1   **Raman Spectroscopy Study of Manganese Oxides – Layer Structures   <u>Revision 1</u>**

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Abstract

14   Raman spectra were collected for an extensive set of well-characterized layer-structure

15   Mn oxide mineral species (phyllomanganates) employing a range of data collection conditions.

16   We show that the application of a variety of laser wavelengths, such as 785, 633, and 532 nm, at

17   low power levels (30 – 500 µW) in conjunction with the comprehensive database of standard

18   spectra presented here, makes it possible to distinguish and identify the various phyllomanganate

19   minerals. The Raman mode relative intensities can vary significantly as a function of crystal

20   orientation relative to the incident laser light polarization direction as well as incident laser light

21   wavelength. Consequently, phase identification success is enhanced when using a standards

22   database that includes multiple spectra collected for different crystal orientations and with

23   different laser light wavelengths. The position of the highest frequency Raman mode near 630-

24   665 cm^{-1} shows a strong linear correlation with the fraction of Mn^{3+} in the octahedral Mn sites.

25   With the comprehensive Raman database of well-characterized Mn oxide standards provided

26   here (and available online as supplemental materials), and use of appropriate data collection

27   conditions, micro-Raman is a powerful tool for identification and characterization of biotic and

28   abiotic Mn oxide phases from diverse natural settings, including on other planets, as well as for

29   laboratory and industrial materials.

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32   Keywords: Manganese Oxide, Raman Spectroscopy, Phyllomanganates, Birnessite

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INTRODUCTION

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37   Layer-structure Mn oxide minerals, also called phyllomanganates, are found in a wide

38 variety of geological settings and are important constituents in many soils and sediments (Post,

39 1999). These phases can precipitate from solution as the result of macro or microscale changes

40 in redox conditions, pH, or composition; additionally, natural and laboratory Mn oxides that

41 form by biologically mediated processes are predominantly phyllomanganates (McKeown and

42 Post 2001; Tebo et al. 2004; Santelli et al. 2011). Phyllomanganates having a birnessite-like

43 structure readily participate in redox and cation-exchange reactions and exhibit high adsorption

44 capacities for a variety of organic pollutants and toxic metallic ions (Le Goff et al. 1996;

45 Manning et al. 2002; Feng et al. 2007; Lopano et al. 2009; Kwon et al. 2013; Fleeger et al. 2013;

46 Shumlas et al., 2016; Kong et al. 2019). They also have been identified as promising

47 heterogeneous compounds for water-oxidation catalysis (Sauer and Yachandra, 2002; Jiao and

48 Frei, 2010; Wiechen et al., 2012; Frey et al.; 2014; Feng et al., 2017). Phyllomanganates are

49 critical battery materials and are being investigated for their applications as catalysts and cation-

50 exchange agents, as well as for their potential to mitigate hazardous materials in the environment

51 (Ghodbane et al. 2009; Li et al. 2012; Nam et al. 2015).

52   Phyllomanganates are constructed of sheets of MnO_6 octahedra. The Mn is

53 predominantly Mn^{4+} but can be substituted by Mn^{3+} and vacancies, with the resulting layer

54 charges being compensated by various interlayer cations in the different phases (Fig. 1). Most

55 phyllomanganates also have interlayer water molecules. Natural samples commonly are fine-

56 grained and poorly crystalline, and the particular phyllomanganate mineral phases are difficult to

57 distinguish visually in the field or in hand specimens. They also can occur as fine-scale

58 intergrowths of two or more phases that readily alter from one to another. In many cases, X-ray

59   diffraction (XRD) of these phases also fails to identify them, since the XRD patterns often

60   exhibit broad peaks from multiple disordered phases, making basic phase identification difficult

61   or impossible (Ling et al. 2020). Consequently, many researchers employ other methods in

62   addition to XRD to characterize natural phyllomanganates, such as X-ray absorption

63   spectroscopy (XAS), Fourier transform infrared spectroscopy (FTIR), transmission electron

64   microscopy (TEM), and combined energy-dispersive X-ray spectroscopy and scanning electron

65   microscopy (EDS-SEM). These techniques also have experimental limitations and requirements,

66   such as special sample preparation methods, large sample sizes, or synchrotron X-ray sources.

67   Due to the difficulties of working with complex and typically poorly crystalline natural

68   phyllomanganate samples, many researchers use synthetic phases that are presumed to be

69   suitable analogs of the minerals. Offsetting the advantages of working with pure, relatively well-

70   crystalline laboratory-produced samples is the difficulty of assessing their relevancy to natural

71   phases or systems. Additionally, complexities and confusion introduced using multiple synthesis

72   methods, and terminology, can cause problems comparing results among different research

73   groups.

74   In a recent paper, we demonstrated the advantages of using micro-Raman spectroscopy to

75   routinely identify and characterize tunnel-structure Mn oxide phases for a variety of natural and

76   synthetic samples (Post et al. 2020). Here we extend that work to the phyllomanganates. During

77   the past few decades, numerous reports have described applications of Raman spectroscopy to

78   Mn oxides, primarily as an identification tool, but also for investigating changes in response to

79   certain redox, cation-exchange, and other reactions (Bernard et al. 1993). There are several

80   studies that have used Raman spectroscopy to study phyllomanganates (e.g. Bernard et al. 1993;

81   Kim and Stair 2004; Julien et al. 2003; Julien et al. 2004; Hsu et al. 2011; Burlet and Vanbrabant

82   2015; Yang et al. 2019; Boumaiza et al. 2019; and Bernardini et al. 2019) with various degrees

83   of success. Such work has been invigorated in part by advancements in micro-Raman techniques

84   that have resulted in greater availability of in-house Raman systems. Modern systems typically

85   offer multiple laser options with high-sensitivity detectors that provide a range of data collection

86   conditions that can be optimized for particular samples. Additionally, Raman spectrometers

87   fitted with high quality microscopes permit rapid *in situ* interrogation of samples with spatial

88   resolution approaching one micron or less. Micro-Raman systems have the potential to provide

89   phase identification and structural information quickly and easily from discrete areas on natural

90   or synthetic Mn oxide samples. In particular, the combination of Raman microscopy and

91   analytical SEM provides unparalleled insights into the micro-mineralogy and -chemistry of

92   complex samples.

93   Our study of the tunnel structure Mn oxides (Post et al. 2020) confirmed the importance

94   of using low laser powers (e.g. < 0.35 mW) and multiple laser wavelengths (e.g. 532, 633, and

95   785 nm) in order to obtain the most useful Raman spectra for phase identification and for

96   elucidating structure information. These considerations are critical for the large tunnel-structure

97   Mn oxides, such as todorokite and romanechite, but are equally so for the phyllomanganates, and

98   in particular, for the birnessite-like phases that are important in many natural systems.

99   In the work presented here, we provide results from the most comprehensive-to-date

100   Raman spectroscopy study of layer-structure Mn oxide phases. Raman spectra were collected

101   from a large number and variety of natural and synthetic samples, drawing from the Smithsonian

102   Institution mineral collection, and additional samples from various sources, which had been

103   characterized in detail as part of our long-term research program on Mn oxides. Raman spectra

104   were collected using multiple Raman systems with a range of laser wavelengths in order to

105   provide comparisons and to determine optimal data collection conditions. Additionally, we

106   present representative spectra from different specimens, localities, and crystal orientations. A

107   major goal of this study is to provide a spectral database for identifying the various layer-

108   structure Mn oxide mineral phases, with an emphasis on natural samples. Finally, we explore

109   spectral trends and details for some specific phases that provide insights about composition,

110   symmetry, and in some circumstances, Mn oxidation states.

111

EXPERIMENTAL METHODS

113   **Specimens**

114   The layer-structure Mn oxide mineral samples for which spectra are presented here are

115   listed in Table 1, including information about individual compositions. Structure symmetry and

116   factor group analyses (Fateley et al. 1972) for the various phases are presented in Table 2. A

117   variety of samples were included to represent variations in composition, structural disorder, and

118   locality. All samples were checked by powder X-ray diffraction (XRD) to confirm phase

119   identification and purity. Energy-dispersive X-ray spectroscopy (EDS) analyses and

120   backscattered electron imaging were used to determine composition and assess chemical

121   homogeneity. Where possible, single crystals, or crystal fragments, were selected for Raman

122   measurements; fine-grained samples were lightly crushed, or in some cases, prepared as polished

123   sections that were also used for chemical analyses. For some Raman measurements, loose

124   sample grains were placed on glass slides without adhesive, which can introduce strong

125   luminescence. The synthetic triclinic Na-birnessites included the same material studied by Post

126   and Veblen (1990) as well as samples more recently synthesized and described in Ling et al.

127   (2018). Synthetic birnessites with different compositions were prepared by cation-exchange,

128   following the procedure of Golden et al. (1986). The hexagonal birnessite samples were

129   prepared by reacting Na-birnessite with a pH 2 HCl solution.

130   **X-ray diffraction (XRD)**

131   Samples were characterized by powder XRD using a Rigaku II D/MAX-RAPID micro-

132   diffractometer (Department of Mineral Sciences, Smithsonian Institution) equipped with a

133   graphite monochromator and a curved image plate area detector. A Mo tube (50 kV, 40 mA) was

134   used as the X-ray source with a 0.3 mm collimator. Small (~1 mm) balls of powdered samples

135   (with added super-glue as needed), or fragments of fine-grained polycrystalline materials, were

136   mounted on tips of glass fibers. During exposure to X-rays, the sample was rotated at 1°/min on

137   phi to minimize the effects of sample heterogeneity and preferred orientation. The full set of

138   Debye-Scherrer diffraction rings from the imaging plate data were integrated using Rigaku-

139   provided software, and interpretation of XRD patterns was performed using the JADE 9 software

140   package. Phase identifications were confirmed using the ICDD PDF-4 Minerals database and an

141   in-house collection of well-characterized Mn oxide mineral standards. Representative XRD

142   patterns are deposited as supplementary data with *American Mineralogist*.

143

144   **Scanning electron microscopy**

145   Uncoated samples (which then could also be used for Raman analysis) were mounted on

146   carbon tape adhered to an aluminum stub and analyzed with scanning electron microscopy

147   (SEM) using a field emission source (FEI Apreo) equipped with an EDAX Octane Silicon Drift

148   EDS detector (Department of Mineral Sciences, Smithsonian Institution). Backscattered electron

149   (BSE) images were collected, and EDS analysis was used to determine the chemical composition

150   and homogeneity of the Mn oxide samples (with beam current of 1.6 nA). The images were

151 collected and analyses performed in low vacuum (0.31 torr) at an accelerating voltage of 15 kV.

152 The data were processed using the Noran System Six 3 (NSS 3) software.

153

154 **Raman spectroscopy**

155   The reproducibility of the Raman spectra and the optimal data collection conditions were

156 evaluated by using four different micro-Raman systems at 25 °C in back-scattering geometry

157 using a single-grating spectrograph with notch filters. Two HORIBA LabRam HR Evolution

158 systems were employed (Department of Mineral Sciences, Smithsonian Institution; and Materials

159 Characterization Laboratory, Penn State University), both equipped with Synapse back-

160 illuminated deep depleted, Peltier cooled 1024 x 128 element CCD cameras. The spectra

161 presented in this paper were collected using 532, 633 (Penn State), and 785 nm solid state lasers

162 with 300 and 600 gr/mm spectrograph gratings, respectively, for spectral resolutions near 4 cm^{-1}.

163 An Olympus 100x or 50x objective was used to focus the incident laser light onto the sample.

164 The characteristic 520 cm^{-1} line from a Si wafer standard was used for Raman frequency

165 calibration. The laser power at the sample was measured using a Thorlabs power meter

166 (PM100USB) for the various combinations of microscope objectives and lasers. Typically,

167 spectra were collected using laser powers of 540 μW or less for the 532 nm laser and 350 μW or

168 less for the 633 and 785 nm lasers. Some phases, e.g. chalcophanite and lithiophorite, did not

169 exhibit obvious spectral changes at laser powers up to 2 mW, but birnessite-like phases showed

170 evidence of sample degradation or phase transformation at laser powers above ~500 μW at the

171 sample. For the 532 nm laser, spectra for birnessite-like phases exhibited changes at powers as

172 low as 30 μW. The laser power measurements are intensities of the focused incident laser beam

173   at the sample, not power densities, which vary depending upon the laser spot size, determined by

174   the objective used, laser focus, and certain other instrumental and sample surface characteristics.

175   The second system (Vitreous State Laboratory, Catholic University) consists of a WITec

176   alpha-300 RA+ micro-Raman system, where 633 nm solid state diode and 532 nm DPSS lasers

177   were used with a 600 gr/mm grating to disperse the Raman scattered light on to a 1024 x 128

178   element Peltier cooled CCD camera (Andor Technology Model DV401A-BVF-352). 50x and

179   100x Zeiss objectives were used producing a ~1 μm laser spot size on the sample. The spectra

180   were frequency calibrated to the Si 520 cm^{-1} mode. The spectral resolution of the data produced

181   from these system configurations is near 6 cm^{-1}. Spectra for birnessite-like phases showed phase

182   alteration at powers as low as 150 μW using 633 nm laser light.

183   A third system (Vitreous State Laboratory, Catholic University) consists of a Melles-Griot

184   Model 45 Ar^{+} laser that provided 457.9 and 514.5 nm wavelength light that was guided through a

185   long working distance Mitutoyo 10x microscope objective and focused to a 10 μm diameter spot

186   on the sample. The scattered light proceeded through holographic notch and super-notch filters

187   (Kaiser Optical Systems), which reduced the Rayleigh (or elastically) scattered light intensity by

188   ten optical densities. The Horiba HR460 spectrograph used a 1200 gr/mm grating (Richardson

189   Grating Laboratory) to disperse the Stokes scattered light from the sample on to a 2048 x 512

190   element Peltier cooled CCD detector (Andor Technology Model DU440BV). Due to the

191   relatively broad spectral features for most samples measured, the spectrograph incident slits were

192   set to 6 cm^{-1} spectral resolution. The spectrograph was frequency calibrated using CCl_4,

193   such that recorded Raman mode frequencies for all spectra are accurate to within ±1 cm^{-1} of the

194   actual values. The laser power for this system was minimized to <0.1 mW at the sample to avoid

195   sample heating and alteration.

