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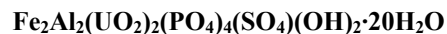
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1 **The application of Raman spectroscopy to the study of the uranyl mineral coconinoite**



3
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5
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7 Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

8
9 ^b National Museum, Václavské náměstí 68, CZ-115 79 Praha 1, Czech Republic.

10
11 **ABSTRACT**

12
13 Raman spectra of the uranyl containing mineral coconinoite,
14 $\text{Fe}_2\text{Al}_2(\text{UO}_2)_2(\text{PO}_4)_4(\text{SO}_4)(\text{OH})_2 \cdot 20\text{H}_2\text{O}$, are presented and compared with the mineral's
15 infrared spectra. Bands connected with $(\text{UO}_2)^{2+}$, $(\text{PO}_4)^{3-}$, $(\text{SO}_4)^{2-}$, $(\text{OH})^-$ and H_2O stretching
16 and bending vibrations, are assigned. Approximate U-O bond lengths in uranyl, $(\text{UO}_2)^{2+}$, and
17 O-H...O hydrogen bond lengths are calculated from the wavenumbers of the U-O stretching
18 vibrations and $(\text{OH})^-$ and H_2O stretching vibrations, respectively, and compared with
19 published data for similar natural and synthetic compounds.

20
21 **KEYWORDS:** coconinoite, mineral, uranyl, phosphate, sulphate, hydroxyl, water molecules,
22 Raman spectroscopy, infrared spectroscopy

23
24

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25 Introduction

26

27 The mineral coconinoite $\text{Fe}_2\text{Al}_2(\text{UO}_2)_2(\text{PO}_4)_4(\text{SO}_4)(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ [1] is a uranium
 28 bearing mineral with phosphate and sulphate in the structure [2-4]. The mineral is an unusual
 29 mineral as it contains so many cations and anions in its structure. The mineral may be
 30 categorised as a uranyl phosphate and is named after the place of its discovery namely
 31 Coconino in Arizona. The mineral is of monoclinic symmetry with unit-cell parameters $a =$
 32 12.45 ± 0.06 , $b = 12.96 \pm 0.3$, $c = 17.22 \pm 0.05 \text{ \AA}$, $\beta = 105.7^\circ$, space group $C2/c$ [2, 5]

33 . The mineral shows lamellar properties and occurs as platy grains or lathlike
 34 aggregates [4]. The mineral occurs in the oxidised zone of vanadium-poor uranium-
 35 vanadium deposits as are found in Utah and Arizona, USA [1]. The mineral is related to
 36 other uranyl aluminophosphate minerals including furongite, moreauite, and xiangjiangite
 37 [2]. Not approved Al analogues of coconinoite have been mentioned –

38 $\text{Al}_4(\text{UO}_2)_2(\text{PO}_4)_4(\text{SO}_4)(\text{OH})_2 \cdot 18\text{H}_2\text{O}$ from the Kyzylkum uranium-vanadium deposit
 39 (Uzbekistan) [2, 5-7], and an unnamed Al-equivalent of coconinoite

