

QUT Digital Repository:
<http://eprints.qut.edu.au/>



This is the accepted version of the following journal article:

[Frost, Ray L.](#) & [Palmer, Sara J.](#) (2011) Raman spectroscopic study of pascoite $\text{Ca}_3\text{V}_10\text{O}_{28}\cdot 17\text{H}_2\text{O}$. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 78(1), pp. 248-252.

© Copyright 2010 Elsevier B.V. All rights reserved.

Raman spectroscopic study of pascoite $\text{Ca}_3\text{V}_{10}\text{O}_{28}\cdot 17\text{H}_2\text{O}$

Ray L. Frost* and Sara J. Palmer

Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Abstract

Raman spectroscopy has been used to study the molecular structure of the vanadate mineral pascoite. Pascoite, rauvite and huemulite are examples of simple salts involving the decavanadate anion $(\text{V}_{10}\text{O}_{28})^{6-}$. Decavanadate consists of four distinct VO_6 units which are reflected in Raman bands occurring at higher wavenumbers. The Raman spectrum of pascoite is characterised by two intense bands at 991 and 965 cm^{-1} . Raman bands are observed at 991, 965, 958 and 905 cm^{-1} and originate from four distinct VO_6 sites in the mineral structure. In the infrared spectra of pascoite, two wavenumber regions are observed between: 1) 837 and 860, and 2) between 803 and 833 cm^{-1} . These bands are assigned to ν_3 antisymmetric stretching modes of $(\text{V}_{10}\text{O}_{28})^{6-}$ or $(\text{V}_5\text{O}_{14})^{3-}$ units. The spectrum is highly complex in the lower wavenumber region, and therefore the assignment of bands is difficult. Bands observed in the 404 to 458 cm^{-1} region are assigned to the ν_2 bending modes of $(\text{V}_{10}\text{O}_{28})^{6-}$ or $(\text{V}_5\text{O}_{14})^{3-}$ units. Raman bands observed in the 530 to 620 cm^{-1} region are assigned to the ν_4 bending modes of $(\text{V}_{10}\text{O}_{28})^{6-}$ or $(\text{V}_5\text{O}_{14})^{3-}$ units. The Raman spectra of the vanadates in the low wavenumber region are complex with multiple overlapping bands which are probably due to VO subunits and MO bonds.

KEYWORDS: pascoite, huemulite, barnesite, hewettite, meta-hewettite, hummerite, vanadates, Raman spectroscopy, infrared spectroscopy

* Author for correspondence (r.frost@qut.edu.au)

30 INTRODUCTION

31
32 Pascoite is a hydrated calcium vanadate and is named after its place of origin Pasco,
33 Peru. The mineral is based upon the decavanadate polyanion [1]. Linking these
34 decavanadate anions gives the unit cationic group $(\text{Ca}_3(\text{H}_2\text{O})_{17})^{6+}$. A picture of the
35 studied mineral is given in Fig. S1 (Supplementary Information). Vanadium in
36 minerals represents the most complicated of systems because of the variable oxidation
37 state of vanadium, as it relates to mineral species and their crystallisation from
38 solution [2-4]. This complication is exacerbated by the range of oxidation states in the
39 natural environment, including the supergene zone. These include V(III), V(IV),
40 V(V). In aqueous V(V) solutions at low concentrations, only mononuclear species are
41 present, VO_2^+ , $\text{VO}(\text{OH})_3$, $\text{VO}_2(\text{OH})_2^-$, $\text{VO}_3\text{OH}^{2-}$ and VO_4^{3-} . In contrast to this, at
42 higher total V(V) concentrations under acid conditions extensive polymerisation of
43 vanadate occurs according to the following equations.



48
49
50 Protonated analogues are also present in solution. The pyrovanadates, metavanadates
51 and decavanadates are all expressed in a number of mineral structures.

52 Metavanadates, in the solid state, consist of infinite chains of VO_3^- composition,
53 $(\text{VO}_3^-)_n$. The chemistry of polymerisation of vanadate in acidic solution is well
54 understood and is reflected in many examples in the mineral kingdom. Depending
55 upon the prevailing redox potential in solution, from which such species crystallise,
56 highly coloured, mixed V(IV,V) species are formed, are called vanadium bronzes.
57 Polymerisation of V(V) as $(\text{VO}_4)^{3-}$, in more concentrated solutions, gives rise to three
58 types of complex anions. If the pH is between 9 and 13, pyrovanadates $[(\text{V}_2\text{O}_7)^{4-}$,
59 $(\text{HV}_2\text{O}_7)^{3-}, (\text{H}_2\text{V}_2\text{O}_7)^{2-}]$ are formed, in the pH range 5 to 9 metavanadates $[(\text{V}_3\text{O}_9)^{3-}$,
60 $(\text{V}_4\text{O}_{12})^{4-}, (\text{H}_2\text{V}_3\text{O}_{10})^{3-}, (\text{HV}_3\text{O}_{10})^{4-}, (\text{V}_5\text{O}_{15})^{5-},]$ are predominantly formed, and as
61 solutions become more acidic decavanadates $[(\text{V}_{10}\text{O}_{28})^{6-}]$ are formed.