196   For each sample, initial data collection was performed using minimal laser power, e.g. 30

197   µW; the power level was gradually increased until noticeable changes occurred to the spectra,

198   such as variations in peak intensities, the appearance of new peaks, or broad band luminescence

199   with evidence of sample darkening or hole formation at the incident laser light position. Where

200   possible, relatively flat and smooth sample surfaces, as ascertained at 100x or 50x magnification,

201   were selected for data collection, using 5- to 60-second integration times per acquisition, with

202   two to 10 acquisitions per spot to improve signal-to-noise levels in the spectra. Crystal

203   orientation effects were apparent for most layer-structure Mn oxide phases. Phyllomanganate

204   crystals typically have a platy morphology and tended to orient preferentially with the Mn

205   octahedral sheets normal to the direction of the laser beam. When possible, spectra were

206   collected with crystals oriented such that the octahedral sheets were both parallel and

207   perpendicular to the direction of the incident laser light. Polarized spectra were gathered using

208   an analyzer polarizer inserted in the scattered light path. Polarized spectra were labeled VV

209   (vertical-vertical) or VH (vertical-horizontal) to describe collection conditions where the laser

210   light polarization was oriented parallel or perpendicular, respectively, to the polarization

211   direction of the analyzer. For comparison, unpolarized spectra also were collected without an

212   analyzer in the scattered light path between the sample and spectrograph.

213

214   **Lattice Dynamics Calculations**

215   In order to provide guidance for some general vibrational assignments to the observed

216   Raman features, preliminary normal coordinate valence-force lattice dynamics (LD) calculations

217   at zero wavevector (Dowty 1987 and 2007) were performed for several of the phyllomanganate

218   structures. The models included Mn-O stretch as well as O-Mn-O bend force constants to

219   simulate the various bonding environments within the linked MnO_6 octahedra. Interlayer cation-

220   oxygen stretch force constants were also included. The force constants were allowed to vary so

221   that the calculated mode frequencies best matched the set of observed mode frequencies from the

222   Raman spectra for each phase.

223   Overall, LD calculations indicated that Raman-active modes for these Mn-oxides can be

224   divided into two frequency ranges. Consistent with previous interpretations by Julien et al.

225   (2003, 2004), modes above 500 cm^{-1}, are dominated by MnO_6 octahedral deformations,

226   including O-Mn-O bend, Mn-O stretch, as well as expansion and compression of the octahedra in

227   the layer stacking direction, and shear motions of layers of O atoms that are parallel to the MnO_6

228   layers. In structures with higher symmetry Mn-sites, e.g. Mn on a symmetry center, the internal

229   Mn octahedral modes involve O motions, while the Mn atoms are stationary. Modes at

230   frequencies less than 500 cm^{-1} include contributions from displacements of interlayer cations,

231   such as Zn^{2+} in chalcophanite and Na^+ in birnessite, and cation-water and water-water

232   interactions.

233

234
235   **RESULTS**

236   **Chalcophanite Group**

237   Chalcophanite ($ZnMn_3O_7 \cdot 3H_2O$; Space Group R-3) is constructed of sheets of Mn^{4+}-O

238   octahedra with one out of seven octahedra vacant. Single-crystal X-ray diffraction studies (Post

239   and Appleman 1988) indicate that the vacancies are fully ordered within the octahedral sheets.

240   Zn^{2+} cations sit above and below the vacancies and are in octahedral coordination with three O

241   atoms from the octahedral sheet and three O atoms from the interlayer water molecules (Fig. 1).

242   Jianshuiite and ernienickelite are isostructural with chalcophanite, but have Mg^{2+} and Ni^{2+},

243 respectively, as the dominant interlayer cations. Chalcophanite group minerals commonly occur

244 as euhedral platy crystals.

245   Chalcophanite typically gives strong Raman features, especially for 532 and 633 nm laser

246 light that are consistent for laser powers less than ~0.5 mW. Chalcophanite spectra are highly

247 sensitive to laser light polarization, especially the Mn-O vibrational modes near 670 cm^{-1} that are

248 intense in parallel polarized light but almost absent in the crossed polarized spectrum (Fig. 2).

249 Similar polarization behavior for these modes is also observed for other phyllomanganates. By

250 contrast, there are only small intensity differences for analogous peaks in crossed versus parallel

251 polarized spectra for the large tunnel structure phases such as todorokite and romanechite (Post

252 et al. 2020). Raman spectra for chalcophanite using 532, 633 and 785 nm lasers are similar (Fig.

253 3). The 670 cm^{-1} mode for chalcophanite has the greatest frequency of any of the layer Mn

254 oxides, presumably because all the Mn is in the 4+ valence state, which imposes the shortest

255 possible average Mn-O distance, and correspondingly the highest frequency vibrational motions.

256 As discussed below, substitution of Mn^{4+} by the larger Mn^{3+}, with its attendant Jahn-Teller

257 distortions, shifts the corresponding peaks to lower frequencies and increases the number of

258 internal MnO_6 modes.

259   The Raman spectra for chalcophanite, jianshuiite, and ernienickelite are similar, but

260 some variations, e.g. extra peaks near 533 and 590 cm^{-1}, suggest some fundamental differences

261 in the Ni-bearing ernienickelite (Fig. 4). A detailed structure refinement has not been reported

262 for ernienickelite. Spectra collected from chalcophanite with the laser light polarization

263 direction parallel versus perpendicular to the octahedral sheets (Fig. 5a) show modest variations

264 in intensities of several modes. Spectra collected with the laser polarization perpendicular to the

265 layers for chalcophanite and ernienickelite show modes at ~3320 and 3390 cm^{-1} (Fig. 5b) that

266   correspond to OH stretch vibrations from the interlayer water molecules; these modes were

267   absent in spectra collected with the laser polarization parallel to the octahedral sheets, indicating

268   that the predominant OH stretch motion is perpendicular to the sheets.

269   Lattice dynamic calculations for the chalcophanite structure (Figs. 6a and b) indicate that

270   modes above ~500 cm^{-1} are due primarily to internal MnO_6 deformation, as well as expansion

271   and compression of the MnO_6 layers. There are also Zn-O stretch contributions with Zn

272   translating perpendicular to the octahedral layers, but as there are more MnO_6 octahedra than

273   ZnO_6 octahedra, these modes are dominated by internal MnO_6 displacements. Modes below 500

274   cm^{-1} arise from mixtures of MnO_6 deformations and motions involving the interlayer Zn^{2+}

275   cations and water molecules in ZnO_6 octahedra, where three of the coordinating oxygens are

276   from water molecules. The $Zn-H_2O$ stretch and the water motions become more dominant in the

277   lower frequency modes. The lower frequency parallel polarized A_g modes arise from Zn

278   translations perpendicular to the octahedral layers, while lower frequency crossed polarized B_g

279   modes result primarily from Zn translations parallel to the octahedral layers. Not surprisingly,

280   the most obvious differences among the spectra for chalcophanite compared with those for

281   jianshuiite and ernienickelite are in this lower frequency region, presumably related to the

282   different sizes and bonding properties of the Zn^{2+} versus Mg^{2+} and Ni^{2+} interlayer cations,

283   respectively.

284

285   **Ranciéite Group**

286   Ranciéite, a Ca-rich phyllomanganate, has been found as an abiotic product in low-

287   temperature alpine vein deposits and in oxidized zones of Fe and Mn deposits (Ertle et al. 2005).

288   Recent studies, however, of naturally occurring phyllomanganates from fresh-water

289   environments revealed Ca to be the predominant interlayer cation, sometimes associated with

290   Mg, Ba, and/or K (Bargar et al. 2009; Tan et al. 2010; Ling et al. 2020). Furthermore, ranciéite-

291   like structures play critical roles in water-oxidation catalysis and as the oxygen-evolving

292   complex within the enzyme photosystem II (PSII) (Umena et al. 2011; Zhang et al. 2015;

293   Yamaguchi et al. 2017).

294   Ranciéite has a hexagonal structure (P-3), and like chalcophanite consists of sheets of

295    $Mn^{4+}O_6$ octahedra, but with one out of ten (or eleven) octahedra vacant, and Ca^{2+} and water

296   molecules in the interlayer regions (Kim 1991, Post et al. 2008). X-ray diffraction and selected

297   area electron diffraction patterns show no superstructure reflections, indicating that vacancies are

298   not ordered in the octahedral sheets, presumably because of the relatively fewer vacancies, and

299   therefore less energetic drive to order, compared with chalcophanite. The interlayer cations

300   occupy sites above and below the octahedral vacancies and are predominately Ca^{2+} in ranciéite

301   and Mn^{2+} in takanelite; other similar sized divalent cations, such as Ba^{2+}, Sr^{2+}, and Mg^{2+} are

302   commonly found in ranciéite and takanelite specimens (Table 1 and Kim 1991). The interlayer

303   cations are coordinated to three octahedral O atoms and three interlayer water O atoms. The

304   interlayer-cation to Mn octahedral site ratio is ~0.2 (compared to 0.33 in chalcophanite), and the

305   total interlayer cation charge is approximately +0.75. The larger sizes of the interlayer cations in

306   ranciéite relative to those in chalcophanite group minerals might limit the numbers of cations that

307   can fit into the interlayer region. The chemical analyses for the ranciéite samples used in this

308   study, as well as Mn and interlayer cation occupancy factors determined by Rietveld refinements

309   (Post et al. 2008), indicate that Mn^{2+} is absent or present in only minor amounts as an interlayer

310   cation. The powder X-ray diffraction patterns and Raman spectra suggest that the ranciéite

311   structure is like those of the synthetic Ca-birnessites generated when Na-birnessite is exchanged

312   at low pH and low Ca concentrations (Elmi et al. 2020).

313   As with chalcophanite, the parallel and crossed polarized spectra ofranciéite (Fig. 7)

314   reveal a strong polarization response, especially for the A_g internal MnO_6 modes near 667 and

315   578 cm^{-1}, which arise from mostly symmetric stretch vibrations that can only effectively scatter

316   light polarized in the same direction as the incident laser beam; hence, these prominent high

317   frequency features nearly disappear in the cross polarized spectrum. Unpolarized ranciéite

318   spectra collected using 532, 633 and 785 nm laser wavelengths are plotted in Figure 8, and for

319   several different ranciéite specimens in Figure 9. Not surprisingly, there is a resemblance

320   between the chalcophanite and ranciéite spectra, but the ranciéite peaks generally are broader,

321   presumably because of the lower crystal structure symmetry for ranciéite (P-3 vs. R-3), and the

322   disordered vacancies in the octahedral sheets. Also, modes below 300 cm^{-1} are weaker or absent

323   for ranciéite, relative to chalcophanite, likely resulting from interlayer cation disorder related to

324   the random Mn site vacancies, and the variety of interlayer cations commonly found in natural

325   samples. Powder XRD patterns for ranciéite samples typically exhibit broad diffraction peaks

326   that also suggest structural disorder. The highest frequency Raman modes observed for various

327   ranciéite specimens (near 667 cm^{-1}) are comparable to those seen in the chalcophanite spectra,

328   suggesting that the Mn is tetravalent; this is consistent with Rietveld refinements (Post et al.

329   2008) showing ranciéite Mn-O bond distances comparable to those reported for chalcophanite

330   (Post and Appleman 1988).

331   Ranciéite structure LD calculations (Fig. 10) include A_g modes at ~665 and 564 cm^{-1}

332   dominated by expansion - compression motions of the MnO_6 octahedral sheets parallel to the c-

333   axis, the layer stacking direction, with some Ca^{2+} translation parallel to the c-axis. Calculated E_g

334   modes at 621 and 396 cm^{-1} arise from MnO_6 octahedral shear within the layer. The lower

335   frequency modes are dominated by interlayer water translations parallel (443 and 508 cm^{-1}) or

336   perpendicular (363, 384, and 420 cm^{-1}) to the layer stacking direction. The calculations do not

337   explain the observed A_g mode near 605 cm^{-1}, nor most observed modes below 400 cm^{-1} (Fig. 8)

338   that may be due to motions of the interlayer cations (Ca^{2+}) near MnO_6 octahedra layer defects or

339   water molecules.

340

341   **Birnessite-like Phases**

342   Birnessite was first described by Jones and Milne (1956) as a natural phase discovered in

343   Aberdeenshire, Scotland with a chemical formula of $Na_{0.7}Ca_{0.3}Mn_7O_{14} \cdot 2.8 \cdot H_2O$. Subsequently,

344   numerous natural phases with "birnessite-like" structures have been described, including

345   ranciéite (Post et al. 2008), takanelite (Nambu and Tanida 1971; Kim 1991), and lagalyite

346   (Witzke et al. 2017). They commonly occur as fine-grained, poorly crystalline aggregates and

347   coatings, making the studies of their structures and behaviors challenging. Additionally, various

348   synthetic birnessite-like structures containing almost every possible alkali and alkaline earth

349   element, as well as many of the transition metals, have been synthesized (*e.g.*, McKenzie, 1971;

350   Golden et al., 1986) in attempts to elucidate the structural and chemical features of birnessite-like

351   phyllomanganates (*e.g.*, Post and Veblen, 1990; Drits et al., 1997; Silvester et al., 1997; Lanson

352   et al., 2000; Post et al., 2002; Feng et al., 2004; Händel et al., 2013) and their reactivities (*e.g.*,

353   (Manceau et al., 2002; Feng et al., 2007; Lopano et al., 2007, 2011; Landrot et al., 2012; Wang et

354   al., 2010; Kwon et al., 2013; Lefkowitz et al., 2013; Yin et al., 2013; Fischel et al., 2015; Hinkle

355   et al., 2016; Zhao et al., 2016; Fischer et al. 2018). Laboratory studies have also demonstrated

356   that formation of birnessite-like phases can be initiated, or enhanced, by certain microbes and

357   fungi (Tebo et al. 2004; Webb et al. 2005; Grangeon et al. 2010; Santelli et al. 2011), and it is

358   therefore likely that biologically mediated birnessite-like phyllomanganates are important in

359   natural systems.

