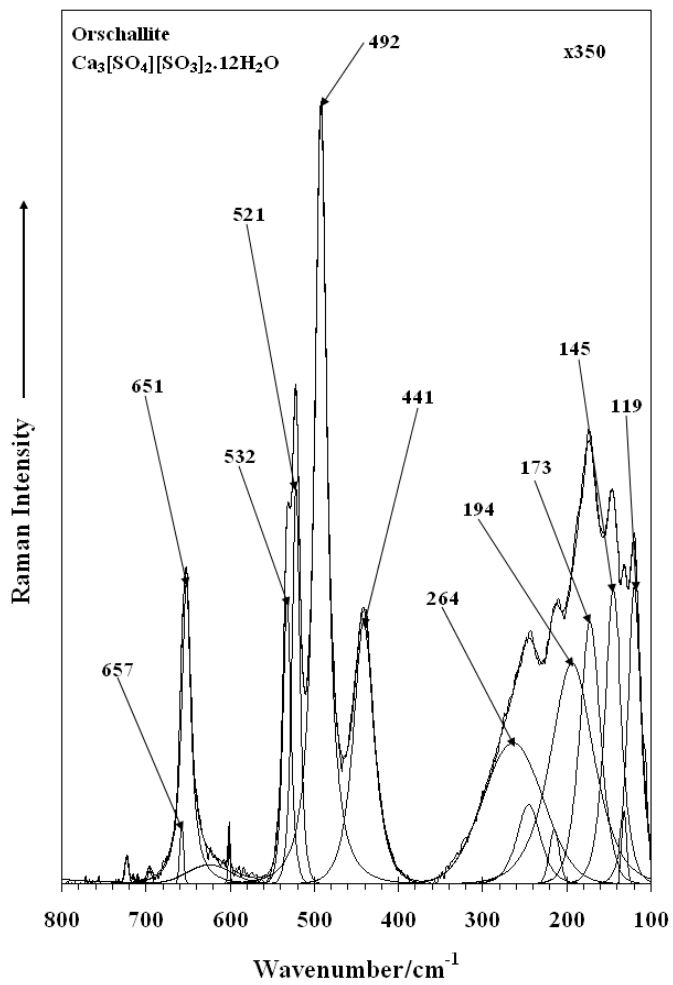
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308 **Fig. 2**



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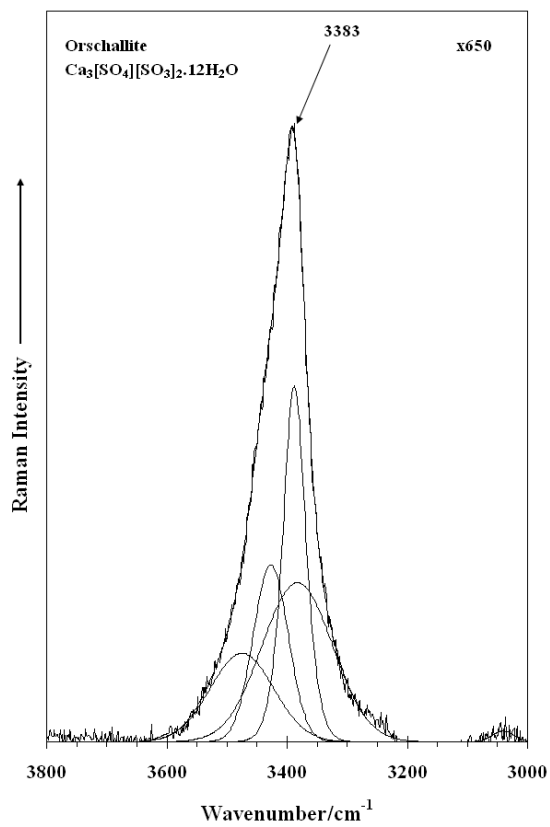
310 **Fig. 3**



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312

313 **Fig. 4**



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315

316 **Fig. 5**