63 As part of our on-going studies of the vibrational spectroscopy of minerals
64 particularly secondary minerals, we report the Raman of the vanadium containing
65 mineral pascoite. The Raman spectra of pascoite are studied and compared with the
66 Raman spectrum of pascoite from the RRUFF data base, where it has been published
67 without any interpretation. The Raman spectra are related to the molecular structure of
68 the mineral pascoite. It is necessary to get a full understanding of this mineral as it is a
69 secondary mineral occurring as a leachate of near-surface vanadium oxides by ground
70 waters and as efflorescences in mine tunnels.

71

72 **EXPERIMENTAL**

73 ***Minerals***

74

75 The pascoite $\text{Ca}_3\text{V}_{10}\text{O}_{28}\cdot 17\text{H}_2\text{O}$ was obtained by one of the authors (AVC) and
76 originated from the Vanadium Queen Mine, San Juan County, Utah, USA. For
77 comparison, a Raman spectrum of pascoite was also downloaded from the RRUFF
78 mineral data base. This mineral originated from Arrowhead Claim, Slick Rock, San
79 Miguel County, Colorado, USA. The spectra from the RRUFF data base is provided
80 in the supplementary information

81

82 ***Raman spectroscopy***

83

84 The crystals of pascoite were placed and orientated on the stage of an Olympus
85 BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw
86 1000 Raman microscope system, which also includes a monochromator, a filter
87 system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe
88 laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} .
89 Repeated acquisition using the highest magnification was accumulated to improve the
90 signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon
91 wafer. In order to ensure that the correct spectra are obtained, the incident excitation
92 radiation was scrambled. Spectra at controlled temperatures were obtained using a
93 Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).
94 Spectral manipulation such as baseline adjustment, smoothing and normalisation was

95 performed using the GRAMS® software package (Galactic Industries Corporation,
96 Salem, NH, USA).

97

98 **Infrared absorption spectroscopy**

99 Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a
100 smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm⁻¹
101 range were obtained by the co-addition of 64 scans with a resolution of 4 cm⁻¹ and a
102 mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise
103 ratio. The minerals were used as is. No sample preparation was involved.

104

105 **RESULTS AND DISCUSSION**

106

107 **Background**

108

109 The infrared spectra of selected minerals containing pentavalent vanadium have been
110 published by Farmer [5]. There are four vibrations for (VO₄)³⁻, namely the A₁
111 symmetric stretching mode observed at around 824 cm⁻¹, the E bending mode in the
112 region between 305 and 345 cm⁻¹, the F₂ antisymmetric stretching mode between 780
113 and 855 cm⁻¹ and the F₂ bending mode between 340 and 345 cm⁻¹. The F₂ modes are
114 both Raman and infrared active whereas the A₁ and E modes are Raman active only.
115 Farmer reported the infrared spectrum of the vanadium containing mineral pucherite.
116 Frost *et al.* Provided the Raman spectra of pucherite, clinobisvanite, and namibite [6]
117 and have also undertaken studies of uranyl vanadates [7] including carnotite,
118 curienite, francevillite, tyuyamunite and metatyuyamunite. The minerals are
119 characterized by an intense band in the 800-824 cm⁻¹ region, assigned to the ν₁
120 symmetric stretching vibrations of the (UO₂)²⁺ units. Frederickson and Hausen made
121 infrared spectra-structure correlation study of compounds containing vanadium and
122 oxygen [8]. Among the compounds studied were the polyvanadates hummerite,
123 metahewettite and pascoite. These authors stated that these minerals are the
124 decavanadates and can be distinguished from the hexavanadates by having only one
125 intense band in the infrared spectrum attributed to the V-O stretch near 975 cm⁻¹, as
126 opposed to two bands for the hexavalent vanadates[8]. Recently Frost *et al.* reported
127 the vibrational spectroscopy of simple vanadate containing minerals [9, 10]. The

128 Raman band at 844 cm^{-1} , assigned to the ν_1 symmetric (VO_4^-) stretching mode for
129 descloizite, is shifted to 814 cm^{-1} for mottramite. The ν_3 mode of descloizite is
130 observed as a single band at 777 cm^{-1} but this mode is more complex for mottramite
131 with three bands observed in the 77K spectrum at 811 , 785 and 767 cm^{-1} . The
132 bending mode (ν_2) is observed at 437 cm^{-1} for descloizite and at 426 cm^{-1} for
133 mottramite.

134

135 The free vanadate ion has tetrahedral T_d symmetry. Ross reports the free aqueous
136 vanadate ion as having a ν_1 (A_1) mode at 874 cm^{-1} , the ν_2 mode of E symmetry at
137 345 cm^{-1} , the ν_3 mode of F_2 symmetry at 855 cm^{-1} and the ν_4 mode also of F_2
138 symmetry at 345 cm^{-1} . For perfect T_d symmetry the first two modes are Raman
139 active/infrared inactive and the last two modes both Raman and infrared active. The
140 presence of a cation in the aqueous vanadate solution as an ion pair reduces this
141 symmetry.

