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1   **Raman spectroscopic study of the tellurite minerals: graemite $CuTeO_3.H_2O$ and**
2   **teineite $CuTeO_3.2H_2O$**
3
4   **Ray L. Frost [•] and Eloise C. Keeffe**
5

6   Inorganic Materials Research Program, School of Physical and Chemical Sciences,
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8   Australia.
9
10

11   **Tellurites may be subdivided according to formula and structure.**
12   **There are five groups based upon the formulae (a) $A(XO_3)$, (b)**
13   **$A(XO_3).xH_2O$, (c) $A_2(XO_3)_3.xH_2O$, (d) $A_2(X_2O_5)$ and (e) $A(X_3O_8)$. Raman**
14   **spectroscopy has been used to study the tellurite minerals teineite and**
15   **graemite; both contain water as an essential element of their stability.**
16   **The tellurite ion should show a maximum of six bands. The free**
17   **tellurite ion will have C_{3v} symmetry and four modes, $2A_1$ and $2E$.**
18   **Raman bands for teineite at 739 and 778 cm^{-1} and for graemite at 768**
19   **and 793 cm^{-1} are assigned to the v_1 $(TeO_3)^{2-}$ symmetric stretching mode**
20   **whilst bands at 667 and 701 cm^{-1} for teineite and 676 and 708 cm^{-1} for**
21   **graemite are attributed to the the v_3 $(TeO_3)^{2-}$ antisymmetric stretching**
22   **mode. The intense Raman band at 509 cm^{-1} for both teineite and**
23   **graemite is assigned to the water librational mode. Raman bands for**
24   **teineite at 318 and 347 cm^{-1} are assigned to the $(TeO_3)^{2-}$ v_2 (A_1) bending**
25   **mode and the two bands for teineite at 384 and 458 cm^{-1} may be**
26   **assigned to the $(TeO_3)^{2-}$ v_4 (E) bending mode. Prominent Raman bands,**
27   **observed at 2286, 2854, 3040 and 3495 cm^{-1}, are attributed to OH**
28   **stretching vibrations. The values for these OH stretching vibrations**
29   **provide hydrogen bond distances of 2.550(6) Å (2341 cm^{-1}), 2.610(3) Å**
30   **(2796 cm^{-1}) and 2.623(2) Å (2870 cm^{-1}) which are comparatively short**
31   **for secondary minerals.**
32

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INTRODUCTION

Selenites and tellurites may be subdivided according to formula and structure [1]. There are five groups based upon the formulae (a) $A(XO_3)$, (b) $A(XO_3) \cdot xH_2O$, (c) $A_2(XO_3)_3 \cdot xH_2O$, (d) $A_2(X_2O_5)$ and (e) $A(X_3O_8)$. Of the selenites, molybdomenite is an example of type (a); chalcomenite, clinochalcomenite, cobaltomenite and ahlfeldite are examples of type (b) mandarino is an example of type (c). There are no known examples of selenite minerals with formula (d) and (e). The tellurite group, however, consists of minerals that can be categorised into each of the five formula types. Fairbankite, balyakinite, plumbotellurite, mocktezumite, magnolite and smirnite are examples of type (a); graemite, teineite and chaloalite are examples of type (b); zemmanite and emmonsite are examples of type (c); rajite and denningite are examples of type (d) and spiroffite, winstanleyite, carlfreisite and pingguite are examples of type (e). A further group, of alternate formula and structure, is one in which the minerals contain water and/or OH units. Of this group are the minerals rodalquilarite, sonoraite, cesbronite, guilleminite, marthozite, demesmaekerite and haynesite. The two related minerals teineite $Cu(TeO_3) \cdot 2H_2O$ [2-7] and graemite $Cu(TeO_3) \cdot H_2O$ [8,9] are examples of hydrated tellurites. Further information may be obtained by consulting the MINDAT website http://www.mindat.org/dana.php?a=34.