40 $\text{Al}_4(\text{UO}_2)_2(\text{PO}_4)(\text{SO}_4)(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ from the La Creusat uranium prospect (Valais,
 41 Switzerland) [8]. The chemistry of xiangjiangite, $(\text{Fe}^{3+}, \text{Al})(\text{UO}_2)_4(\text{PO}_4)_2(\text{SO}_4)_2(\text{OH}) \cdot 22\text{H}_2\text{O}$,
 42 is similar to that of coconinoite [1]. The infrared spectrum of xiangjiangite is essentially
 43 similar to that of torbernite, autunite, and furongite [9]. Five strong absorption bands at 264,
 44 923, 1044, 1617 and 3390 cm^{-1} , three medium to strong absorption bands at 468, 534, and
 45 613 cm^{-1} , weak absorption bands at 795, 845, 1400 and 1720 cm^{-1} and shoulders at 1163
 46 3520 cm^{-1} were observed in the infrared spectrum of xiangjiangite and assigned to stretching
 47 and bending vibrations of $(\text{PO}_4)^{3-}$, $(\text{SO}_4)^{2-}$, $(\text{UO}_2)^{2+}$, $(\text{OH})^-$ and water molecules [10]. The
 48 comparable interpreted infrared spectrum of furongite, which does not contain any sulphate
 49 anions, was characterized by the absorption bands at 470, 540, 810, 912, 1055, 1635 and
 50 3400 cm^{-1} and attributed to the stretching and bending vibrations of $(\text{PO}_4)^{3-}$, $(\text{UO}_2)^{2+}$, $(\text{OH})^-$
 51 and water molecules [11]. Neither X-ray single-crystal structure data, nor infrared and Raman
 52 spectra of coconinoite are available. An abstract of crystal structure of furongite [12] and a
 53 comparison of furongite from Kobokobo (Kivu, Zaire) and from Furong, China were
 54 published [5-7, 13]. Some other uranyl aluminophosphate minerals were described and
 55 approved [1, 14-16] some were synthesized [17]. Visible-near infrared spectrum of
 56 coconinoite has been discussed [18]. Raman and infrared spectra of this coconinoite mineral
 57 has not been reported or analysed. Such work is important in the undersading of the
 58 structure of uranyl containing minerals. The identification of coconinoite sample (RRUFF

59 database, R060952) is not yet confirmed and its Raman spectrum (presented as usually
60 without any interpretation) cannot be therefore used for discussion.

61
62

63 Raman spectroscopy has proven most useful for the study of diagenetically related
64 minerals as often occurs with minerals containing uranyl groups. Raman spectroscopy is
65 especially useful when the minerals are X-ray non-diffracting or poorly diffracting as can
66 occur for many uranyl containing minerals. This paper is a part of systematic studies of
67 vibrational spectra of minerals of secondary origin in the oxide supergene zone. In this work
68 bands at various wavenumbers are attributed to vibrational modes of coconinoite using
69 Raman spectroscopy complimented with infrared spectroscopy and we relate the spectra to
70 the structure of the mineral.

71

72 **Experimental**

73

74 **Mineral**

75 The mineral coconinoite samples were supplied by The Mineralogical Research
76 Company. The structure and composition of the mineral sample were confirmed by X-ray
77 powder diffraction and by electron probe analysis.

78

79 **Raman spectroscopy**

80

81 Crystals of coconinoite were placed on a polished metal surface on the stage of an
82 Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The
83 microscope is part of a Renishaw 1000 Raman microscope system, which also includes a
84 monochromator, a filter system and a CCD detector (1024 pixels). The mineral was excited
85 by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and
86 collected at a nominal resolution of 2 cm^{-1} and a precision of $\pm 1\text{ cm}^{-1}$ in the range between
87 100 and 4000 cm^{-1} . Repeated acquisition on the crystals using the highest magnification (50x)
88 were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated
89 using the 520.5 cm^{-1} line of a silicon wafer. 64 scans were collected at 30 second time
90 intervals.

91

92 Infrared spectroscopy

93

94 Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a
 95 smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm⁻¹ range
 96 were obtained by the co-addition of 64 scans with a resolution of 4 cm⁻¹ and a mirror velocity
 97 of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio. It is noted that no
 98 spectra were obtained below 525 cm⁻¹ as the cell absorbs all radiation below this
 99 wavenumber.

100

101 Band component analysis of both the Raman and infrared spectra was undertaken
 102 using the Jandel ‘Peakfit’ (Erkrath, Germany) software package which enabled the type of
 103 fitting function to be selected and allowed specific parameters to be fixed or varied
 104 accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the
 105 minimum number of component bands used for the fitting process. The Lorentz-Gauss ratio
 106 was maintained at values greater than 0.7 and fitting was undertaken until reproducible
 107 results were obtained with squared correlations (r^2) greater than 0.995. Band fitting of the
 108 spectra is quite reliable providing there is some band separation or changes in the spectral
 109 profile.