142

143 **Raman Spectroscopy**

144

145 The Raman spectra of the vanadium containing mineral pascoite are shown in Fig. 1
146 and S1. The results of the band component analysis of the Raman spectra are reported
147 in Table 1. Three distinct bands are observed in the Raman spectrum of pascoite from
148 Utah at 991 , 961 and 958 cm^{-1} with bandwidths (FWHM) of 9.6 , 11.8 and 8.9 cm^{-1} .
149 The band at 958 cm^{-1} appears as a shoulder on the 961 cm^{-1} band. The Raman
150 spectrum of pascoite from the RRUFF data base (Fig. S2) displays two distinct bands
151 at 953 and 993 cm^{-1} . A broad Raman peak centred at 1080 cm^{-1} . This band is
152 attributed to an impurity in the mineral, possibly silicate. Solid solution involving
153 anionic substitution is ubiquitous in vanadate minerals. Phosphate and arsenate
154 frequently substitute for vanadate in these minerals, albeit to different extents. The
155 vanadate ion, VO_4^{3-} , is somewhat larger than phosphate and arsenate ions, whose radii
156 are 230 and 237 pm , respectively [11]. Other comparable ions such as silicate may
157 also substitute with charge balance compensation. Thus, many of the formulae of the
158 vanadate minerals conceal more complex compositions for natural materials, although
159 substitution for vanadate is more limited in many cases than is found for mutually
160 soluble phosphate and arsenate analogues and related minerals.

161

162 In contrast to the Raman spectrum, the infrared spectrum of the San Juan mineral
163 shows three overlapping bands at 945, 987 and 1030 cm^{-1} (Fig. 2). Other infrared
164 bands are observed at 746, 816 and 840 cm^{-1} . The published infrared spectra gave
165 bands at 975 and 960 cm^{-1} [8]. These bands are attributed to ν_1 symmetric stretching
166 modes of $(\text{V}_6\text{O}_{16})^{2-}$ units and terminal VO_3 units. According to Frederickson and
167 Hausen, decavanadates can be distinguished from hexavanadates by having only one
168 band in the infrared spectrum in the V-O stretching region at around 975 cm^{-1} as
169 opposed to two bands for hexavanadates. In the infrared spectrum of pascoite in this
170 work three bands are observed at 945, 987 and 1030 cm^{-1} which are broad with
171 bandwidths of 56.0, 15.8, 37.9 cm^{-1} . In the transmission infrared spectrum of pascoite
172 given by Frederickson and Hausen three bands were observed [8]. Pascoite and
173 huemulite are decavanadates containing the polyoxyanion $(\text{V}_{10}\text{O}_{28})^{6-}$. In the infrared
174 spectrum of hummerite, given by Frederickson and Hausen, two bands were shown at
175 around 975 and 960 cm^{-1} with the former as a shoulder on the latter band [8]. In our
176 infrared spectrum only a single band was observed at 952 cm^{-1} . The band is broad
177 with a bandwidth of 41.6 cm^{-1} . A low intensity band is observed as a slight shoulder
178 at 982 cm^{-1} . Hummerite is an example of a mineral containing the $(\text{V}_5\text{O}_{14})^{3-}$ anion.
179 Pascoite has multiple bands around 975 cm^{-1} and the latter only a single band at
180 952 cm^{-1} . In the Raman spectrum there are two sharp bands for both minerals. It
181 would appear that the ‘rule’ suggested by Frederickson and Hausen for distinguishing
182 between hexa and decavanadates is of questionable validity.

183

184 In the Raman spectrum of pascoite (Fig. 3), bands are observed in the 775 to 875 cm^{-1}
185 region. In the Raman spectrum of pascoite from the RRUFF data base, Raman bands
186 are observed at 542, 695 and 878 cm^{-1} . Considerable differences are observed in this
187 spectral region for the two minerals. In contrast to the bands assigned to the
188 symmetric stretching modes, these Raman bands tend to be broad. In the Raman
189 spectrum of pascoite, two bands are observed at 815 and 841 cm^{-1} with bandwidths of
190 26.3 and 40.1 cm^{-1} . In the published infrared spectrum of pascoite two bands were
191 observed at 840 and 805 cm^{-1} [8]. An additional quite broad band was observed at
192 750 cm^{-1} [8]. In our infrared spectrum of pascoite, four overlapping bands are
193 observed at 746, 816 and 840 cm^{-1} . These bands are attributed to the ν_3
194 antisymmetric stretching modes of $(\text{V}_6\text{O}_{16})^{2-}$ units.