360   The birnessite structure is constructed of stacked layers of nominally $Mn^{4+}O_6$ octahedra;

361   substitution of Mn^{3+} or other lower valence cations and vacancies for Mn results in a net negative

362   charge on the octahedral sheets (Fig. 1). The charge is offset by addition of large mono- or

363   divalent cations (e.g. Na^+, Ba^{2+}, K^+, Ca^{2+}) into the interlayer region, along with water molecules.

364   Birnessite-like phases with predominantly Mn^{4+} exhibit overall hexagonal (trigonal) or near-

365   hexagonal symmetry. As the proportion of Mn^{3+} increases, the associated Jahn-Teller distortions

366   lower the symmetry to triclinic (Silvester et al. 1997; Ling et al. 2018). Birnessite-like structures

367   exhibit a characteristic ~7 Å repeat in the layer stacking direction. In buserite phases, a double

368   layer of water molecules between the octahedral sheets expands the layer spacing to ~10 Å.

369   Raman spectra collected using a 785 nm laser are shown for triclinic synthetic Na-

370   birnessite and hexagonal-birnessite in Figure 11. The octahedral layers in Na-birnessite

371    $[(Na^+_{0.29}, Mn^{2+}_{0.02}, H^+_{0.05}) (Mn^{3+}_{0.38}, Mn^{4+}_{0.62}) O_2 \cdot 0.75H_2O]$ (Post et al. 2002) have ~38% Mn^{3+}

372   (Ilton et al 2016) and no vacancies. H-birnessite has ~20% Mn^{3+} (Ilton et al 2016), mostly in the

373   interlayer region, and ~10% of the Mn octahedra are vacant (Ling et al 2018). The Raman

374   spectra collected for Na-birnessite using 457.9, 633 and 785 nm lasers are plotted in Figure 12a.

375   All spectra for birnessite-like phases collected using 532 nm laser light, even with power levels

376   at 0.03 mW, show significant evidence of alteration due to laser heating, presumably related to

377   the higher energy of the shorter wavelength light. Other observations suggest that 785 nm laser

378   light consistently yields reproduceable spectra with no evidence of sample degradation for laser

379   powers below about 0.3 mW. Spectra collected with 457.9 and 633 nm laser light at power

380   levels near 0.1 mW are similar to those for 785 nm (Fig. 12a), with indications of sample

381   alteration at powers as low as 0.15 mW (Fig. 12b).

382   LD calculations for Na-birnessite used a simplified higher symmetry $C2/m$ monoclinic

383   structure (the triclinic structure is close to having monoclinic symmetry), due to uncertainties

384   arising from disorder among the H, Na, and O(w) positions. Similar to other phyllomanganates,

385   LD calculations (Fig. 13) indicate that the highest frequency Raman peaks, e.g. the A_g mode at

386   640 cm^{-1} for Na-birnessite, arise primarily from MnO_6 octahedral expansion and compression

387   motions parallel to the layer stacking direction. The next highest frequency modes, A_g and B_g at

388   ~586 and 566 cm^{-1}, respectively, arise from shear motions of O atoms parallel to the MnO_6

389   layers. At frequencies below 500 cm^{-1}, calculated modes are dominated by translations of the

390   interlayer Na and H_2O.

391   Raman spectra collected from synthetic birnessite-like phases having different interlayer

392   cations are plotted in Figure 14. The spectra are similar at frequencies above 300 cm^{-1}, indicating

393   that the MnO_6 octahedral sheets were not generally affected by the exchanges of the interlayer

394   cations. A notable exception, however, involves the positions of the highest frequency peaks,

395   ranging from 651 cm^{-1} for Ca-birnessite to 636 cm^{-1} for K-birnessite. As described below, these

396   disparities likely reflect variations in Mn^{3+} concentration, which in turn depends on the valence

397   charges and sizes of the interlayer cations. The most noticeable differences among the various

398   birnessite spectra are in the lower frequency modes, which are governed by interlayer cation

399   motions, as shown by our LD calculations. These modes are most intense for triclinic structures

400   whose interlayer cations occupy positions at or near the midpoint between the MnO_6 layers, e.g.

401   for Na^+-, K^+-, Li^+-, and Ba^{2+}-birnessites (Post and Veblen 1990; Lopano et al. 2007). In some

402   cases, the Raman spectra might reveal the identity of the predominant interlayer cation and its

403   site symmetry; for example, a strong peak near 97 cm^{-1} is present only for K-birnessite (Fig. 14).

404   Also, compared with other compositions, K-exchanged birnessite typically showed sharper

405   Raman peaks, suggesting that K^+ is particularly well accommodated by the birnessite structure.

406

407   **Vernadite**

408   Vernadite is a poorly crystalline natural Mn oxide phase characterized by a powder XRD

409   pattern with broad peaks at 2.46, 1.42, and rarely at 2.2 Å. It was first described and named by

410   Betekhtin (1940). Vernadite is commonly described as a birnessite that is turbostratically

411   disordered in the layer stacking direction, or a birnessite with crystallites with so few MnO_6

412   layers that powder XRD patterns show no basal reflections (Buser et al. 1954; Bricker 1965;

413   Giovanoli, 1980; Drits et al. 1997; Grangeon, 2012). Chukrov et al. (1987) concluded, however,

414   that birnessite and vernadite are distinct. Chemical analyses of vernadite typically show minor

415   amounts of K, Mg, Ca, Ba, and Fe with 15-25 wt.% water as compared with approximately 12

416   wt.% water in Na-birnessite (Chukrov et al. 1978). Vernadite is found in the oxidized zone of

417   Mn-rich deposits and might be a major phase in ocean Mn nodules and crusts (Chukrov et al.

418   1987). Vernadite often is assumed to be analogous to the synthetic phase δ-MnO_2 (Villalobos et

419   al. 2003; Grangeon, 2010; Lee et al. 2019), although the term δ-MnO_2 has been applied very

420   broadly in recent years. Some have suggested that its formation is primarily mediated by biota

421   (Chukrov et al. 1987; Grangeon et al. 2012). Unpolarized and polarized Raman spectra for

422   vernadite from a Pacific Ocean crust (Table 1) contain a few broad peaks consistent with its

423   disordered nature (Fig. 15).

424

425 **Lithiophorite and Asbolane**

426   Lithiophorite is constructed of stacked sheets of MnO_6 octahedra alternating with sheets

427 of $Al(OH)_6$ octahedra in which one-third of the octahedra are vacant (Fig. 1). In the idealized

428 structure, Li^+ cations fill the vacancies in the Al layer, and charge balance is maintained by Mn^{3+}

429 replacing one-third of the Mn^{4+} cations (Post and Appleman 1994). The layers are cross-linked

430 by H-bonds between the hydroxyl H^+ ions on the Al/Li layer and O atoms in the MnO_6 octahedra

431 sheet. Chemical analyses show that transition elements such as Ni, Co, and Cu commonly

432 substitute into the structure. Reported Li concentrations range from 0.2 to 3.3 weight % oxide

433 (Ostwald 1984). Lithiophorite typically occurs in oxidized zones of Mn deposits and in some

434 soils.

435   Polarized Raman spectra collected for lithiophorite (Fig. 16) show strong polarization

436 effects for the higher frequency peaks, similar to that observed for most other phyllomanganates.

437 The Raman spectra for lithiophorite from South Africa showed a curious for wavelengths of

438 514.5, 532, 633, and 785 nm laser light (Figs. 16 and 17), where Raman mode frequencies

439 increase by 10 to 30 cm^{-1} as laser wavelengths became shorter. One possible explanation for the

440 shift is that the shorter wavelength laser light oxidizes some of the Mn^{3+} to Mn^{4+}. We did not see

441 this effect for other lithiophorite, or phyllomanganate samples. The large broad band centered

442 near 340 cm^{-1} in the relatively weak 785 nm spectrum may be due to luminescence effects and

443 appears to overwhelm the Raman mode near 380 cm^{-1} seen in the shorter laser wavelength

444 spectra. This feature was especially prominent for the South African lithiophorite and less

445 obvious in 785 nm spectra for other lithiophorite samples. It is possible that the cause of the

446 luminescence is trace impurities unique to this sample. It also could be an orientation effect, as

447   this is the only samplethat consisted of large plate-like crystals, which were oriented with their

448   flat surface perpendicular to the laser beam. Other lithiophorite samples typically were fine-

449   grained with random crystal orientations.

450

451   Because lithiophorite has alternating layers of $(Mn^{4+},Mn^{3+}) O_6$ and $(Al,Li)O_6$ octahedral

452   sheets, the structure contains a variety of octahedral environments: 1) Mn^{4+} in two-thirds of the

453   Mn octahedra, with average Mn-O distances of ~1.89 Å (Post and Appleman 1994); 2) Jahn-

454   Teller distorted Mn^{3+} octahedra in one-third of the Mn sites, with average Mn-O distances of

455   ~2.04 Å (Shannon 1976); and 3) two-thirds $Al(OH)_6$ and one-third $Li(OH)_6$ in the Al,Li

456   octahedral sheet, with Al-OH = 1.88 Å and Li-OH = 2.10 Å (Shannon 1976).   This range of

457   octahedral environments likely contributes to the typically broader peaks in the spectra for

458   lithiophorite compared with those for chalcophanite. The lithiophorite spectra show no clear

459   features below 350 cm^{-1}, presumably because there are no interlayer cations or water molecules,

460   as there are in birnessite and chalcophanite phases.

461   LD calculations for lithiophorite (Fig. 18) indicate that A_{1g} modes above 500 cm^{-1} are

462   due to MnO_6 and $Al(OH)_6$ octahedral sheet compression-expansion motions parallel to the c-

463   axis, whereas the higher frequency E_g modes are due to MnO_6 and $Al(OH)_6$ octahedral sheet

464   shear motions perpendicular to the c-axis. Calculated modes below 500 cm^{-1} have major

465   contributions from O-H stretches parallel to the c-axis (A_{1g}) and H translations within the a-b

466   plane (E_g).

467   Asbolane is a lithiophorite-like phase with transition-metal cations such as Co, Cu and

468   Ni replacing some of the Al, and possibly Mn (Chukhrov et al. 1982; Manceau et al. 1987).   The

469   asbolane structure has not been determined, but Chukhrov et al. (1982) propose that it likely has

470   hexagonal symmetry, and the lithiophorite $Al(OH)_6$ layer is largely replaced by poorly structured

471   "islands" of $(Co, Ni, Cu)O_6$ octahedra. Figure 19 shows that spectra for several asbolane

472   samples (Table 1) are similar to that of lithiophorite; a major difference is that the peak near 540-

473   560 cm^{-1} is relatively stronger for the asbolane spectra, increasing in intensity with greater Co

474   concentrations. Burlet and Vanbrabant (2015), based on results from a peak-fitting procedure,

475   suggested a correlation between certain peak positions and intensities and the compositions of

476   asbolane-lithiophorite samples; they also observed an intensity increase for a peak at ~540 cm^{-1}

477   for asbolane relative to lithiophorite.

478

479   **Feitknechtite**

480   The crystal structure for feitknechtite is not known. The formula is assumed to be

481   MnOOH, and some have speculated that the structure consists of layered MnO_6 octahedra (Luo

482   et al. 1996, Grangeon et al. 2017). Our XPS data (unpublished results) confirm that all Mn is

483   trivalent. Natural feitknechtite samples typically include hausmannite, which presumably is an

484   alteration product of the feitknechtite. Feitknechtite occurs as an intermediate phase in syntheses

485   of birnessite by oxidation of $Mn(OH)_2$ (Min and Kim 2019), and also has been reported in

486   biogenically precipitated Mn oxides (Mandernack et al. 1995). Polarized Raman spectra for

487   synthetic feitknechtite shown in Figure 20, and unpolarized spectra collecting using different

488   laser lines are compared in Figure 21.

489

490

491

492   **DISCUSSION**

493   **Phase Identification**

494   In a recent study, we concluded that when users employ appropriate data collection

495   conditions, Raman spectroscopy is an effective tool for the identification and characterization of

496   tunnel-structure Mn oxide phases (Post et al. 2020). The current work extends those conclusions

497   to layer-structure Mn oxides. Raman spectra for the various layer structure Mn oxide phases are

498   compared in Figure 22. As all phyllomanganates are constructed of similar MnO_6 octahedra, it is

499   not surprising that there are general similarities among the spectra, especially in the region from

500   ~300 to 665 cm^{-1} that is dominated by internal MnO_6 octahedra modes. The spectra have

501   sufficiently unique characteristics, especially at frequencies below 500 cm^{-1}, to make it possible,

502   in most cases, to identify specific phases. Additionally, the phyllomanganate spectra are

503   distinctly different from large tunnel Mn oxide spectra (Fig. 23) as discussed below.

504

505   Recent studies have shown that Mn oxide minerals from a variety of nonmarine sources

506   and in particular those assumed to form biogenically typically have layer or large-tunnel

507   structures, or are mixtures of both (McKeown and Post 2001, Bargar et al 2009, Ling et al.

508   2020). Furthermore, laboratory experiments indicate that various environmental conditions

509   transform phyllomanganates into tunnel structures, thereby significantly altering the reaction

510   potentials for the Mn oxides in soils and sediments (Atkins et al. 2014, Grangeon et al. 2014,

511   Yang et al. 2019). Routine Raman identification of specific tunnel or layer Mn oxides, even for

512   fine-grained samples and mixtures, and surface coatings, can be critical to understanding and

513   modeling their behaviors in a variety of natural settings.