110

111 RESULTS and DISCUSSION

112

113 The mineral coconinoite is an interesting mineral because it contains five different
 114 vibrating units. These are the uranyl cation, (UO₂)²⁺, phosphate, (PO₄)³⁻, sulphate, (SO₄)²⁻,
 115 and hydroxyl, (OH)⁻ anions and water molecules [19-21][26-28]. The formula of the mineral
 116 coconinoite is given by Fe₂Al₂(UO₂)₂(PO₄)₄(SO₄) (OH)₂·20H₂O. Thus the spectroscopy of
 117 this mineral coconinoite will be made up of the spectroscopy of the subunits. The D_{∞h}
 118 symmetry of the free uranyl, (UO₂)²⁺, and T_d symmetry of the (PO₄)³⁻ and (SO₄)²⁻ groups are
 119 lowered causing infrared and Raman activation of all (UO₂)²⁺, (SO₄)²⁻ and (PO₄)³⁻ vibrations
 120 and splitting of doubly and triply degenerate vibrations in the spectra of coconinoite. The
 121 factor group analysis of the uranyl, phosphate and water units are given in Tables S1-4
 122 respectively.

123 The irreducible representation is given by $\Gamma = 24A_u + 26A_g$. According to Hawthorne [22-
 124 24][29-31] from the general point of view, and the conclusions by Burns concerning uranium

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125 minerals, hydrogen bonding is of fundamental importance to the stability of the structure of
 126 minerals. Burns [\[25\]\[32\]](#) and Burns *et al.* [\[26, 27\]\[33, 34\]](#) also proposed hydrogen bonding
 127 network in the crystal structures on the basis of crystal-chemical and bond-valence
 128 parameters arguments. This may be applied also to coconinoite. Thus possible assignment of
 129 the bands observed is therefore made with regard to all these assumptions.

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130
 131 The Raman spectrum of coconinoite in the 100 to 1200 cm^{-1} range is provided
 132 in Fig. 1. The complete spectrum is subdivided into sections for convenience based upon the
 133 type of vibrating unit. The Raman spectrum of coconinoite in the 750 to 1150 cm^{-1} range is
 134 provided in Fig. 2. This spectral region is where the symmetric stretching vibrations of the
 135 oxyanions are observed. Two distinct sets of bands are observed. The first set is observed at
 136 826, 837 and 847 cm^{-1} . Based upon empirical calculations, it was estimated that the bands
 137 between 800 and 850 cm^{-1} are assignable to the ν_1 symmetric stretching mode of $(\text{UO}_2)^{2+}$
 138 units [\[28\]\[35\]](#). The spectral profile centered upon 842 cm^{-1} is strongly asymmetric on the low
 139 wavenumber side of the band and thus three bands may be resolved. This data provides
 140 evidence for the non-equivalence of the uranyl units in the coconinoite structure. Low
 141 intensity bands are observed at 783 and 832 cm^{-1} in the infrared spectrum (Fig. 3). These may
 142 be also attributed to the ν_1 $(\text{UO}_2)^{2+}$; however, the infrared band at 783 cm^{-1} may be connected
 143 with the libration mode of water molecules and/or δ M^{3+} -OH bending vibration. The spectral
 144 profile of the infrared spectrum is very complex with many overlapping band components.
 145 Approximate U-O bond lengths in uranyl, $(\text{UO}_2)^{2+}$, inferred from the wavenumbers of the ν_1
 146 $(\text{UO}_2)^{2+}$ symmetric stretching vibration observed in the Raman and infrared spectra, are
 147 ($\text{\AA}/\text{cm}^{-1}$) [\[29\]\[36\]](#): 1.77/847, 1.77/837, 1.79/826 (Raman); 1.78/832, 1.83/783 (infrared). They
 148 are close to ~ 1.8 \AA as presented by Burns [\[15, 30-32\]\[15, 37-39\]](#) for synthetic and natural
 149 uranyl compounds on the basis of their X-ray single crystal structure analysis.