195

196 The Raman spectrum of pascoite in the low wavenumber region is displayed in Fig. 4.
197 Raman bands are observed at 292, 320, 337 and 360 cm^{-1} . The Raman spectrum of
198 the RRUFF sample is very different in this spectral region (Fig. S3). Raman bands
199 are observed at 241, 282 and 330 cm^{-1} . Additional bands are observed at 406 and 428
200 cm^{-1} which appear unrelated to the vanadate anion. The bending mode (ν_2) of the
201 vanadate anion was observed at 426 cm^{-1} and 437 cm^{-1} for descloizite and mottramite.
202 The Raman spectrum of the free vanadate ion shows the ν_2 mode of E symmetry at
203 345 cm^{-1} and the ν_4 mode also of F_2 symmetry at 345 cm^{-1} . The Raman spectra in the
204 200 to 345 cm^{-1} region are complex to say the least and consist of several overlapping
205 bands. The question arises as to the significance of these bands. One possibility is
206 that the bands are from the ν_4 bending modes. Another possibility is that the bands are
207 due to subunits such as the V_2O_2 units. Band assignment in this region is realistically
208 not possible. Bands below 240 cm^{-1} are attributed to MO bonds and lattice vibrations.
209

210 The Raman spectrum in the 1300 to 1800 cm^{-1} region is shown in Fig. 5. A broad
211 band is observed at 1514 cm^{-1} along with a sharp band at 1646 cm^{-1} with a shoulder at
212 1668 cm^{-1} . The first broad band is attributed to an overtone band. The two bands at
213 1646 and 1668 cm^{-1} are assigned to the bending modes of water. The position of
214 these bands provides evidence for strongly hydrogen bonded water. Water is found in
215 the $(\text{Ca}_3(\text{H}_2\text{O})_{17})^{6+}$ units. Based upon Raman spectroscopy it is suggested that two
216 non equivalent water molecules exist in the pascoite mineral structure with slight
217 differences in hydrogen bond lengths. The Raman spectrum of the OH stretching
218 region is shown in Fig. 6. The spectrum is complex with multiple overlapping bands
219 with bands observed at 3125, 3254, 3405, 3466 and 3570 cm^{-1} . These bands are
220 attributed to water stretching vibrations. The observation of multiple bands supports
221 the concept of non-equivalent water molecules in the pascoite structure. The position
222 of the water stretching vibrations is a function of the hydrogen bond distances. The
223 bands at 3125 and 3254 cm^{-1} are associated with strong hydrogen bonds and as the
224 wavenumber increases with the other peaks the bond distances become larger.

225

226

227 **CONCLUSIONS**

228

229 The Raman spectra of the vanadate mineral pascoite from the Vanadium Queen Mine,
230 San Juan County, Utah, USA. have been collected and the spectra related to the
231 molecular structure of the mineral. A comparison of the spectra obtained in this work
232 with the Raman spectra of pascoite from the Arrowhead Claim, Slick Rock, San
233 Miguel County, Colorado, USA from the RRUFF data base is made. Bands attributed
234 to the stretching and bending modes of $(V_{10}O_{28})^{6-}$ units or $(V_5O_{14})^{3-}$ units have been
235 assigned. In summary (a) terminal V=O bonds occur in the 900 to 1000 cm^{-1} region;
236 (b) Bridging V-O-V bonds vibrate in the ~500 and 700 cm^{-1} region as symmetric and
237 antisymmetric stretching modes respectively;. V-O bending modes occur in the 300 to
238 400 cm^{-1} region. The decavanadate ion consists of four distinct distorted VO_6 units
239 which are observed as V=O bonds at the highest wavenumbers.

240

241 **Acknowledgements**

242

243 The financial and infra-structure support of the Queensland University of Technology
244 Inorganic Materials Research Program of the School of Physical and Chemical
245 Sciences is gratefully acknowledged. The Australian Research Council (ARC) is
246 thanked for funding.

247

248

249

250 **REFERENCES**

- 251 [1] J.M. Hughes, M. Schindler, C.A. Francis, *Canadian Mineralogist* 43 (2005) 1379-1386.
- 252 [2] W.F. Hillebrand, H.E. Merwin, F.E. Wright, *Zeitschrift fuer Kristallographie und Mineralogie*
253 54 (1914) 209-231.
- 254 [3] W.F. Foshag, F.L. Hess, *Proc. U. S. Nat. Museum* 72 (1927) 1-12.
- 255 [4] W.H. Barnes, *Am. Mineralogist* 40 (1955) 689-693.
- 256 [5] V.C. Farmer, *Mineralogical Society Monograph 4: The Infrared Spectra of Minerals*,
257 Mineralogical Society, London, 1974.
- 258 [6] R.L. Frost, D.A. Henry, M.L. Weier, W. Martens, *Journal of Raman Spectroscopy* 37 (2006)
259 722-732.
- 260 [7] R.L. Frost, J. Cejka, M.L. Weier, W. Martens, D.A. Henry, *Vibrational Spectroscopy* 39
261 (2005) 131-138.
- 262 [8] L.D. Frederickson, Jr., D.M. Hausen, *Anal. Chem.* 35 (1963) 818-827.
- 263 [9] R.L. Frost, M. Crane, P.A. Williams, J.T. Kloprogge, *Journal of Raman Spectroscopy* 34
264 (2003) 214-220.
- 265 [10] R.L. Frost, P.A. Williams, J.T. Kloprogge, P. Leverett, *J. Raman Spectrosc.* 32 (2001) 906-
266 911.
- 267 [11] D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, Cleveland, Ohio, 1977.
- 268 [12] R.L. Frost, K.L. Erickson, M.L. Weier, *Spectrochimica Acta, Part A: Molecular and*
269 *Biomolecular Spectroscopy* 60A (2004) 2419-2423.
- 270 [13] R.L. Frost, K.L. Erickson, M.L. Weier, O. Carmody, *Spectrochimica Acta, Part A: Molecular*
271 *and Biomolecular Spectroscopy* 61A (2005) 829-834.