514

515   The spectra plotted in Figure 23 suggest that a reliable method for distinguishing large

516   tunnel and layer structures is the presence or absence of a moderate-to-strong Raman mode near

517   725-740 cm^{-1}; this peak is present for all tunnel structures with predominantly Mn^{4+}, especially

518   for those with large tunnels, e.g. romanechite and todorokite, but is absent in all

519   phyllomanganate spectra – even layer structures containing only Mn^{4+}, such as chalcophanite.

520   This tunnel-structure marker peak is particularly strong when spectra are collected using 633 or

521   785 nm laser light. Post et al. (2020) suggested that this high frequency Mn-O stretch mode

522   arises from Mn^{4+}-O bonds in rigid octahedral tunnel structure frameworks. Phyllomanganate

523   octahedral sheets, on the other hand, are more elastic, softening the Mn-O stretches. This

524   behavior becomes even more pronounced with the replacement of some Mn^{4+} by the larger Mn^{3+}

525   or by vacancies.

526   As mentioned above, spectra collected from many phyllomanganates show strongly

527   polarized features, with strong intensities in the VV (laser light polarization parallel to analyzer

528   polarization direction) spectra, and weak intensities in the VH (laser light polarization

529   perpendicular to analyzer polarization direction) spectra. This behavior is particularly evident at

530   the highest frequencies that are dominated by internal MnO$_6$ octahedral motions. Spectra

531   collected under similar conditions for large-tunnel structures, however, showed little or no

532   polarization dependence (Post et al. 2020).

533

534   **Mn Oxidation State**

535   Post et al. (2020) concluded that Raman frequencies of certain internal MnO$_6$ octahedral

536   modes vary as a function of Mn^{3+}/(Mn^{4+}+Mn^{3+}) ratio. Increasing concentrations of the larger,

537   Jahn-Teller distorted Mn^{3+}O$_6$ octahedra cause a lengthening of the average Mn-O bond and a

538   more distorted octahedral environment, thereby decreasing the associated vibrational

539   frequencies. This is true in general for tunnel-structure Mn oxides, but is particularly true for the

540   hollandite group minerals, where a linear relationship was found between $Mn^{3+}/(Mn^{4+}+Mn^{3+})$

541   ratio and frequency of the internal MnO_6 octahedral mode near 630 cm^{-1}.

542

543   In the present study of phyllomanganates, we similarly noted a strong linear correlation

544   ($R^2 = 0.984$) between the $Mn^{3+}/(Mn^{4+}+Mn^{3+})$ ratios and the frequencies for certain internal

545   MnO_6 octahedral modes (Fig. 24). The highest frequency mode for chalcophanite and ranciéite

546   occur near 669 cm^{-1}. This mode is dominated by internal MnO_6 octahedral vibrations, and might

547   be expected to appear at high frequencies for phases where all Mn is tetravalent. In contrast,

548   one-third of the Mn in triclinic Na- and K-birnessite is trivalent, and the comparable modes for

549   these phases were observed near 638 cm^{-1}. Cation exchange of triclinic Na-birnessite can

550   significantly alter the Mn redox state. For example, substitution of interlayer Na^+ with Ca^{2+}

551   (Elmi et al 2020) and H^+ (Sylvester et al. 1997) will significantly reduce the $Mn^{3+}/(Mn^{4+}+Mn^{3+})$

552   ratio (Ilton et al. 2016). In our Raman spectra of Ca- and H-birnessite, the internal MnO_6

553   octahedral mode peaks were shifted to higher frequencies relative to those for K-, Na-, and Li-

554   birnessites. The high-frequency modes plot approximately along the same trend line, with some

555   uncertainty arising from the broadness of the associated Raman peaks. Additionally, for certain

556   phases, some or all the Mn^{3+} will be in the interlayer region above or below octahedral

557   vacancies, and this different bonding environment will likely modify (broaden) some Raman

558   features.

559

560   The observed correlation of $Mn^{3+}/(Mn^{4+}+Mn^{3+})$ with the highest frequency Raman modes

561   suggests that Raman spectroscopy might be used to assess the approximate Mn^{3+} concentration

562   for birnessite-like phases, or for comparing Mn oxidation state before and after, or monitoring

563   during, certain types of reactions. It also offers the potential of using Raman spectroscopy to

564   map differences in Mn oxidation state in environmental or other complex samples.

565

566   **Birnessite Symmetry**

567   There has been considerable interest in recent years in establishing methods to distinguish

568   triclinic and hexagonal birnessite-like samples, as the structural symmetry correlates with the

569   Mn^{3+} and Mn site vacancy concentrations, which determine certain types of chemical

570   reactivities, and can be an indicator of the formation mechanism, e.g. biotic or abiotic (Tebo et

571   al. 2004, Webb et al. 2005). Commonly, powder X-ray diffraction patterns of natural birnessites

572   show only a few broad peaks resulting from small crystallite sizes or possibly long-range

573   structural disorder that cannot provide definitive long- or short-range symmetry characterization.

574   In recent years, some researchers used specific, although sometimes subtle, differences in X-ray

575   absorption spectroscopy features to distinguish triclinic from hexagonal birnessite-like phases

576   (e.g. Webb, 2005). Others use pair distribution function modeling to assess the symmetry and

577   other structural details (Yang et al. 2019; Lee et al. 2019). A drawback of both approaches is

578   that data must be collected using synchrotron sources. Additionally, the results are not always

579   conclusive, and in most cases *in situ* measurements are not routine.

580   Our results suggest that Raman spectroscopy offers several advantages for determining

581   the structural symmetry for birnessite-like phases. In addition to not requiring a synchrotron

582   source, Raman spectroscopy routinely enables the investigation of samples *in situ* with ~1 μm

583 spatial resolution. Moreover, several features robustly differentiate between the spectra for

584 triclinic (Na-birnessite) and hexagonal birnessite (H- birnessite) phases (Fig. 11). The internal

585 MnO_6 octahedral modes between 500 and 650 cm^{-1} correspond to at least three partially

586 resolved peaks in the Na-birnessite spectrum, and typically less resolved for H-birnessite. The

587 prominent, low-frequency peaks below 500 cm^{-1} in the Na-birnessite spectrum are absent or

588 significantly weaker, or shifted, for H-birnessite (Fig. 11). The position of the highest frequency

589 mode for Na-birnessite is shifted to lower frequency by approximately 10 cm^{-1} relative to that

590 for H-birnessite, reflecting the greater concentrations of Mn^{3+} in Na-birnessites. Additionally,

591 Figure 11 shows that the relative intensities for the two highest frequency modes (at about 580-

592 590 and 640-650 cm^{-1}) are reversed in the hexagonal and triclinic birnessites, as previously

593 observed by Julien et al. (2003), Hsu (2011), Yang et al. (2015), Boumaiza (2019), and

594 Bernardini (2019). These distinctly different spectra indicate that Raman spectroscopy, using the

595 appropriate data collection conditions, is perhaps the most conclusive method for readily

596 distinguishing triclinic from hexagonal birnessite. Furthermore, information derived from

597 Raman peak frequencies, relative intensities, and widths provide opportunities to explore

598 detailed structural variations among different birnessite-like phases beyond a simple triclinic or

599 hexagonal designation. Our results complement the study by Ling et al. (2017) that demonstrated

600 Fourier transform infra-red spectra effectively distinguish hexagonal and triclinic birnessite-like

601 structures, but Raman offers the advantages of better resolved spectral features and *in situ*

602 microanalyses.

603

604 **Vernadite**

605   Vernadite is reported as a major phase in ocean Mn nodules and crusts, and as indicated

606   above, is widely assumed to be a birnessite-like phase for which the basal reflection is largely

607   absent in powder X-ray diffraction patterns. The missing basal reflection is thought to arise

608   either from turbostratically disordered layer stacking, from crystallites with so few layers that

609   interference effects are minimized, or a combination of both of these factors. The phase is

610   characterized by a diffraction pattern showing broad peaks at ~2.44 and 1.45 Å. Synthetic

611   samples that exhibit similar XRD patterns are commonly referred to as δ-MnO$_2$ and are assumed

612   to be analogues of vernadite. The unpolarized Raman spectrum from an ocean Mn crust that

613   gave an XRD pattern consistent with vernadite is shown in Figure 25 along with spectra for

614   hexagonal birnessite, synthetic δ-MnO$_2$, and asbolane. The natural vernadite spectrum most

615   closely resembles that for asbolane, or perhaps a mixture of asbolane and hexagonal birnessite,

616   and is distinctly different from that of δ-MnO$_2$ (Villalobos et al. 2003), which is more similar to

617   that of hexagonal birnessite. This observation brings into question the assumption that δ-MnO$_2$

618   is always an appropriate analogue for vernadite. The issue is complicated by the fact that there

619   are reported variations in composition, and presumably structures, for vernadites. In addition,

620   different synthesis methods and treatments have been employed to produce "δ-MnO$_2$" phases,

621   which are not always identical. Lee et al. (2019) concluded from their TEM and PDF studies of

622   ocean crust vernadite that this phase is best modeled by interstratified structures with 7 and 10 Å

623   interlayer spacings. Our preliminary results suggest that Raman spectroscopy is a useful tool for

624   characterizing and comparing similarities and differences among natural vernadites and synthetic

625   δ-MnO$_2$ phases. More in-depth Raman studies of a range of natural and synthetic vernadite-like

626   phases is ongoing.

627

628   **IMPLICATIONS**

629   We present here a comprehensive Raman spectroscopy study of layer structure Mn oxide

630   phases from a large assortment of well-characterized natural and synthetic samples, using a

631   variety of data collection conditions (Fig. 22). We demonstrate here and in our previous study of

632   tunnel structure Mn oxides that when using multiple lasers, especially at 785 and 633 nm

633   wavelengths, with low laser powers at the sample (30 – 500 µW, depending upon the laser

634   wavelength and the sample), we were able to consistently identify the Mn oxide phases for most

635   samples. In particular, it is routinely possible to distinguish phases with large tunnels from those

636   with layers (Fig. 23). Additionally, for birnessite-like phases, we observed that the position of

637   the highest frequency Raman mode correlates with $Mn^{3+}/(Mn^{4+}+ Mn^{3+})$, suggesting that Raman

638   spectroscopy might be an effective tool for assessing approximate absolute and relative

639   Mn^{3+} concentrations in this important group of phyllomanganates. With the comprehensive

640   Raman database of well-characterized Mn oxide standards from Post et al (2020), and provided

641   here and as supplementary data[1] with the *American Mineralogist*, micro-Raman is a powerful

642   tool for identification and characterization of biotic and abiotic Mn oxide phases from diverse

643   natural settings, and thereby can provide new insights into the roles of these phases in our

644   environment and on other planets. Current plans for the next NASA Mars lander include a

645   Raman system, where one of the primary targets will be black rock coatings that resemble rock

646   varnishes on Earth (Marnocha 2017). As Mn oxides in terrestrial varnishes are thought to be

647   biologically precipitated (McKeown and Post 2001; Northup et al. 2010; Marnocha and Dixon

648   2014), Raman identification of similar appearing Mn oxide minerals on Mars might be

649   interpreted as indicators of past or possibly current biotic processes on Mars (Marnocha 2017).

650   A comprehensive database of high-quality Raman spectra from well-characterized Mn oxide

651 minerals will be useful for such Martian studies. Additionally, the method is equally applicable

652 for identification and characterization of laboratory produced Mn oxides and those used

653 industrially.

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936   all readers and found on the MSA website, via the specific issue's Table of Contents (go to

937   http://www.minsocam.org/MSA/AmMin/TOC/20XX/XXXX_data/ XXXX_data.html).

938

939

FIGURE CAPTIONS

941

942 **Figure 1.** Polyhedral drawings of manganese oxide layer structures. The blue octahedra contain

943 Mn; in chalcophanite, the green octahedra contain Zn, and for lithiophorite the magenta

944 octahedra are 2/3 Al and 1/3 Li. The yellow spheres in the birnessite structure represent

945 disordered Na atoms and water molecules.

946

947 **Figure 2.** Raman spectra (633 nm) for chalcophanite (NJ #C1814) with plate-like crystals (and

948 MnO_6 octahedral sheets) perpendicular to incident laser light direction. Spectra are labeled

949 Unpolarized (black), VV (blue), and VH (red). VV and VH spectra were collected using parallel

950 and crossed polarization conditions, respectively.

951

952 **Figure 3.** Raman spectra for chalcophanite (NJ #C1814) collected using 532 (0.03 mW), 633

953 (0.05 mW) and 785 (0.11 mW) nm laser light. Spectra are rescaled and offset for clarity.

954

955 **Figure 4.** Raman spectra (532 nm) for chalcophanite (NJ #C1814), ernienickelite (#171561), and

956 jianshuiite (MD) with plate-like crystals (and MnO_6 octahedral sheets) parallel to laser

957 polarization (laser light direction perpendicular to plate-like crystals).

958

959 **Figures 5a and b.** Raman spectra (532 nm) for: a) chalcophanite (NJ #C1814) with crystals

960 oriented with MnO_6 octahedral sheets parallel (top) and perpendicular (bottom) to the laser

961 polarization direction, and b) chalcophanite (NJ #C1814) and ernienickelite (#171561) showing

962   OH stretch modes with the polarization symbol indicating laser polarization perpendicular to the

963   MnO_6 octahedral sheets (or laser light direction parallel to MnO_6 octahedral sheets).

964

965   **Figure 6a and b.** a) Raman modes determined from lattice dynamics (LD) calculations for

966   chalcophanite (#C1814) plotted as vertical lines below their respective Raman spectra (633 nm),

967   and b) an eigenmode drawing of the highest calculated frequency Ag mode for chalcophanite:

968   (110) projection with the c-axis vertical, showing MnO_6 octahedral deformation, O-Mn-O bend

969   and Mn-O stretch, and Zn-O stretch with Zn translating along the c-axis.

970   **Figure 7.** Raman spectra (633 nm) for rancieite (#128319) with plate-like crystals (and MnO_6

971   octahedral sheets) perpendicular to incident laser light direction. Spectra labeled VV and VH

972   were collected using parallel and crossed polarization conditions, respectively.