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150
 151 In the second set of the Raman bands, peaks are found at 985, 998, 1020, 1044, 1085 and
 152 1103 cm^{-1} . The first two bands at 985 and 998 cm^{-1} are assigned to the ν_1 symmetric
 153 stretching modes of the $(\text{PO}_4)^{3-}$ units. In the structure of the mineral, the symmetry of the
 154 phosphate units is reduced. This means the infrared bands of the symmetric stretching mode
 155 will become activated and will be observed in the infrared spectrum. The observation of two
 156 phosphate stretching modes in the Raman spectrum gives credence to two non-equivalent
 157 phosphate units in the coconinoite mineral structure. In the infrared spectrum, bands are

158 observed at 929, 959, 981 and 1002 cm^{-1} . The two infrared bands at 959, 981 cm^{-1} are
 159 assigned to the infrared active ν_1 symmetric stretching modes of $(\text{PO}_4)^{3-}$ units and that at 929
 160 cm^{-1} to the ν_3 $(\text{UO}_2)^{2+}$ antisymmetric stretching band. U-O bond length in uranyl, $(\text{UO}_2)^{2+}$,
 161 inferred from this wavenumber (1.76 Å) [29][36] is also in agreement with that proposed for
 162 such uranyl compounds by Burns [15, 31, 32][15, 38, 39]. The set of infrared bands are in
 163 harmony with the Raman bands. No Raman band which could be assigned to the ν_3 $(\text{UO}_2)^{2+}$
 164 antisymmetric stretching vibration was observed. The only possibility is that at 974 cm^{-1} , but
 165 the calculated U-O bond length (1.73 Å) is relatively too low when compared with ~ 1.8 Å
 166 according to Burns [15, 31, 32][15, 38, 39]. The Raman band at 1020 cm^{-1} is also very sharp
 167 and may be attributed to the ν_1 symmetric stretching modes of the $(\text{SO}_4)^{2-}$ anions. In the
 168 infrared spectrum the sharp infrared band at 1002 cm^{-1} may be assigned to the ν_1 symmetric
 169 stretching modes of the $(\text{SO}_4)^{2-}$ units. The low intensity Raman bands at 1044, 1085 and 1103
 170 cm^{-1} are assigned to the split triply degenerate ν_3 antisymmetric stretching modes of the
 171 $(\text{PO}_4)^{3-}$ and $(\text{SO}_4)^{2-}$ units. In the infrared spectrum, bands are resolved at 1071, 1112, 1142
 172 and 1173 cm^{-1} . These bands are attributed to the overlap of the split triply degenerate ν_3
 173 antisymmetric stretching modes of the $(\text{PO}_4)^{3-}$ and $(\text{SO}_4)^{2-}$ units.

174
 175 The Raman spectrum of coconinoite in the 300 to 700 cm^{-1} region is reported in Fig.
 176 4. This spectral region is where the oxyanion bending modes are observed. The bending
 177 modes of the uranyl units occur at much lower wavenumbers. Ross [33][40] investigated the
 178 infrared spectra of selected sulphate minerals, and reported the split triply degenerate ν_4
 179 $(\text{SO}_4)^{2-}$ bending modes at 595, 618 and 680 cm^{-1} . Thus the two Raman bands at 620 and 637
 180 cm^{-1} are assigned to this vibration. In the infrared spectrum of coconinoite (Fig. 5) a complex
 181 spectral profile in the 550 to 700 cm^{-1} is observed. Infrared bands are observed at 608, 615,
 182 625, 635 and 647 cm^{-1} . It is likely that these bands are assignable to the ν_4 $(\text{SO}_4)^{2-}$ bending
 183 modes. The Raman bands at 492 and 551 cm^{-1} are assigned to the split triply degenerate ν_4
 184 $(\text{PO}_4)^{3-}$ bending modes. This splitting is a function of the site and symmetric splitting. A
 185 sharp band in the infrared spectrum at 578 cm^{-1} is attributed to this vibrational mode. The
 186 Raman bands at 409 and 447 cm^{-1} are attributed to the split doubly degenerate ν_2 $(\text{SO}_4)^{2-}$
 187 bending modes. It is possible that the two Raman bands at 320 and 377 cm^{-1} are assignable
 188 to the split doubly degenerate ν_2 $(\text{PO}_4)^{3-}$ bending modes. Alternatively the Raman band at
 189 320 cm^{-1} may be assigned to the ν_2 (δ) $(\text{UO}_2)^{2+}$ bending vibration. The Raman spectrum in

190 the 75 to 275 cm^{-1} region is shown in Fig. 6. Raman bands are observed at 110, 147, 181,
191 210 and 229 cm^{-1} . These bands are assigned to lattice vibrations.