Both teineite and graemite are zeolite-like with a negatively charged framework of $[Cu(TeO_3)]$. They have large open channels of 8.28 Å, parallel to [0001] [10]. The structures of teineite and graemite are based on layers of edge-sharing, Cu octahedra which are interconnected by TeO_3 pyramids. The Cu atom has a (4+1) coordination. The Te atom is coordinated with three O atoms to form pyramids [2]. Teineite and graemite appear to be isotypes of chalcomenite [5,6]. They are related to many other tellurite minerals including emmonsite, mackayite and sonoraite. These minerals are often found together in tellurite mineral deposits [11]. Teineite, graemite and some related compounds have been synthesised [2,12-14]. Related minerals kinichilite $Mg_{0.5}[Mn^{2+}Fe^{3+}(TeO_3)_3]_4 \cdot 5H_2O$ [15] and emmonsite, $Fe_2^{3+}Te_3^{4+}O_9 \cdot 2H_2O$ [16,17], are found in the tellurium rich deposits of Mexico [18]. Other

2

67 tellurite minerals are cliffordite $UTe_3^{4+}O_9$ [19,20] and keystoneite

68 $Mg_{0.5}[Ni^{2+}Fe^{3+}(TeO_3)_3]_4 \cdot 5H_2O$ [21,22]. The importance of these tellurium bearing

69 minerals is their open framework structures with negatively charged surfaces and

70 zeolitic pores [23]. The minerals fit into the Dana Classification 8th edition as

71 $A_2(XO_3)_3 \cdot xH_2O$ [web site http://www.mindat.org/dana.php?a=34&b=3].

72

73   Information on the molecular structure of minerals can be obtained by Raman

74 spectroscopy which often cannot be obtained by other methods. [24-34] Diagenetcially

75 related minerals such as graemite and teineite lend themselves to study by Raman

76 spectroscopy. The objective of this research is to present Raman of the natural

77 tellurites, graemite and teineite and discuss the Raman spectra from a molecular

78 structure point of view.

79

80 **EXPERIMENTAL**

81

82 ***Minerals***

83

84 The first teineite mineral sample was sourced from the Moctezuma Mine, Mexico

85 whilst a second sample, the type mineral was sourced from the Teine Mine, Japan

86 and a third sample was sourced from Cole Shaft, Arizona, USA. The graemite

87 mineral sample was also sourced from Cole Shaft, Arizona, USA. The two minerals

88 are related due to graemeite being a partially dehydrated teineite. The compositions

89 of these minerals have been reported by Anthony *et al.* (page 696 (teineite) and 260

90 (graemite)) [35].

91

92

93

94 ***Raman microprobe spectroscopy***

95

96   The crystals of the minerals were placed and orientated on the stage of an

97 Olympus BHSM microscope which was equipped with 10x and 50x objectives as part

98 of a Renishaw 1000 Raman microscope system. The system also includes a

99 monochromator, filter system and Charge Coupled Device (CCD). Raman spectra

100 were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between

Comment [QSOE1]: Is it possible to put these somewhere into the list of tellurites of formula type at e start?

3

101 100 and 4000 cm^{-1}. Further details and the application of Raman spectroscopy to the

102 study of minerals has been published by the corresponding authors. [36-39]

103

104   Spectroscopic manipulation such as baseline adjustment, smoothing and

105 normalisation were performed using the Spectracalc software package GRAMS

106 (Galactic Industries Corporation, NH, USA). Band component analysis was

107 undertaken using the Jandel 'Peakfit' software package, which enabled the type of

108 fitting function to be selected and allows specific parameters to be fixed or varied

109 accordingly. Band fitting was done using a Gauss-Lorentz, cross-product function

110 with the minimum number of component bands used for the fitting process. The

111 Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was

112 undertaken until reproducible results were obtained with squared correlations (r^2)

113 greater than 0.995.

114

115

116 **RESULTS AND DISCUSSION**

117

118   Farmer [40] states that very little research has been undertaken on the vibrational

119 spectroscopy of selenates/selenites or tellurates/tellurites. No minerals with the

120 selenate ion SeO$_4^{2-}$ have been discovered and reported [41]. The tellurite ion should

121 show a maximum of six bands. The free ion will have C_{3v} symmetry and four modes,

122 $2A_1$ and $2E$. Farmer, based upon the work of Siebert [42,43], defines the spectrum of

123 (TeO$_3$)$^{2-}$ as ν_1 (A_1) 758 cm^{-1}, ν_2 (A_1) 364 cm^{-1}, ν_3 (E) 703 cm^{-1} and ν_4 (E) 326 cm^{-1} [40].

124 The comment may be made, that there is very little published on the vibrational

125 spectroscopy of tellurite and/or tellurate minerals, especially the Raman spectroscopy

126 of these minerals.