973

974   **Figure 8.** Raman spectra for rancieite (#128319) collected using 532 (0.03 mW), 633 (< 0.1

975   mW) and 785 (0.11 mW) nm laser light. Spectra are rescaled and offset for clarity.

976

977   **Figure 9.** Raman spectra (785 nm) for a variety of different rancieite specimens. Locations and

978   specimen numbers are indicated (see Table 1). Samples were flattened such that MnO_6

979   octahedral sheets were perpendicular to incident laser light direction. Spectra are rescaled and

980   offset for clarity.

981

982   **Figure 10**. Raman modes determined from LD calculations for rancieite (#128319) plotted as

983   vertical lines below their respective Raman spectra (633 nm laser light).

984

985   **Figure 11a. and b.** Raman spectra for synthetic triclinic Na-birnessite and synthetic hexagonal

986   birnessite, with plate-like crystals (and MnO_6 octahedral sheets) perpendicular to incident laser

987   light direction, using a) 633 nm and b) 785 nm laser light. Spectraare rescaled and offset for

988   clarity.

989

990   **Figure 12a. and b**. a) Raman spectra for Na-birnessite collected using 532 (0.03 mW), 633 (<

991   0.1 mW) and 785 (0.11 mW) nm laser light, and b) Raman spectra (633 nm) for Na-birnessite

992   using different laser power levels at the sample (each measurement was from a different, but

993   nearby point on the sample). Sample alteration is evident at incident powers above 0.1 mW.

994   Sample alteration at 0.15 mW can result in different mixtures of phases as shown for two

995   different points on the sample. Spectra are rescaled and offset for clarity.

996

997   **Figure 13**. Na-birnessite Raman modes determined from LD calculations for the simplified

998   C2/m monoclinic structure plotted as vertical lines below their respective Raman features in the

999   785 nm spectrum.

1000

1001   **Figure 14.** Raman spectra (785 nm) for a variety of synthetic birnessite specimens with different

1002   interlayer cations (see Table 1). Samples were flattened such that MnO_6 octahedral sheets were

1003   perpendicular to incident laser light direction. Spectra are rescaled and offset for clarity.

1004

1005

1006 **Figure 15.** Raman spectra (633 nm) for vernadite (Pacific ocean crust), with plate-like crystals

1007 (and MnO_6 octahedral sheets) perpendicular to incident laser light direction. Spectra labeled VV

1008 and VH were collected using parallel and crossed polarization conditions, respectively.

1009

1010

1011 **Figure 16.** Polarized Raman spectra (514.5 nm) for lithiophorite (#162391), with plate-like

1012 crystals (and MnO_6 octahedral sheets) perpendicular to incident laser light direction and parallel

1013 to the laser polarization. Spectra labeled VV and VH were collected using parallel and crossed

1014 polarization conditions, respectively.

1015

1016 **Figure 17.** Raman spectra for lithiophorite (#162391) collected using 532 (0.03 mW), 633 (< 0.1

1017 mW) and 785 (0.11 mW) nm laser light. Spectra are rescaled and offset for clarity.

1018

1019 **Figure 18**. Raman modes determined using lattice dynamics (LD) calculations for lithiophorite

1020 (#162391) structure; the calculated mode frequency for each mode is plotted as a vertical line

1021 below their respective Raman spectra (514.5 nm laser light).

1022

1023 **Figure 19.** Raman spectra (785 nm laser light) for a variety of different asbolane specimens

1024 (Table 1). The Co/Mn (Table 1) in the samples increases from the top to bottom spectrum.

1025 Spectra are rescaled and offset for clarity.

1026

1027   **Figure 20.** Raman spectra (633 nm) for synthetic feitknechtite. Spectra labeled VV and VH

1028   were collected using parallel and crossed polarization conditions, respectively.

1029

1030   **Figure 21.** Raman spectra for feitknechtite collected using 532 (0.03 mW), 633 (< 0.1 mW) and

1031   785 (0.11 mW) nm laser light. Spectra are rescaled and offset for clarity.

1032

1033   **Figure 22.** Raman spectra for a variety of phyllomanganates, ordered from top to bottom

1034   according to decreasing Mn3+/(Mn4++Mn3+). Specimens measured are: chalcophanite

1035   (R12334), rancieite Austria, synthetic Ca-birnessite, synthetic Na-birnessite, synthetic hexagonal

1036   birnessite, and lithiophorite (162391) (Table 1). Spectra are rescaled and offset for clarity.

1037

1038   **Figure 23.** Raman spectra for a variety of layer- and tunnel-structure Mn oxide phases. Tunnel

1039   structure Mn-oxide spectra originally presented in the tunnel Mn-oxide study, Post et al. (2020);

1040   samples: cryptomelane (NMNH 89104), romanechite (NMNH R2232), todorokite (HU 126232).

1041   Layer structure spectra from: chalcophanite (R12334), rancieite Austria, synthetic Na-birnessite,

1042   synthetic hexagonal birnessite, and lithiophorite (162391). Spectra are rescaled and offset for

1043   clarity.

1044

1045   **Figure 24.** $Mn^{3+}/(Mn^{3+}+Mn^{4+})$ ratio versus Raman shift frequency of the highest frequency

1046   vibrational mode for the different phyllomanganates included in this study.

1047

1048   **Figure 25.** Raman spectra (785 nm) for vernadite (Pacific ocean crust), asbolane (#103709),

1049   synthetic hexagonal birnessite (pH 2), and synthetic δ-MnO$_2$. Spectra are rescaled and offset for

1050   clarity.

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1059   **Table 1 Specimens used for Raman Spectroscopy**

Mineral	Specimen #	Locality	Chemical Formula
Chalcophanite	C1814	Sterling Hill mine, NJ	$ZnMn_3O_7 \cdot 3H_2O$
	R12334	Bisbee, AZ	$ZnMn_3O_7 \cdot 3H_2O$
Ernienickelite	171561	Kalgoorlie-Boulder Shire, Australia	$NiMn_3O_7 \cdot 3H_2O$
Jianshuiite		Medford Quarry, MD	$MgMn_3O_7 \cdot 3H_2O$

Rancieite		Friesach, Austria	$Ca_{0.19}K_{0.01}(Mn^{4+}_{0.91}\square_{0.09})O_2 \cdot 0.63H_2O$
	128318	Rancie Mtn., France	$Ca_{0.14}Mg_{.04}Ba_{.01}K_{0.01}(Mn^{4+}_{0.87}Zn_{.06}\square_{0.07})O_2 \cdot 0.63H_2O$
	29.74	Alsace, France	$Ca_{0.16}Mg_{.01}Ba_{.01}K_{0.01}(Mn^{4+}_{0.91}\square_{0.09})O_2 \cdot 0.63H_2O$
		Spain	$Ca_{0.13}Mg_{.04}Ba_{.02}K_{0.01}(Mn^{4+}_{0.91}\square_{0.09})O_2 \cdot 0.63H_2O$
Na-birnessite		Synthetic[a]	$Na_{0.58}(Mn^{4+}_{1.34}Mn^{3+}_{0.66})O_4 \cdot 1.4H_2O$
K-birnessite		Synthetic[a]	$K_{0.58}(Mn^{4+}_{1.34}Mn^{3+}_{0.66})O_4 \cdot 1.4H_2O$
Li-birnessite		Synthetic[a]	$Li_{0.58}(Mn^{4+}_{1.34}Mn^{3+}_{0.66})O_4 \cdot 1.4H_2O$
Ba-birnessite		Synthetic[a]	$Ba_{0.29}(Mn^{4+}_{1.34}Mn^{3+}_{0.66})O_4 \cdot 1.6H_2O$
Ca-birnessite		Synthetic[a]	$Ca_{0.30}(Mn^{4+}_{1.34}Mn^{3+}_{0.50}\square_{0.16})O_4 \cdot 1.6H_2O$
Hex-birnessite		Synthetic (pH 2)[b]	$Mn^{3+}_{0.2}(Mn^{4+}_{1.34}Mn^{3+}_{0.66}\square_{0.09})O_4 \cdot 1.6H_2O$
Vernadite		Pacific Ocean crust	$Na_{0.47}Ca_{.28}Mg_{.16}K_{0.03}(Fe_{1.18}Si_{.28}Al_{.07}Ti_{.09}\square)(Mn^{4+},Mn^{3+})_2O_4 \cdot nH_2O$
δ-MnO$_2$		Synthetic[c]	$(Na_{.09}Mn^{3+}_{.08}K_{.07})(Mn^{4+}_{.70}Mn^{3+}_{.26}\square_{.04})O_2 \cdot nH_2O$
Feitknechtite[d]		Synthetic	$Mn(OH)_3$ (assumed)
Lithiophorite	162391	Postmasburg, South Africa	$(Al_{0.67}Li_{0.33})(Mn^{4+}_{0.67}Mn^{3+}_{0.33})O_2(OH)_2$
		Georgia, USA	$(Al_{0.80}Co_{0.08})(Mn)O_2(OH)_x$
	46158	Rengersdorf, Germany	$(Al_{.75}Si_{.09}Co_{.06}Ni_{.03})MnO_2(OH)_x$
Asbolane	97579	Kasaigaigori, Japan	$(Al_{.79}Co_{.34}Fe_{.04})MnO_2(OH)_x$

	103709	La Motte mi., Missouri	$(Co_{.69}Cu_{.24}Ni_{.10}Zn_{.04}Al_{.04})MnO_2(OH)_x$
	R2247	Sachsen, Germany	$(Al_{.78}Co_{.14}Fe_{.22})MnO_2(OH)_x$
	R9752	Schneeberg, Germany	$(Al_{.47}Co_{.04}Fe_{.05})MnO_2(OH)_x$

1060 a –Na-birnessite synthesized and sample exchanged with respective interlayer cation following

1061 method of Golden et al (1986)

1062 b – Hexagonal birnessite formed by reacting Na-birnessite with pH 2 HCl solution.

1063 c – sample provided by M. Zhu, synthesized using method of Villilobos et al. (2003)

1064 d – sample provided by E. Elzinga

1065 Note: Li content for lithiophorite from South Africa determined by single crystal X-ray structure

1066 refinement by Post and Appleman (1994); Li concentrations were not determined for other

1067 lithiophorite and asbolane samples. Asbolane cation values were normalized to one Mn.

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1070   Table 2. Factor group analysis (FGA) results of the tunnel structure-type Mn-oxides phases. Γ_{optic}

1071   includes Raman- and IR-active modes; three $\Gamma_{acoustic}$ modes are indicated for each phase. The

1072   space group of each phase are listed in Hermann-Mauguin notations.

Phase	**Space Group:**	**FGA**
Lithiophorite	R-3m (#166)	$\Gamma = 3A_{1g} + 3E_g + 5A_{2u} + 5E_u$ $\Gamma_{Acoustic}: A_{2u}(z) + E_u(xy)$
Chalcophanite	R-3 (#148)	$\Gamma = 14A_g + 14E_g + 14A_u + 14E_u$ $\Gamma_{Acoustic}: A_u(z) + E_u(xy)$
Na-Birnessite	C-1 (#2)	$\Gamma = 6A_g + 6A_u$ $\Gamma_{Acoustic}: 3A_g$
Rancieite	P -3	$\Gamma = 5A_g + 5E_g + 5A_u + 5E_u$ $\Gamma_{Acoustic}: A_u + E_u$

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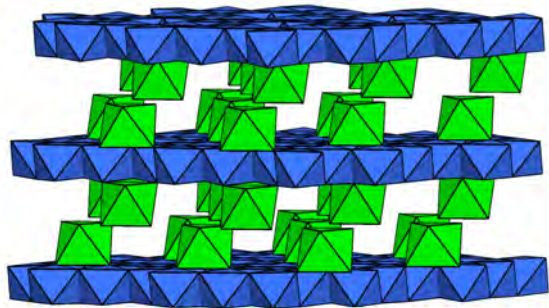
Chalcophanite

Na-Birnessite
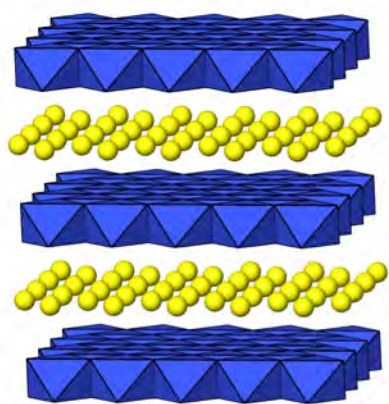
Lithiophorite

Figure 1

Fig. 2

Chalcophanite
Unpolarized

532 nm

633 nm

785 nm

Counts

500

0

0   200   400   600   800   1000   1200

Raman Shift (cm^{-1})

Fig. 3

Unpablarized
(λ = 532 nm)

Ernienickelite (Ni^{2+})

Jianshuiite (Mg^{2+})

Chalcophanite (Zn^{2+})