192
193 The infrared spectrum of coconinoite in the 1400 to 1800 cm^{-1} region is displayed in Fig. 7.
194 The spectrum shows a broad peak centred upon 1636 cm^{-1} with shoulders at 1573 and 1700
195 cm^{-1} . The central peak at 1636 cm^{-1} is assigned to the water δ bending modes. The band at
196 1573 cm^{-1} may be associated with $\delta \text{M}^{3+}\text{-OH}$ bending modes. The infrared spectrum of
197 coconinoite in the 2400 to 3800 cm^{-1} is displayed in Fig. 8. The spectrum is complex with
198 many overlapping bands. The two higher wavenumber bands at 3514 and 3572 cm^{-1} are
199 assigned to the OH stretching vibrations of the free or only weakly hydrogen bonded
200 hydroxyl units. The remaining bands are attributed to the stretching vibrations of hydrogen
201 bonded water molecules; however, bands at 2868, 2887 and 2985 cm^{-1} are probably caused
202 by organic impurities.

203
204 The position of the bands suggests that significant hydrogen bonding exists in the coconinoite
205 structure. It is inferred that there is more than one distinct water molecule in the unit cell.

206 These water molecules may not necessarily be explicitly symmetrically distinct but there is
207 the possibility that the two water molecules are not equivalent. If we use a Libowitzky type
208 empirical equation [34][41], and we assume that we can use infrared data in the equation,
209 estimates of the hydrogen bond distances can be obtained.

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210 The values for the OH stretching vibrations for the OH units give calculated approximate O-
211 H...O hydrogen bond lengths of 2.92 and 3.1 Å. These values suggest that the hydroxyl units
212 are only weakly hydrogen bonding to the adjacent sulphate or phosphate units as mentioned.

213 The approximate O-H...O hydrogen bond lengths calculated for the water stretching
214 vibrations are 2.7 Å (3182 cm^{-1}) and 2.8 Å (3393 cm^{-1}) [35][42]. Thus water molecules with
215 different hydrogen bond distances are found in the coconinoite structure. These results
216 suggest that the water molecules are involved in hydrogen bonding to varying strengths
217 according to their position in the coconinoite structure. Further the water is significantly
218 more strongly hydrogen bonded than the OH units.

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219
220 **Conclusions**

221

222 Coconinoite $\text{Fe}_2\text{Al}_2(\text{UO}_2)_2(\text{PO}_4)_4(\text{SO}_4)(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ is a secondary uranyl mineral, known for
223 many years, containing $(\text{UO}_2)^{2+}$, $(\text{SO}_4)^{2-}$, $(\text{PO}_4)^{3-}$, OH^- units and molecular water. Its X-ray
224 single-crystal structure is not known. However, this paper proves that Raman spectroscopy
225 corroborates and extends knowledge of such natural phases. Observed bands are assigned to
226 the vibrations of $(\text{UO}_2)^{2+}$, $(\text{SO}_4)^{2-}$, $(\text{PO}_4)^{3-}$, OH^- units and water molecules. Some
227 coincidences of bands in the region of the stretching and bending vibrations of these units
228 cannot be excluded. Approximate U-O bond lengths in uranyl, $(\text{UO}_2)^{2+}$, were calculated from
229 the wavenumbers of the ν_1 and ν_3 $(\text{UO}_2)^{2+}$ stretching vibrations. They are close and
230 comparable to the U-O lengths in known uranyl natural and synthetic compounds [15]. O-
231 H...O hydrogen bond lengths were inferred from the wavenumbers of infrared bands assigned
232 to the stretching vibrations of hydroxyl ions and water molecules.