272
273
274
275
276
277

278 **Table 1 Results of the Raman and infrared spectral analysis of pascoite [12, 13]**
 279
 280

Pascoite			Pascoite		Suggested assignments
Raman 298 K [12, 13]	IR	IR published [5]	Raman 298K	Raman RRUFF	
	1108			1085	Impurities-Phosphate?
991 965 958	1025 987 945	975 960	993 961	993 953	ν_1 symmetric stretching of $(V_{10}O_{28})^{6-}$ units and terminal VO_3 units
837 815	845 812	840 805	841	878	ν_3 antisymmetric stretching of $(V_{10}O_{28})^{6-}$ units or $(V_5O_{14})^{3-}$ units
	775 743	750		695	ν_3 antisymmetric stretching of VO_3 units
619 584			621 588		Water librational modes ν_3 antisymmetric stretching of V_2O_2 units ν_4 bending of VO_3 units
546			540	542	ν_4 bending of VO_3 units
458			459	428 406	ν_2 bending of VO_3 units
362 334 317 289 275			360 337 320 292 275	330 282	ν_4 bending of VO_3 units ν_3 antisymmetric stretching of V_2O_2 units
235 192 175			238 193 159	241 159 144	M-O and lattice modes

List of Figs.

Fig. 1 Raman spectrum of pascoite from Utah in the 900 to 1100 cm^{-1} region

Fig. 2 Infrared spectrum of pascoite from Utah in the 600 to 1200 cm^{-1} region

Fig. 3 Raman spectrum of pascoite from Utah in the 400 to 900 cm^{-1} region

Fig. 4 Raman spectrum of pascoite from Utah in the 100 to 400 cm^{-1} region