127

128   The Raman spectrum of teinite in the 500 to 900 cm^{-1} region is shown in Fig.

129 1. A broad spectral profile with Raman bands at 667, 701, 739 and 778 cm^{-1} are

130 found. The bands at 739 and 778 cm^{-1} are assigned to the ν_1 (TeO$_3$)$^{2-}$ symmetric

131 stretching mode. The Raman bands at 667 and 701 cm^{-1} are attributed to the the ν_3

132 (TeO$_3$)$^{2-}$ antisymmetric stretching mode. The Raman spectrum of the graemite

133 sample is shown in Fig. 2. The Raman spectra of the two minerals are very similar

134 which is not unexpected since the mineral graemite is a partically dehydrated teineite.

135 The two Raman bands at 768 and 793 cm^{-1} are assigned to the ν_1 $(TeO_3)^{2-}$ symmetric

136 stretching mode and the two bands at 676 and 708 cm^{-1} are attributed to the ν_3

137 $(TeO_3)^{2-}$ antisymmetric stretching mode.

138

139   A comparison may be made with other tellurite containing minerals such as rajite,

140 denningite, zemmanite and emmonsite. Two Raman bands for rajite, observed at 754

141 and 731 cm^{-1}, are assigned to the ν_1 $(Te_2O_5)^{2-}$ symmetric stretching mode. The two

142 bands at 652 and 603 cm^{-1} are assigned to the ν_3 $(Te_2O_5)^{2-}$ antisymmetric stretching

143 mode. An intense band observed at 734 cm^{-1} for denningite is attributed to the ν_1

144 $(Te_2O_5)^{2-}$ symmetric stretching mode. The Raman band of dennigite at 674 cm^{-1} is

145 assigned to the ν_3 $(Te_2O_5)^{2-}$ antisymmetric stretching mode. Two Raman bands for

146 zemannite are observed at 745 and 647 cm^{-1}. These bands are assigned to the ν_1

147 $(TeO_3)^{2-}$ symmetric stretching mode and the ν_3 $(TeO_3)^{2-}$ antisymmetric stretching

148 mode respectively. Two Raman bands, observed at 763 and 791 cm^{-1} for emmonsite,

149 are assigned to the ν_1 $(TeO_3)^{2-}$ symmetric stretching mode whilst the Raman bands

150 displayed at 679 and 567 cm^{-1} are assigned to ν_3 $(TeO_3)^{2-}$ antisymmetric stretching

151 mode.

152

153   The low wavenumber regions of the teineite and graemite spectra, 100 to 600

154 cm^{-1}, are shown in Fig. 3 and 4. This spectral region displays the bands which are

155 attributable to the $(TeO_3)^{2-}$ bending modes and water librational modes. The intense

156 band at 509 cm^{-1} with a shoulder at 504 cm^{-1} is assigned to water librational mode. In

157 the Raman spectrum of graemite there is an intense band at 507 cm^{-1} which is

158 assigned to the water librational mode. The two bands for teineite at 318 and 347 cm^{-1}

159 are assigned to the $(TeO_3)^{2-}$ ν_2 (A_1) bending mode and the two bands for teineite at

160 384 and 458 cm^{-1} are assigned to the $(TeO_3)^{2-}$ ν_4 (E) bending mode. In this spectral

161 region, the Raman spectrum of graemite appears to be different to that of teineite.

162 Two low intensity bands in the Raman spectrum of graemite at 314 and 358 cm^{-1} may

163 be assigned to the $(TeO_3)^{2-}$ ν_2 (A_1) bending mode. These bands are of very low

164 intensity. One posibilty is that the bands are due to teinite. The intense bands of

165 graemite at 411, 438 and 471 cm^{-1} may be assigned to the $(TeO_3)^{2-}$ ν_4 (E) bending

166 mode. The sharp Raman band for teineite at 235 cm^{-1} and the sharp bands for

167 graemite at 257 and 291 cm^{-1} may be attributed to the CuO stretching vibrations. A

168 comparison may be made with other tellurite containing minerals such as rajite,

169 denningite, zemmanite and emmonsite. Raman bands for rajite, observed at (346,

170 370) and 438 cm^{-1}, are assigned to the $(Te_2O_5)^{2-}$ ν_2 (A_1) bending mode and ν_4 (E)

171 bending modes. The very weak Raman bands of denningite at 450 and 479 cm^{-1} are

172 assigned to the $(Te_2O_5)^{2-}$ ν_4 (E) bending modes and the bands at 349 and 381 cm^{-1} are

173 assigned to the $(Te_2O_5)^{2-}$ ν_2 (A_1) bending modes. Raman bands are observed at 372

174 and 408 cm^{-1} for zemmanite and 397 and 414 cm^{-1} for emmonsite, which may be due

175 to the $(TeO_3)^{2-}$ ν_2 (A_1) bending mode.