233

234 **Acknowledgements**

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238

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294

295 **List of Figs.**

296

297 **Fig. 1** Raman spectrum of coconinoite in the 100 to 1200 cm^{-1} region

298

299 Fig. 2 Raman spectrum of coconinoite in the 750 to 1150 cm^{-1} region.

300

301 Fig. 3 Infrared spectrum of coconinoite in the 750 to 1250 cm^{-1} region.

302

303 Fig. 4 Raman spectrum of coconinoite in the 300 to 700 cm^{-1} region.

304

305 Fig. 5 Infrared spectrum of coconinoite in the 500 to 750 cm^{-1} region.

306

307 Fig. 6 Raman spectrum of coconinoite in the 75 to 275 cm^{-1} region.

308

309 Fig. 7 Infrared spectrum of coconinoite in the 1400 to 1800 cm^{-1} region.

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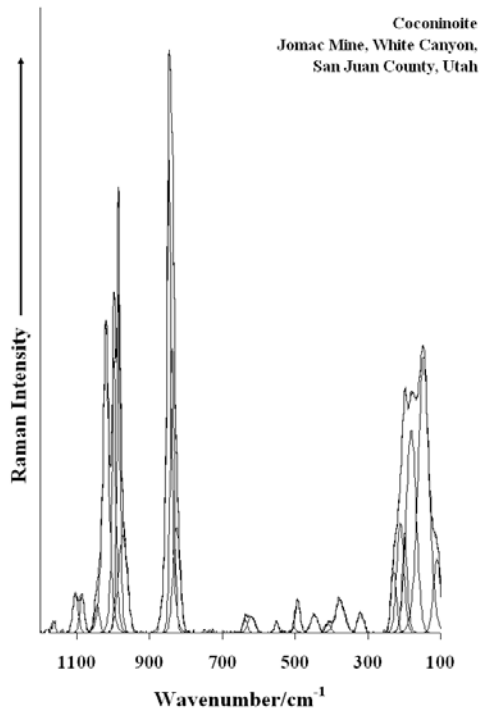
311 Fig. 8 Infrared spectrum of coconinoite in the 2400 to 3800 cm^{-1} region.

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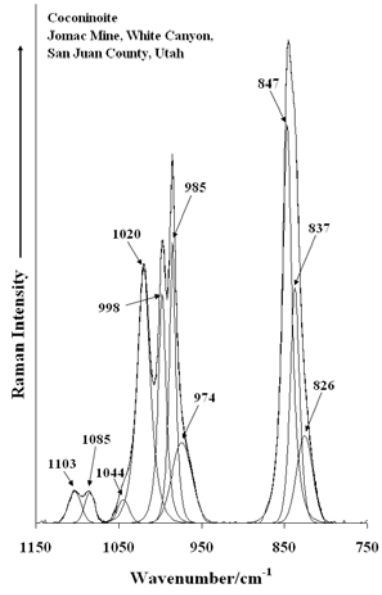
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318 Fig. 1



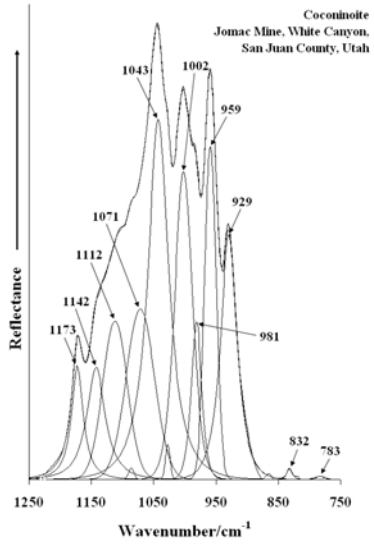
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321 **Fig. 2**