Fig. 5 Raman spectrum of pascoite from Utah in the 1300 to 1800 cm^{-1} region

Fig. 6 Raman spectrum of pascoite from Utah in the 2700 to 3700 cm^{-1} region

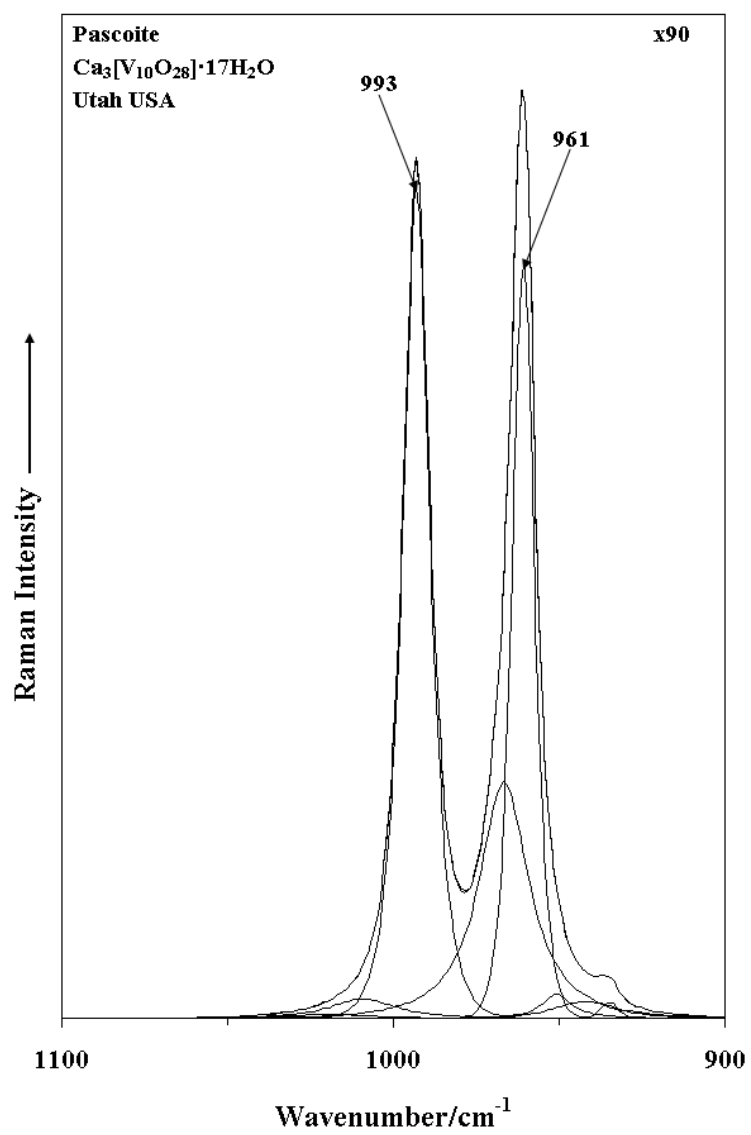


Fig. 1

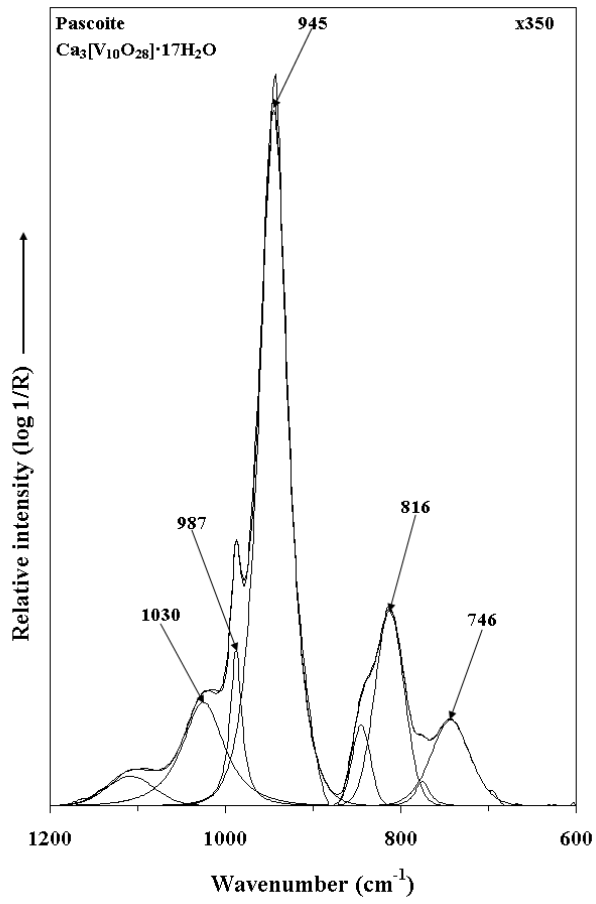


Fig. 2

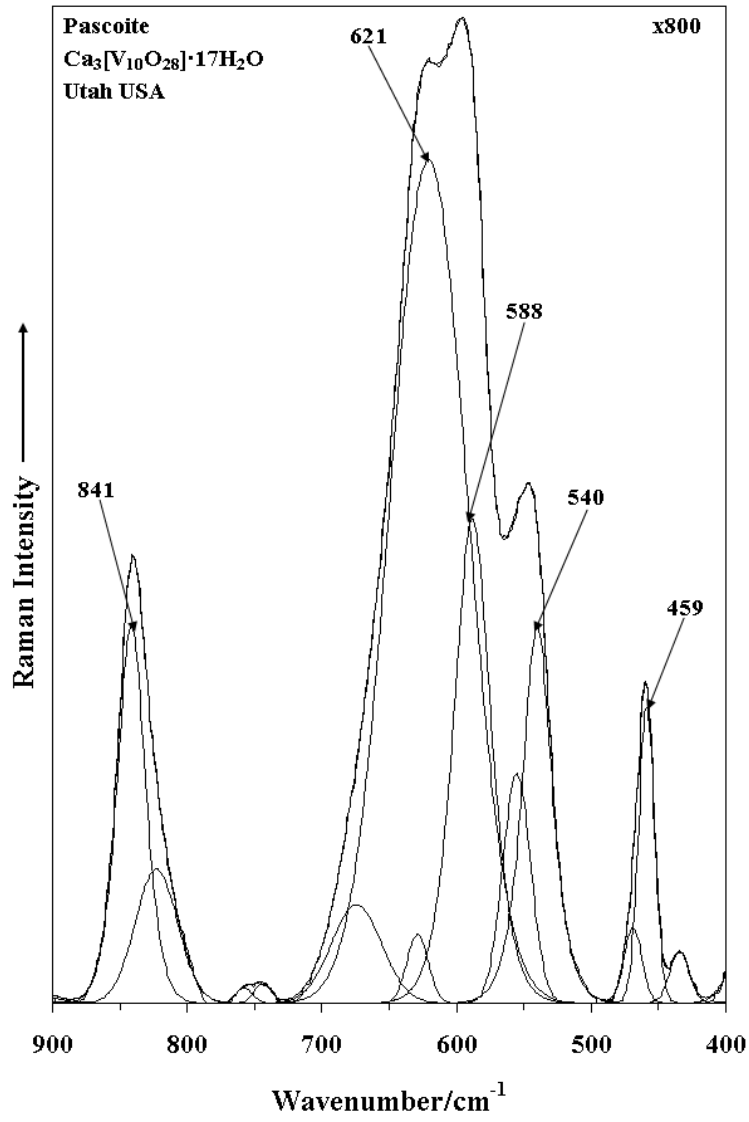


Fig. 3

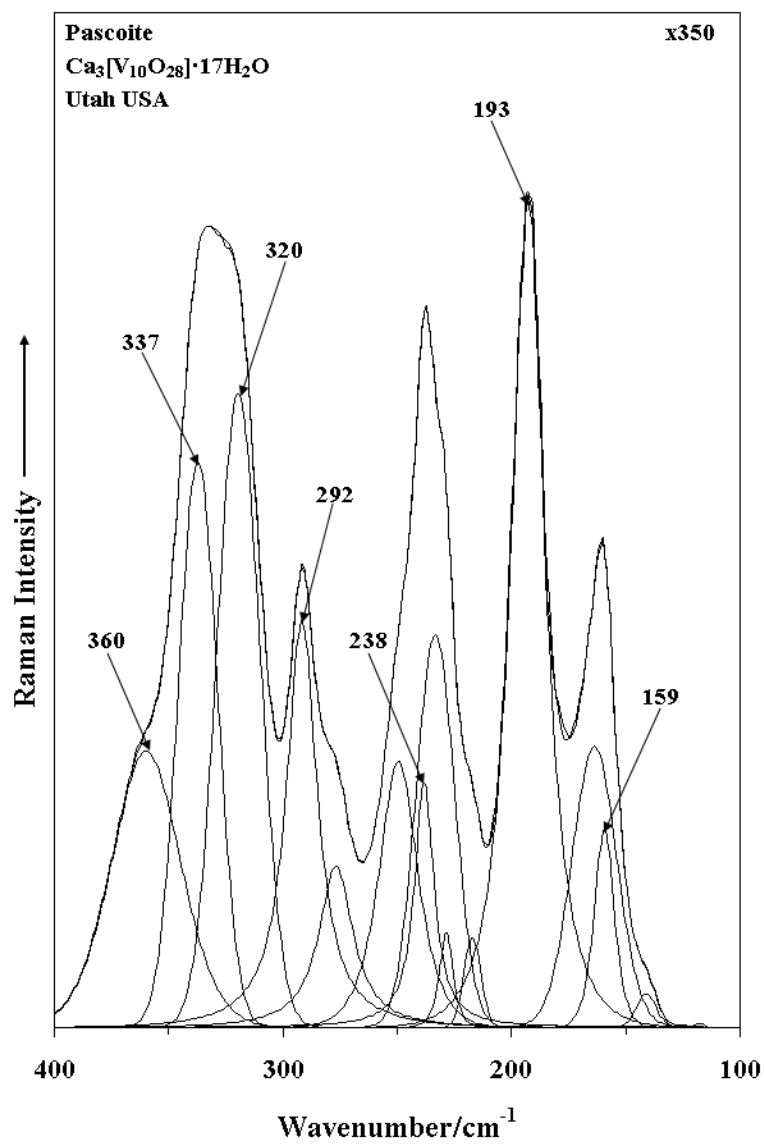


Fig. 4

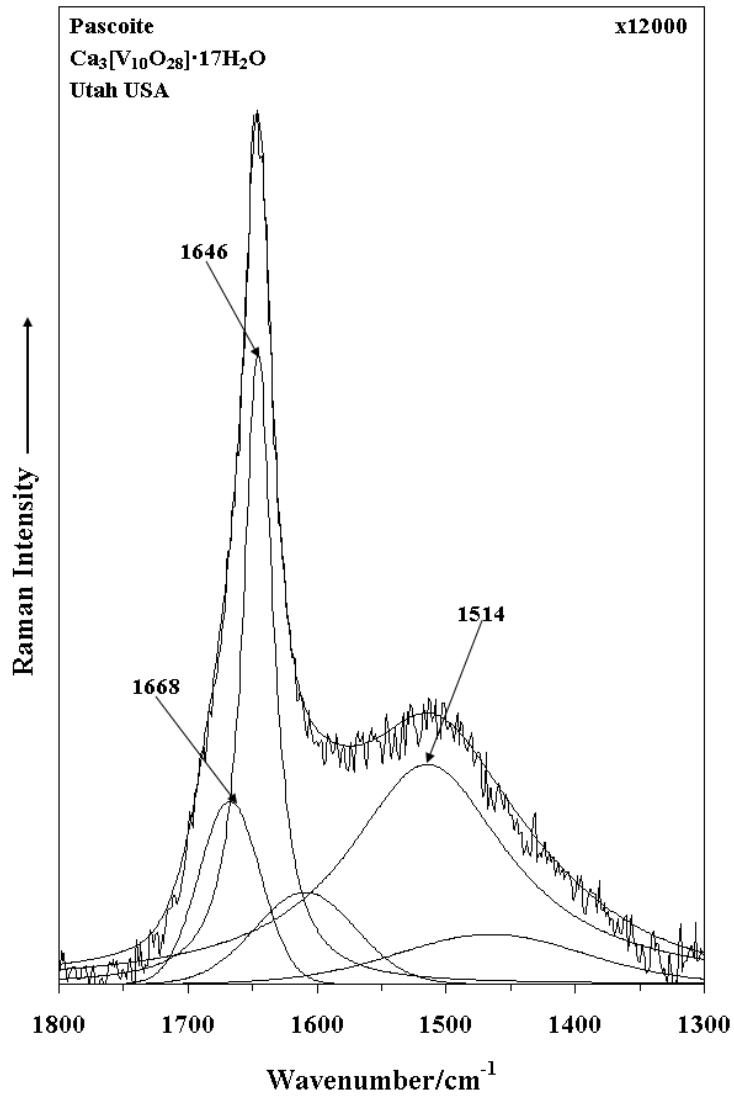


Fig. 5

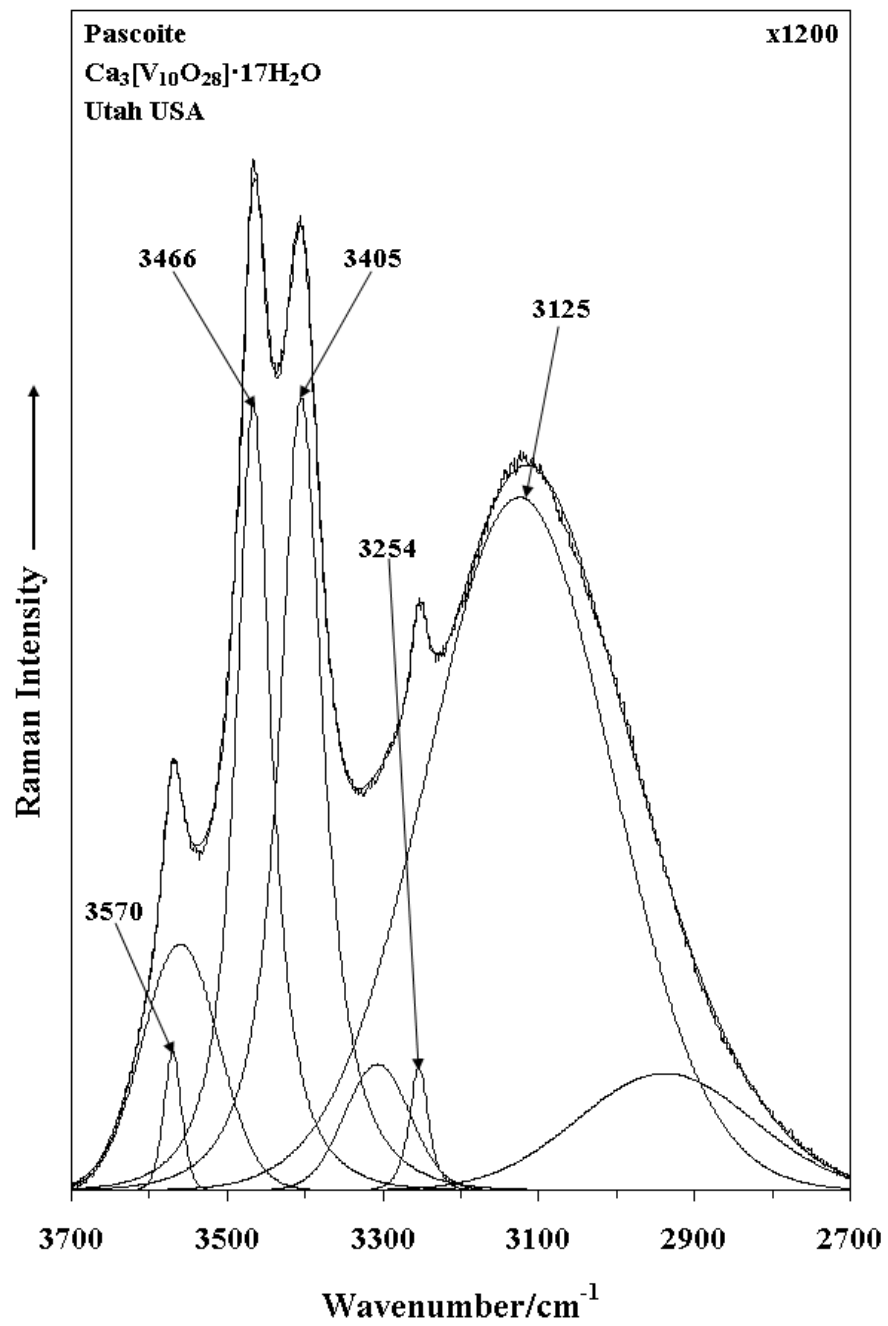


Fig. 6