Counts

Raman Shift (cm^{-1})
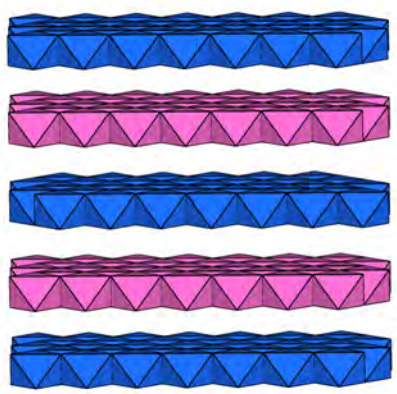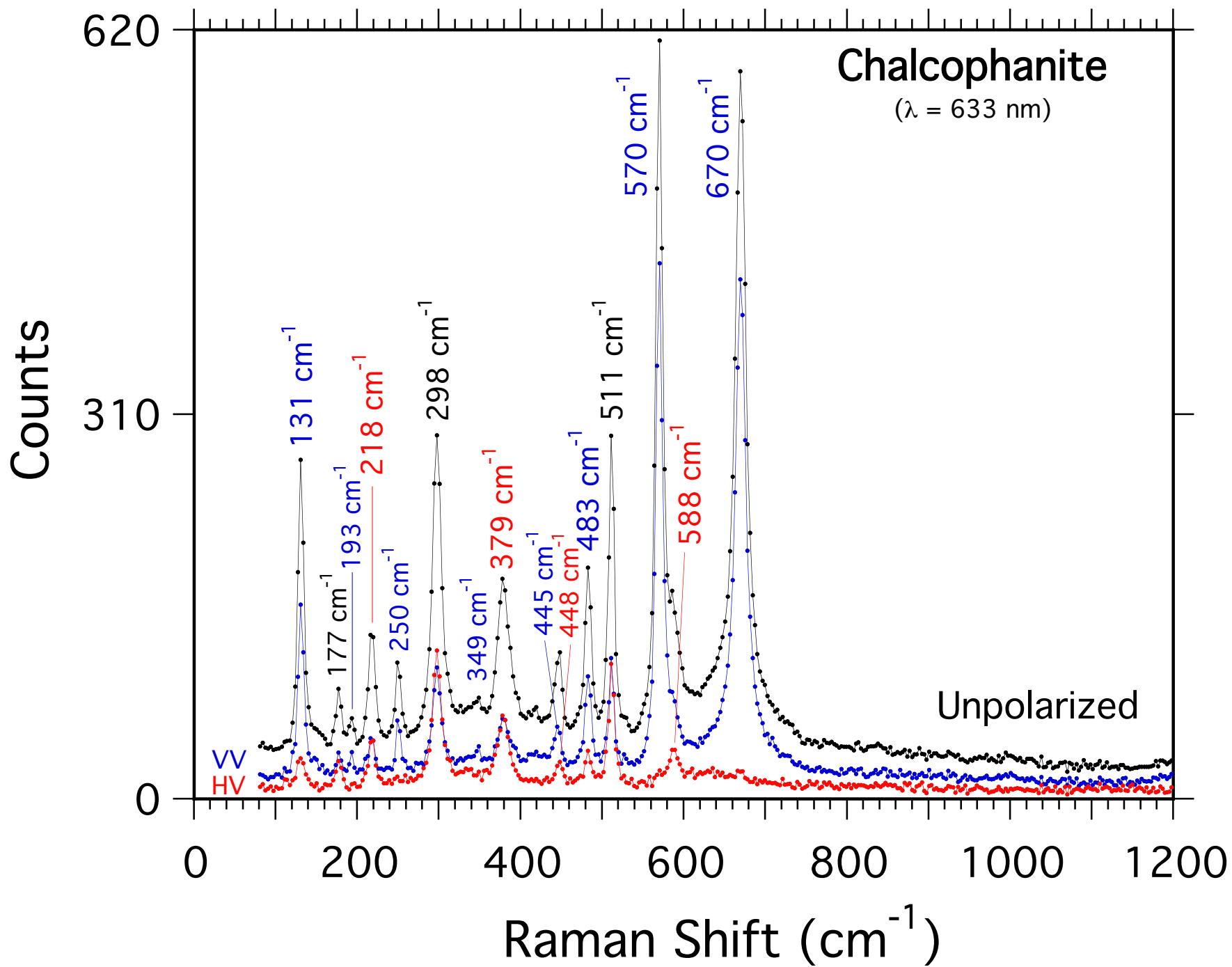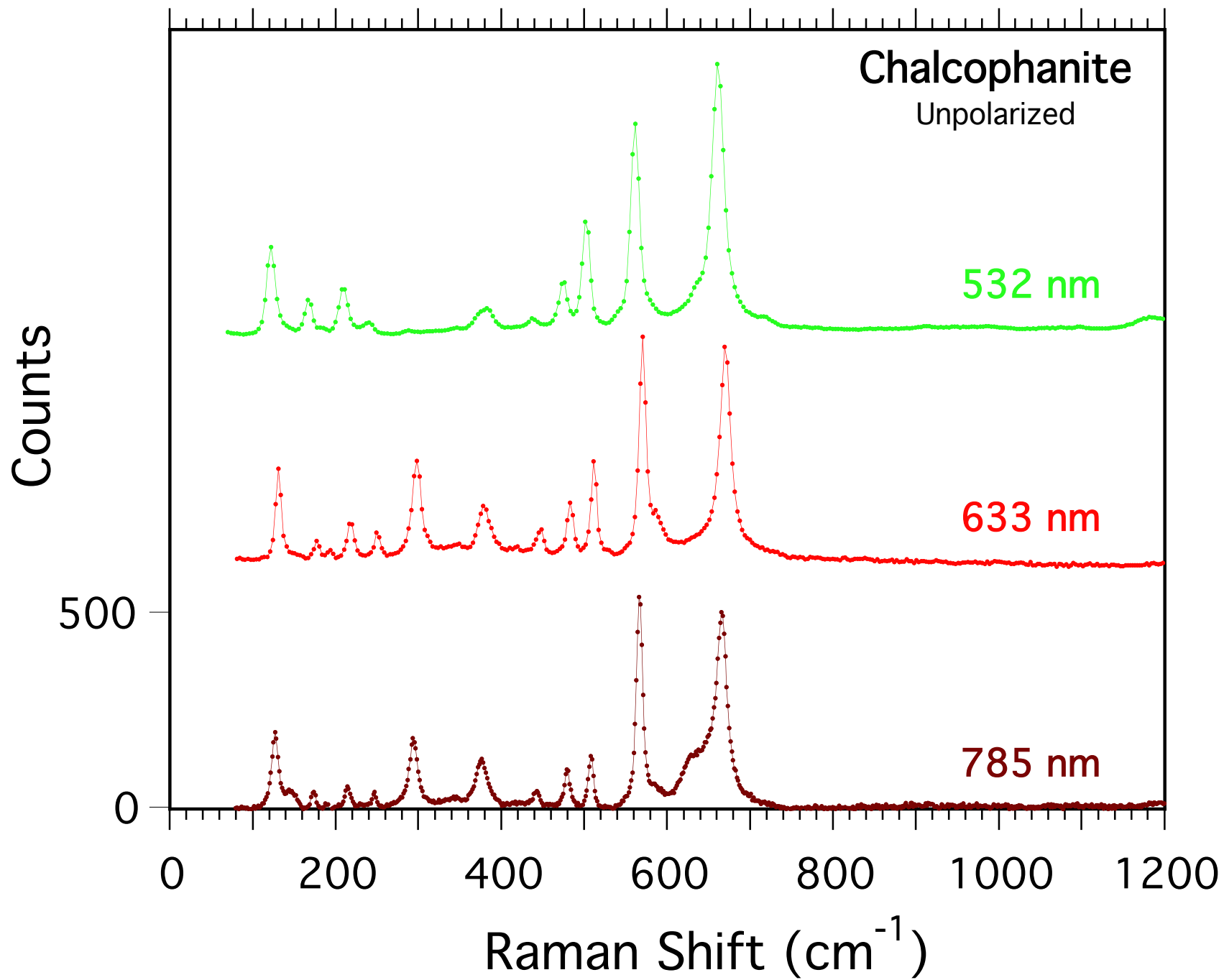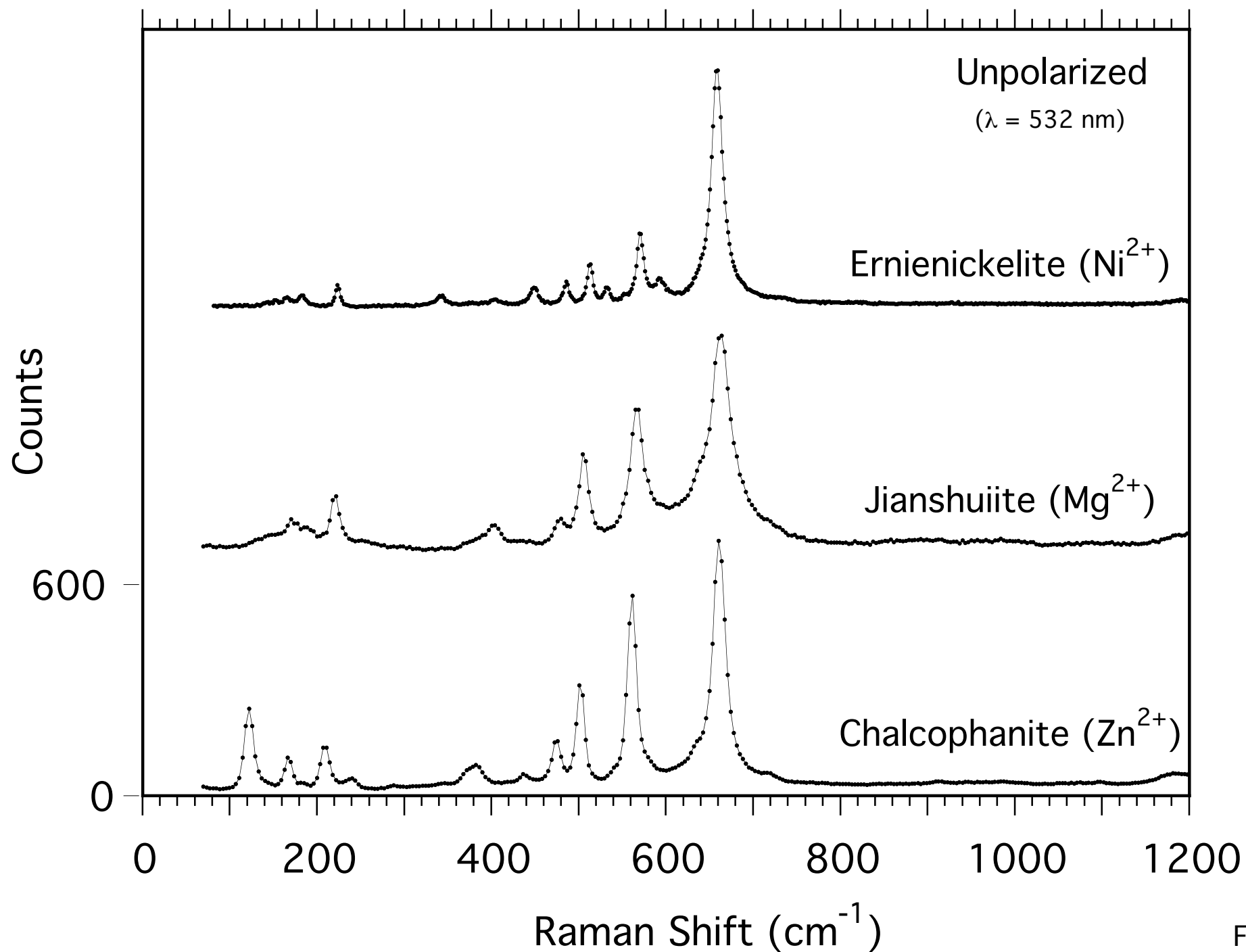