176

177   The Raman spectrum of teineite in the 2100 to 3700 cm^{-1} region is displayed

178 in Fig. 5. Prominent bands are observed at 2286, 2854, 3040 and 3495 cm^{-1}. The

179 Raman bands are not symmetrical and additional components may be observed at

180 2641 and 3139 cm^{-1}. The band at 3495 cm^{-1} appears to be quite distinct and the

181 observation of multiple bands indicates that the water molecules in the teineite

182 structure are not equivalent. The band at 3495 cm^{-1} is very sharp may be well due to

183 OH units in the teineite structure. This band is not observed in the Raman spectrum

184 of graemite although a band component at 3450 cm^{-1} is observed. The bands listed

185 above are attributed to OH stretching vibrations; which are formed by the interaction

186 of the protons with the oxygen of the selenite units. Studies have shown a strong

187 correlation between OH stretching frequencies and both O$^{..}$O bond distances and

188 H$^{..}$O hydrogen bond distances [44-47]. Libowitzky showed that a regression function

189 can be employed relating the hydroxyl stretching frequencies with regression

190 coefficients better than 0.96 using infrared spectroscopy. The function is described

191 as: $\nu_1 = (3592 - 304) \times 109^{\frac{-d(O-O)}{0.1321}}$ cm^{-1}. Thus OH$^{..}$O hydrogen bond distances may be

192 calculated using the Libowitzky empirical function. The values for the OH stretching

193 vibrations listed above provide hydrogen bond distances of 2.544(9) Å (2286 cm^{-1}),

194 2.620(3) Å (2854 cm^{-1}), 2.658(7) Å (3040 cm^{-1}) and 2.988(4) Å (3495 cm^{-1}which are

195 very short, compared with that of many secondary minerals. Normally, large

196 hydrogen bond distances which are present in minerals such as perhamite, can also be

197 seen in other mixed anion minerals such as peisleyite, where the distances range

198 between 3.052(5) and 2.683(6) Å. Such hydrogen bond distances are typical of

199 secondary minerals. A range of hydrogen bond distances are observed from

200 reasonably strong to weak hydrogen bonding. This range of hydrogen bonding

201 contributes to the stability of the mineral. In the case of teineite, the proton-selenite

202 interactions contribute to its stability, as a tellurite mineral. In the Raman spectrum of

203 graemite, three Raman bands are observed at 2937, 3268 and 3450 cm^{-1}. These values

204 give rise to hydrogen bond calculations of 2.636(1), 2.729 (1) and 2.838 (0) Å. The

205 values of the hydrogen bond distances are similar to that found for teineite and are

206 also of a similar magnitude.

207

208

209 **CONCLUSIONS**

210

211 The Raman spectra of the hydrated tellurite minerals teineite, $Cu(TeO_3).2H_2O$, and

212 graemite, $Cu(TeO_3)'H_2O$, have been studied using Raman spectroscopy. Observed

213 bands were assigned to the stretching and bending vibrations of the tellurite anion,

214 $(TeO_3)^{2-}$, hydroxyl and water units in the teineite and graemite structures. A

215 comparison of the Raman spectra of the minerals ,which are hydrated hydroxy

216 tellurite minerals, with the Raman spectra of other tellurite minerals has been made.