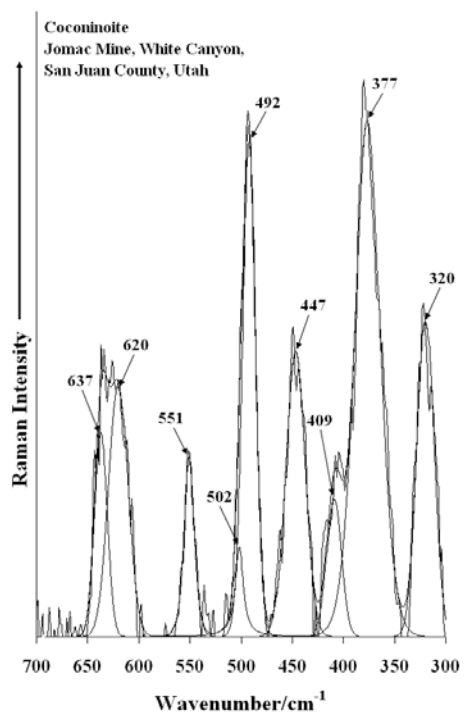
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325 **Fig. 3**



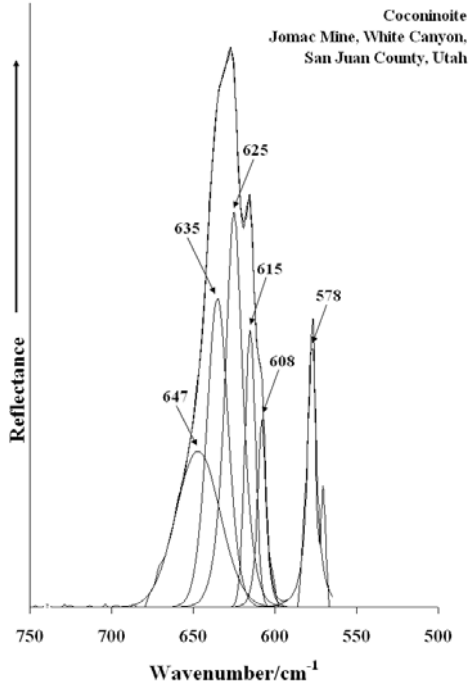
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328 **Fig. 4**

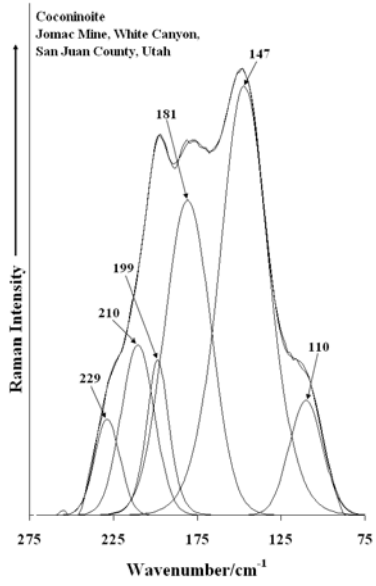
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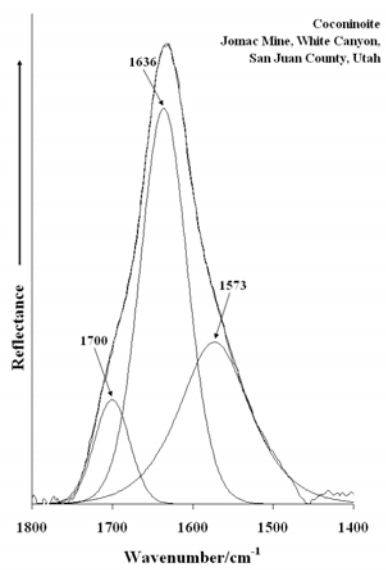
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Fig. 5



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Fig. 6



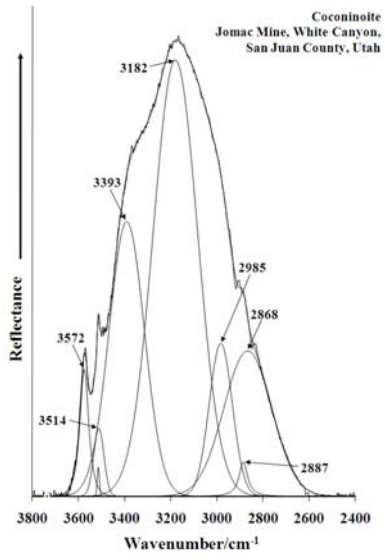
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343 **Fig. 7**

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348 | **Fig. 8**

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