Fig. 4
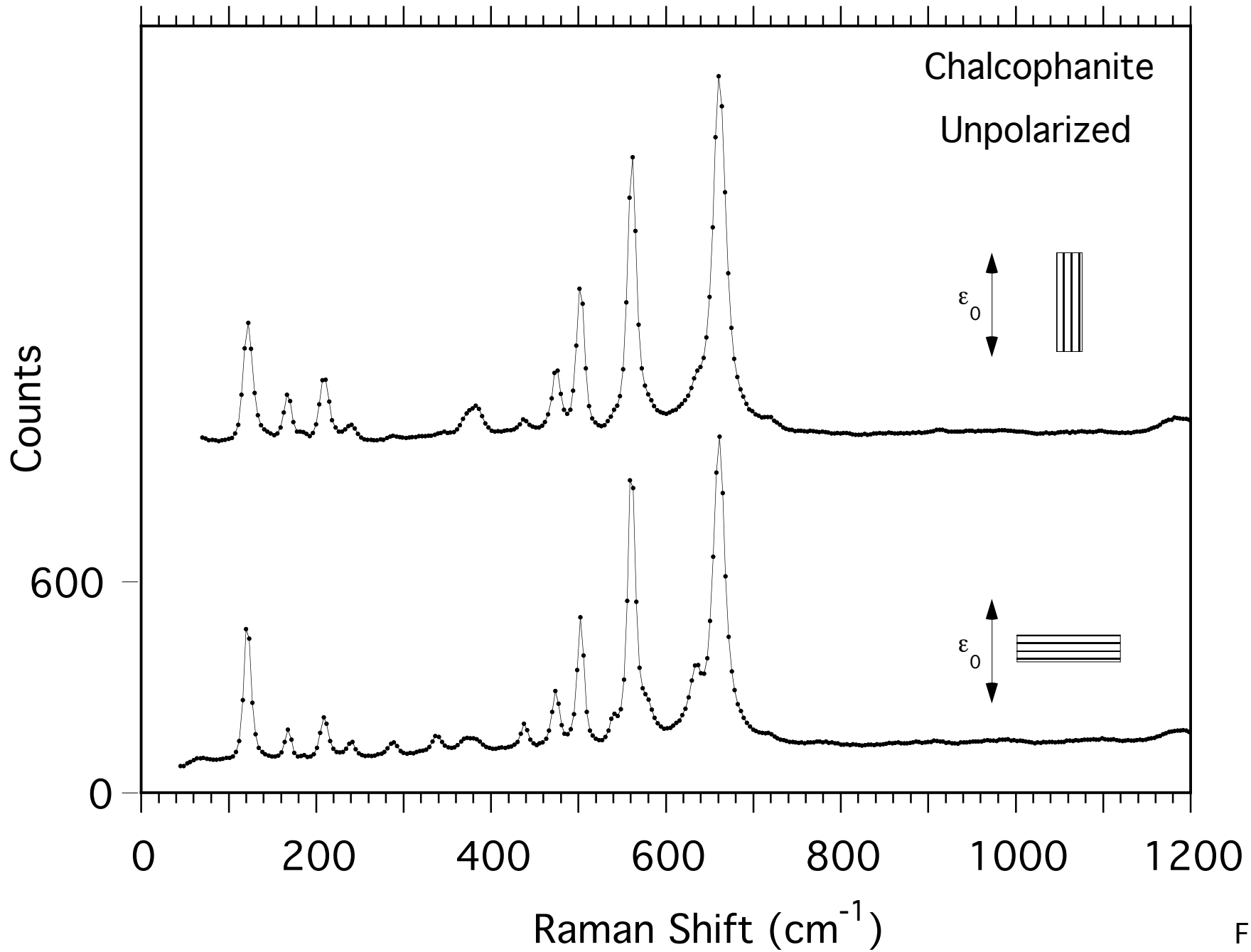
Fig. 5a
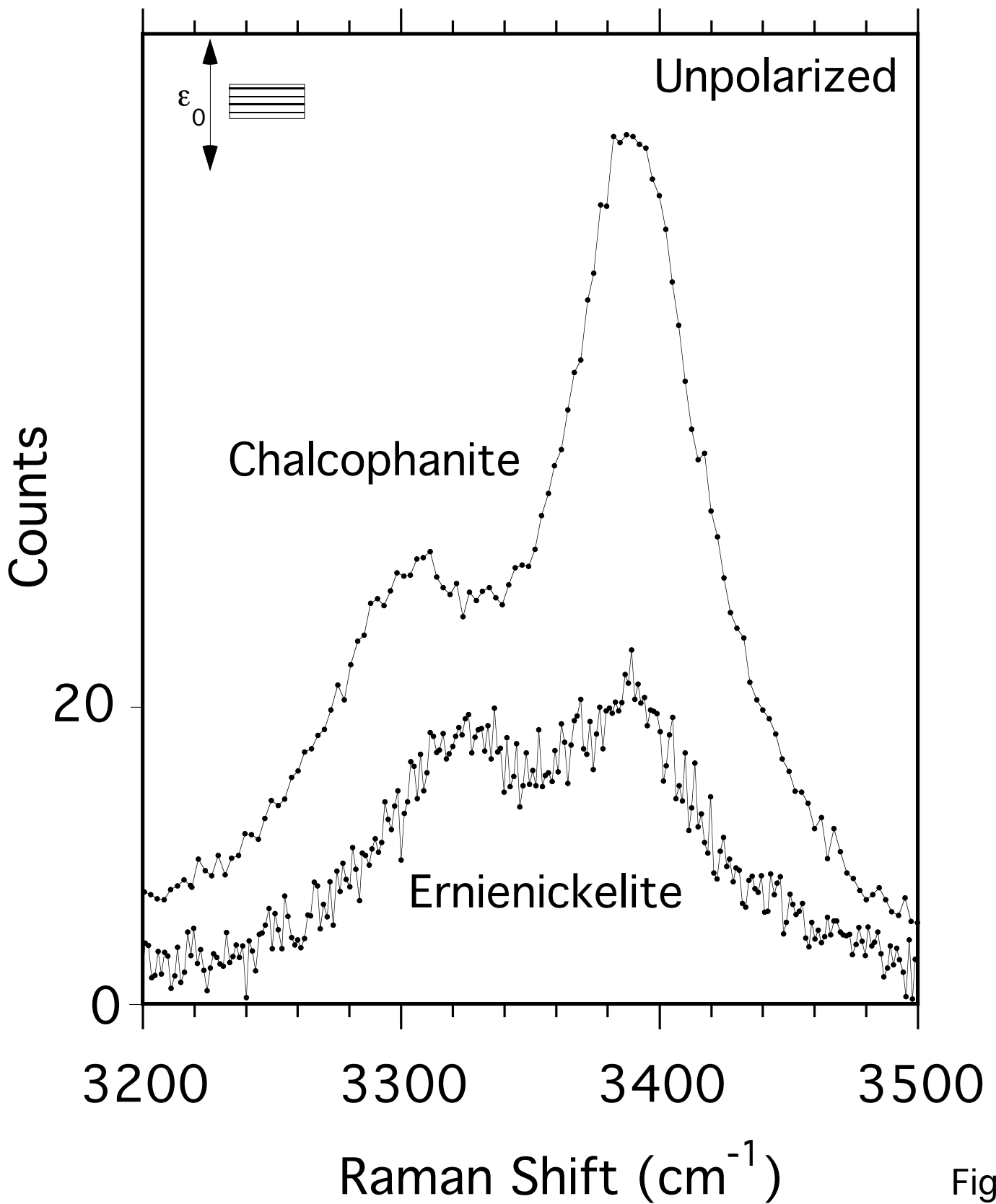
Fig. 5b
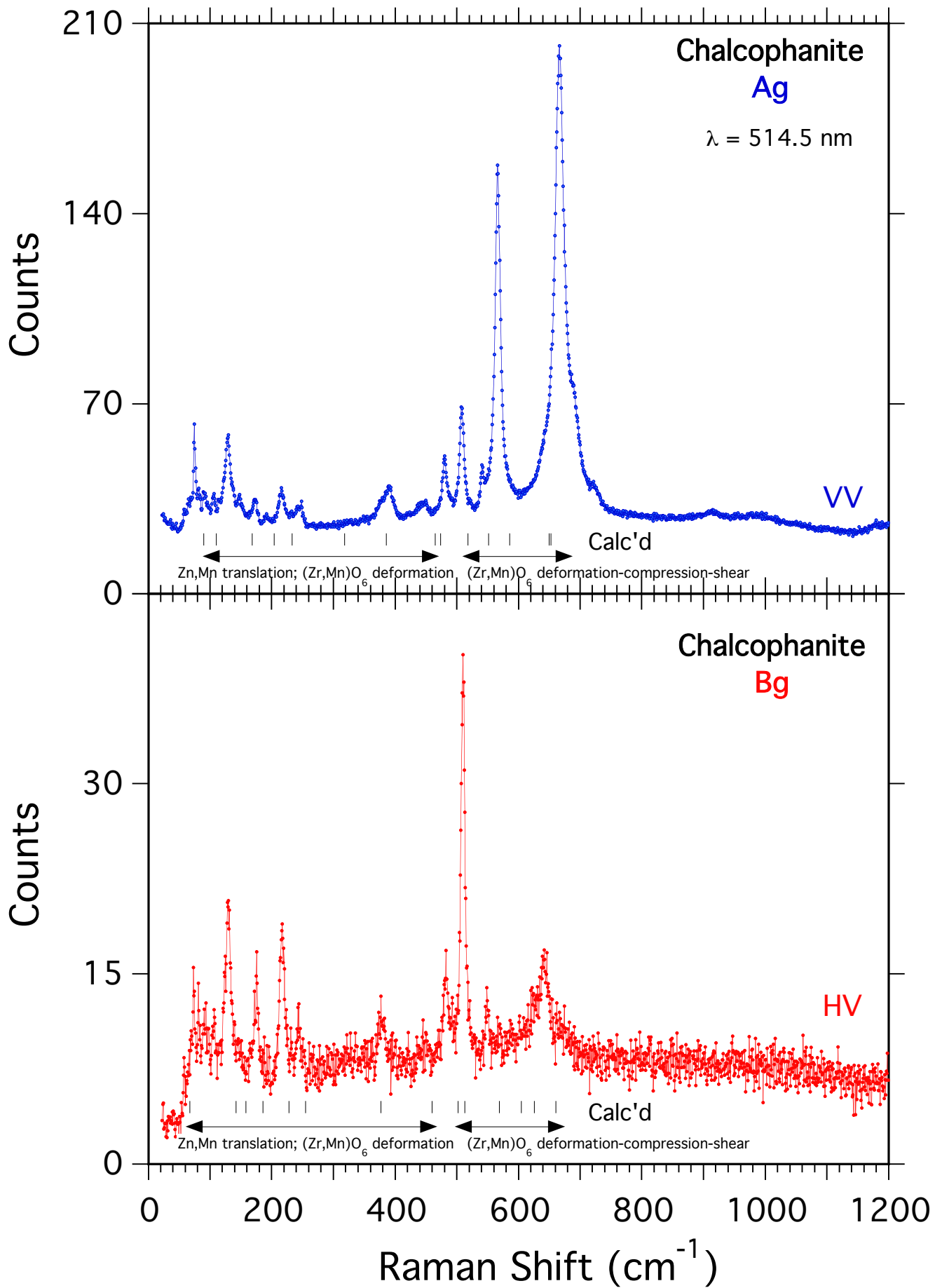
Fig. 6a