217

218 Raman bands for teineite at 739 and 778 cm^{-1} and for for graemite at 768 and 793

219 cm^{-1} are assigned to the ν_1 $(TeO_3)^{2-}$ symmetric stretching mode, whilst bands at 667

220 and 701 cm^{-1} for teineite and at 676 and 708 cm^{-1} for graemite are attributed to the the

221 ν_3 $(TeO_3)^{2-}$ antisymmetric stretching mode. The intense Raman band at 509 cm^{-1} for

222 both teineite and graemite is assigned to the water librational mode. Raman bands for

223 teineite at 318 and 347 cm^{-1} are assigned to the $(TeO_3)^{2-}$ ν_2 (A_1) bending mode and the

224 two bands for teineite at 384 and 458 cm^{-1} may be assigned to the $(TeO_3)^{2-}$ ν_4 (E)

225 bending mode. Prominent Raman bands, observed at 2286, 2854, 3040 and 3495 cm^{-}

226 ^{1} are attributed to OH stretching vibrations providing hydrogen bond distances of

227 2.550(6) Å (2341 cm^{-1}), 2.610(3) Å (2796 cm^{-1}) and 2.623(2) Å (2870 cm^{-1}) which are

228 comparatively short for secondary minerals.

229

230

231 **Acknowledgements**

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240   **References**

241

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309
310

311   *List of* **Figs**

312

313   **Fig. 1 Raman spectrum of teineite in the 600 to 900 cm^{-1} region**

314

315   **Fig. 2 Raman spectrum of graemite in the 600 to 900 cm^{-1} region**

316

317   **Fig. 3 Raman spectrum of teineite in the 100 to 600 cm^{-1} region**

318

319   **Fig. 4 Raman spectrum of graemite in the 100 to 600 cm^{-1} region**

320

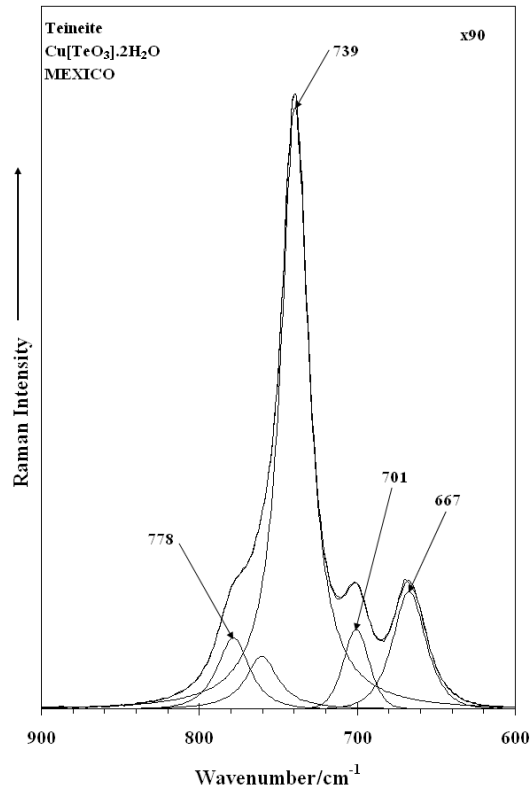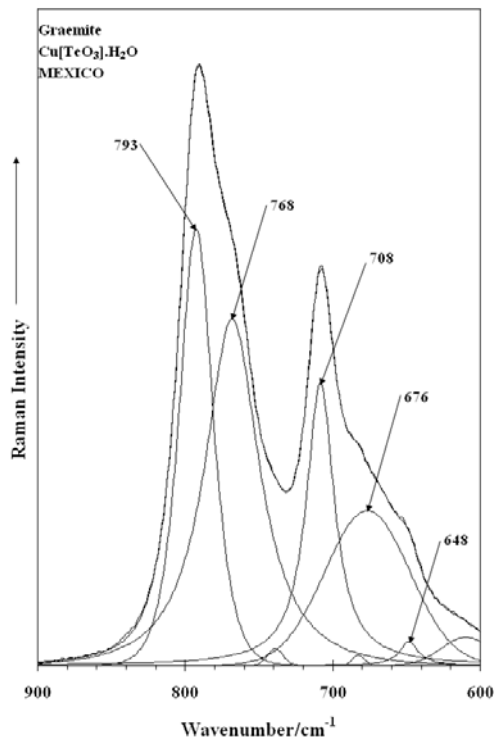321   **Fig. 5 Raman spectrum of teineite in the 2100 to 3700 cm^{-1} region**

322

323   **Fig. 6 Raman spectrum of graemite in the 2500 to 3700 cm^{-1} region**

324

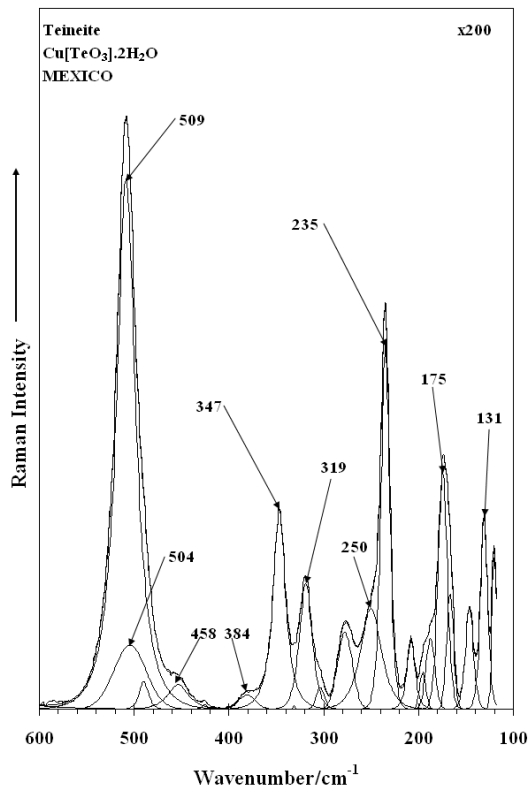325

326

327

Fig. 1 teinite

329

330

Graemite
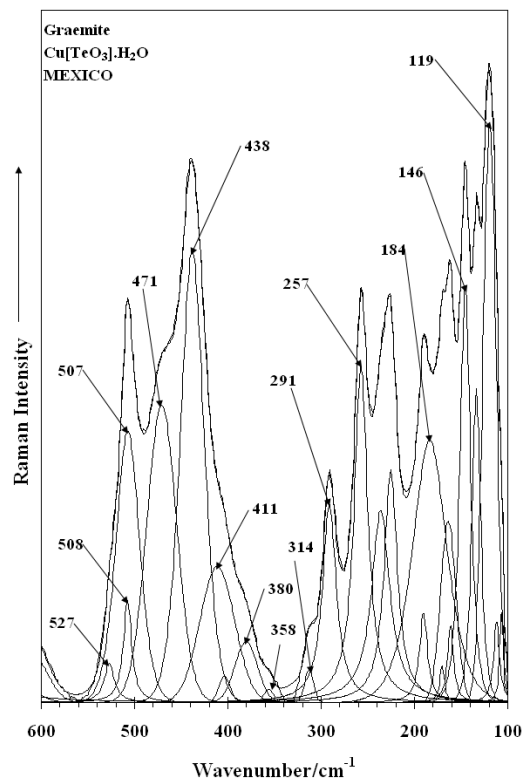$Cu[TeO_3] \cdot H_2O$
MEXICO

331

332

333 **Fig. 2**

Teineite
$Cu[TeO_3].2H_2O$
MEXICO
x200

334

335

336   **Fig. 3**

337

14

338

Fig. 4

339
340
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342
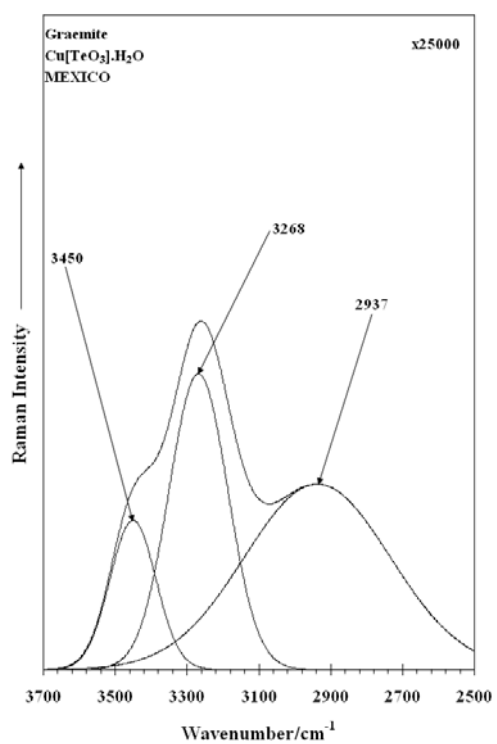343
344

Teineite
Cu[TeO$_3$].2H$_2$O
MEXICO

x2200

345

346

347   **Fig. 5**

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16

349

350

351 **Fig. 6**