Chalcophanite

653 cm^{-1} Ag

Fig. 6b

Fig. 7

Rancieite
Unpolarized

532 nm

633 nm

785 nm

Counts

Raman Shift (cm^{-1})
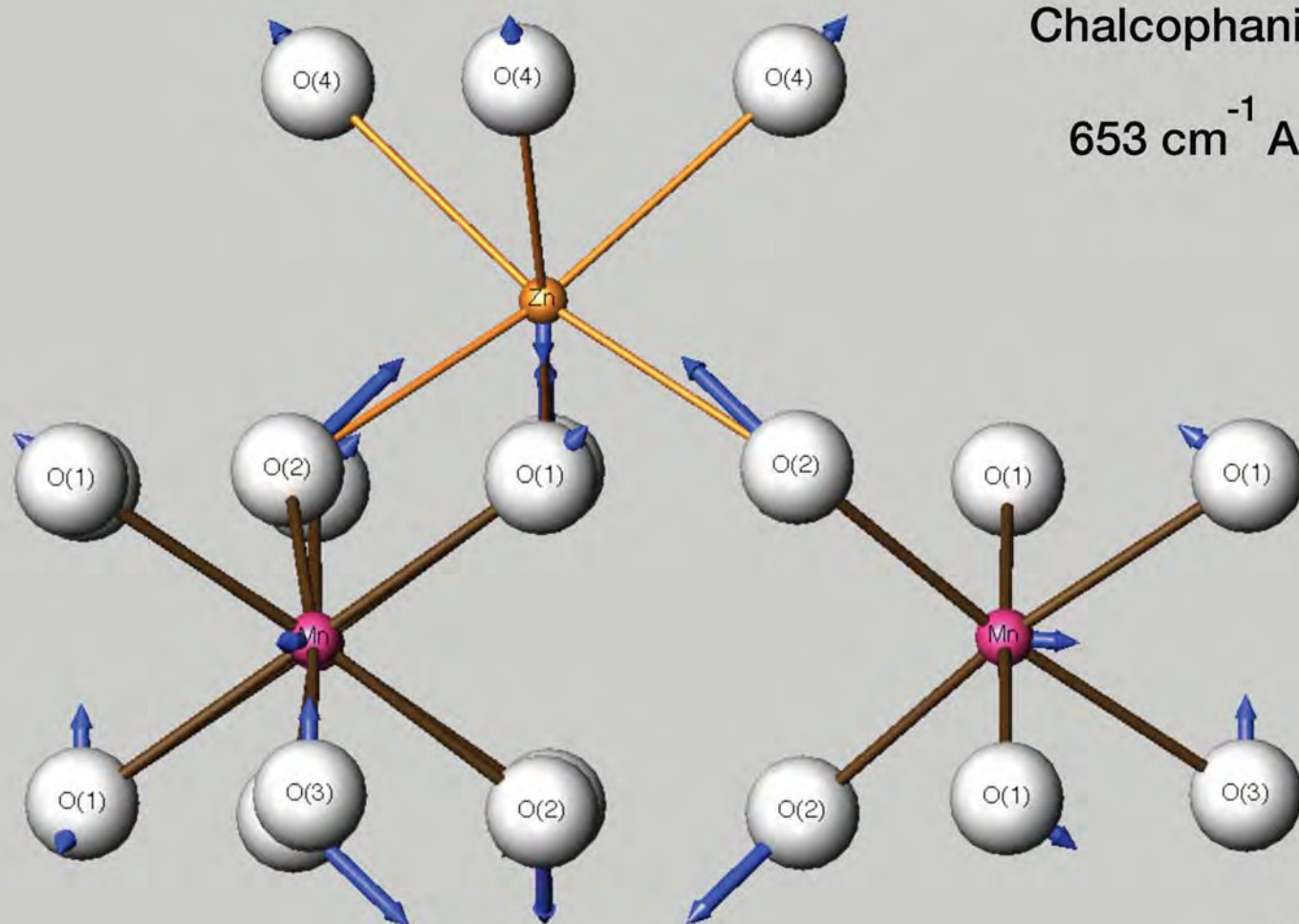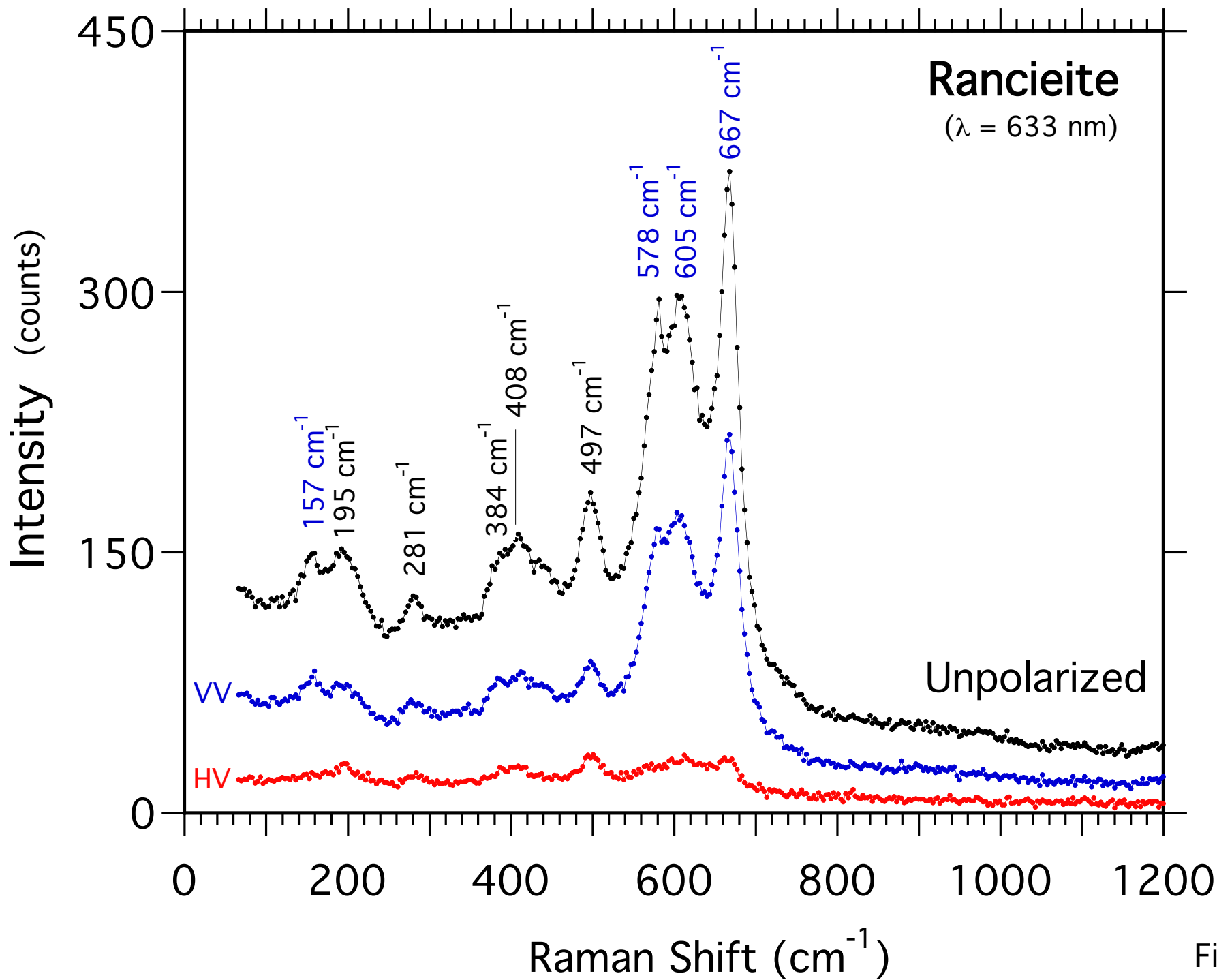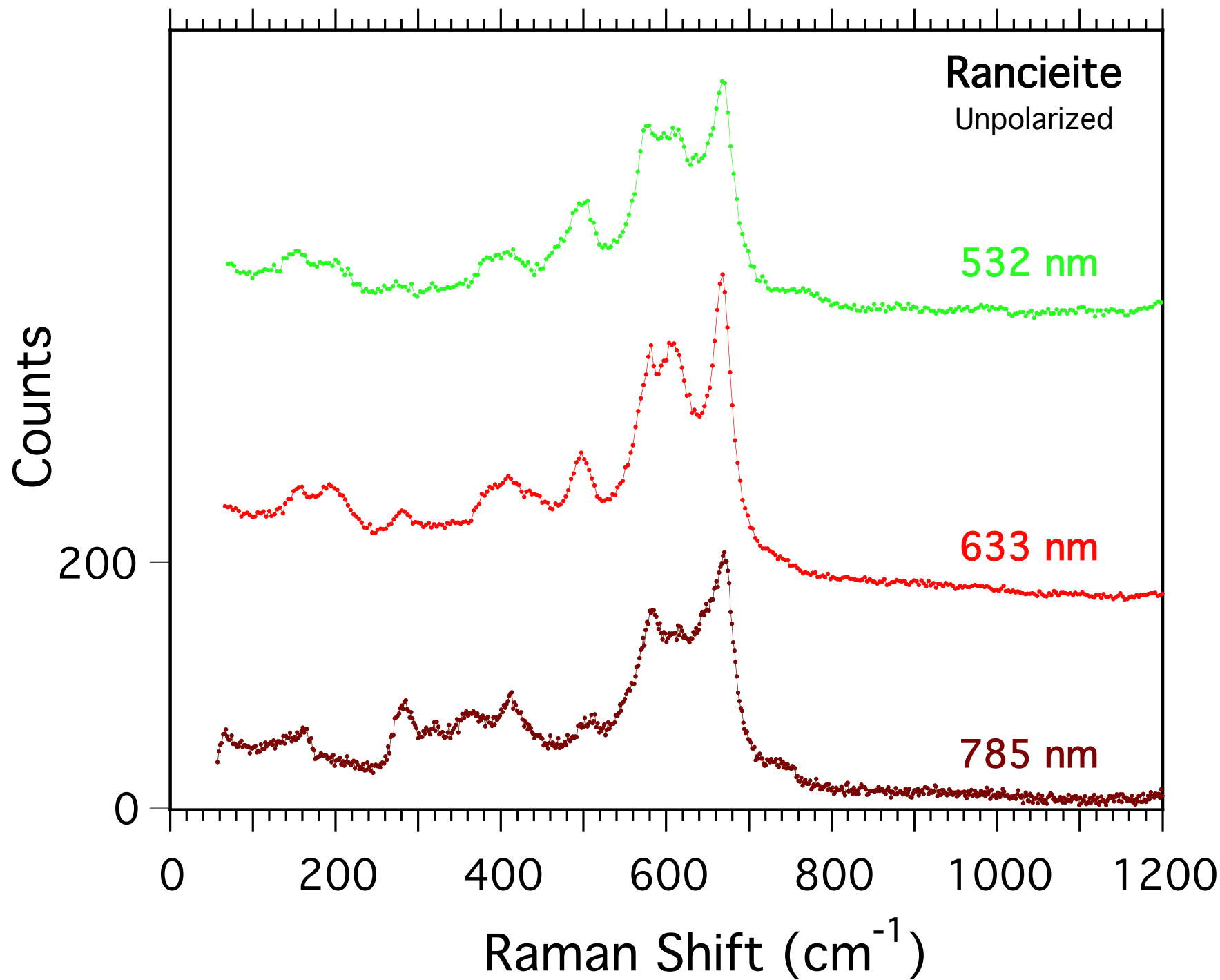
Fig. 8
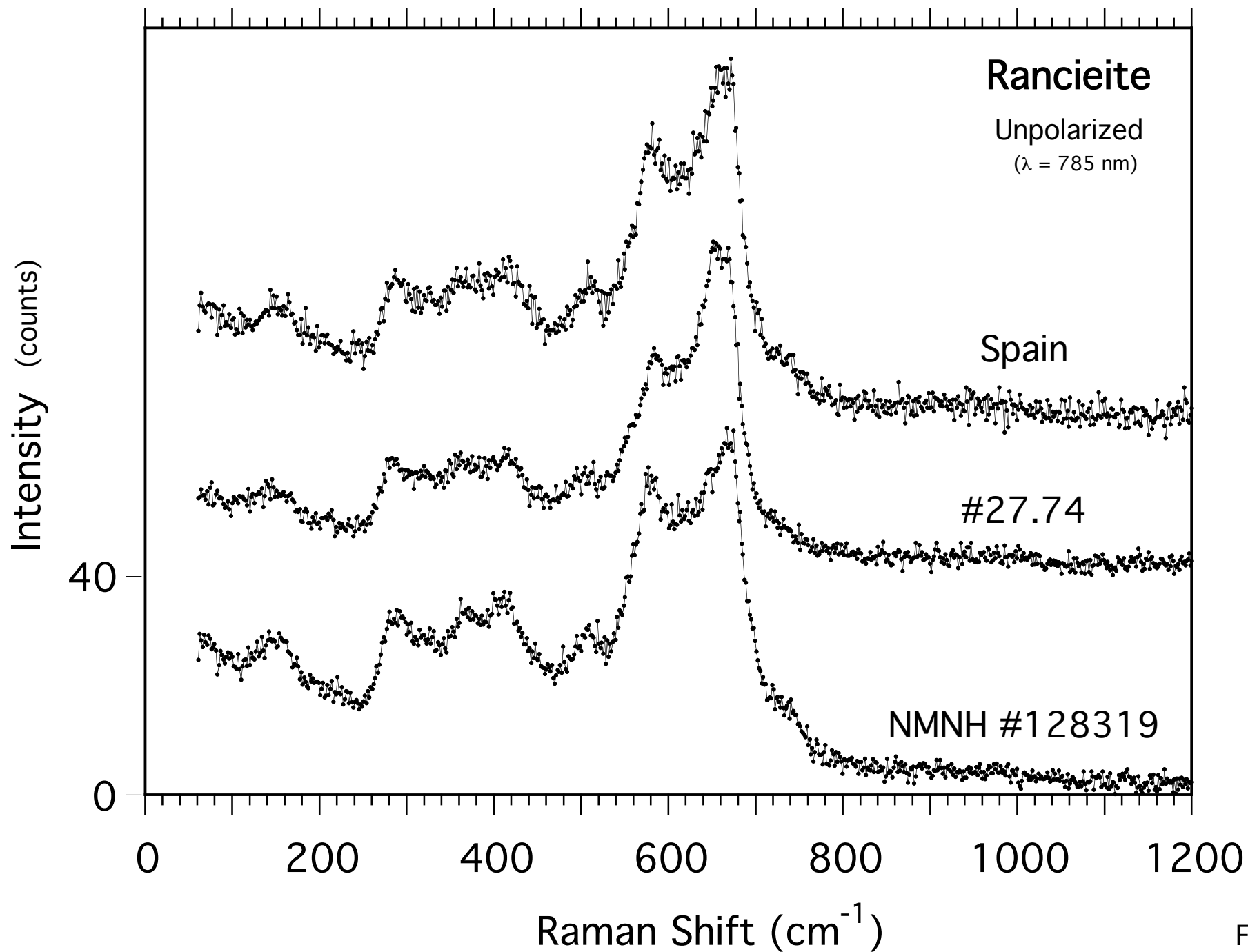
Fig. 9

Fig. 10

Fig. 11a

Fig. 11b

Na-Birnessite
Unpolarized

457.9 nm

633 nm

785 nm

Counts

Raman Shift (cm^{-1})
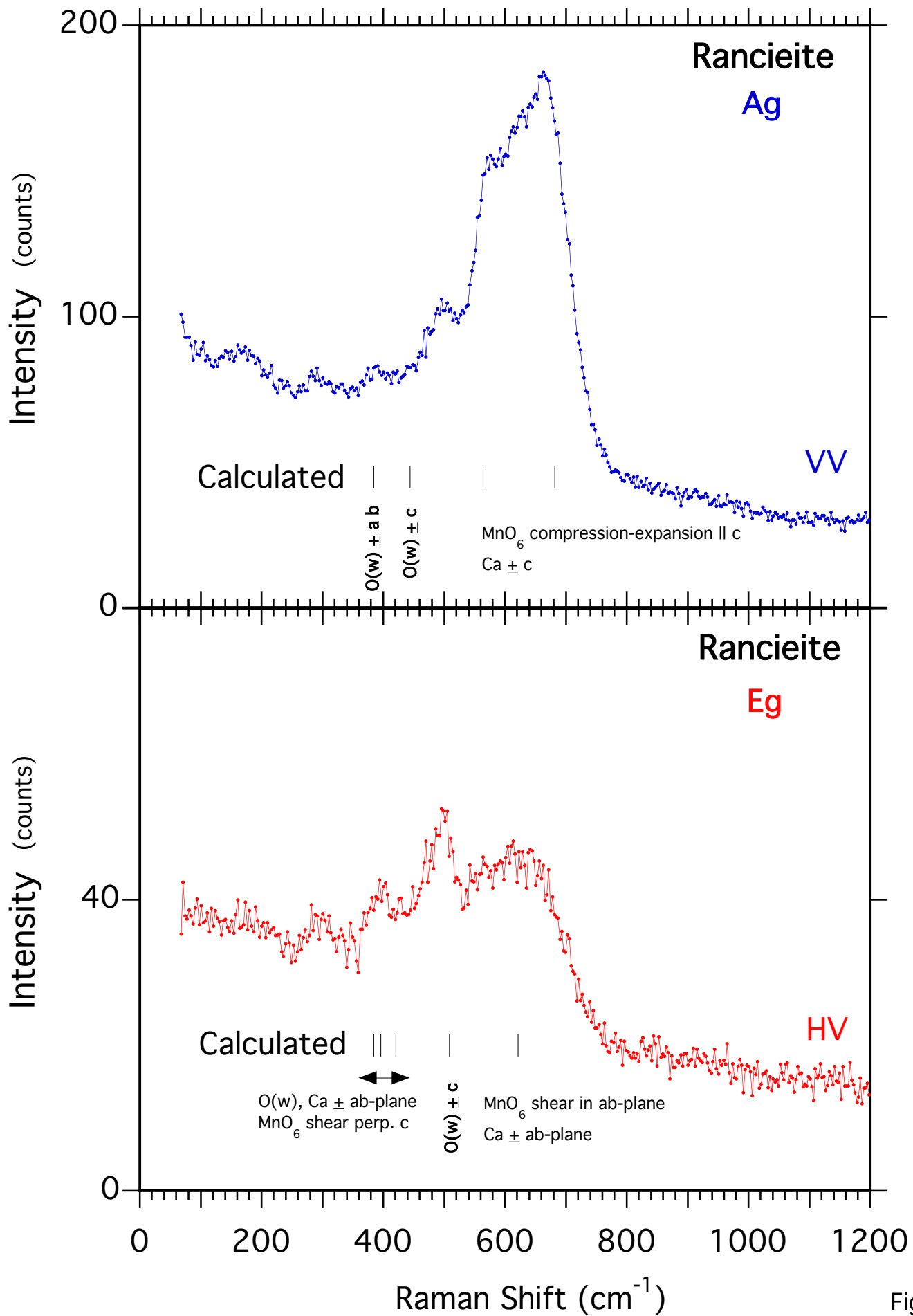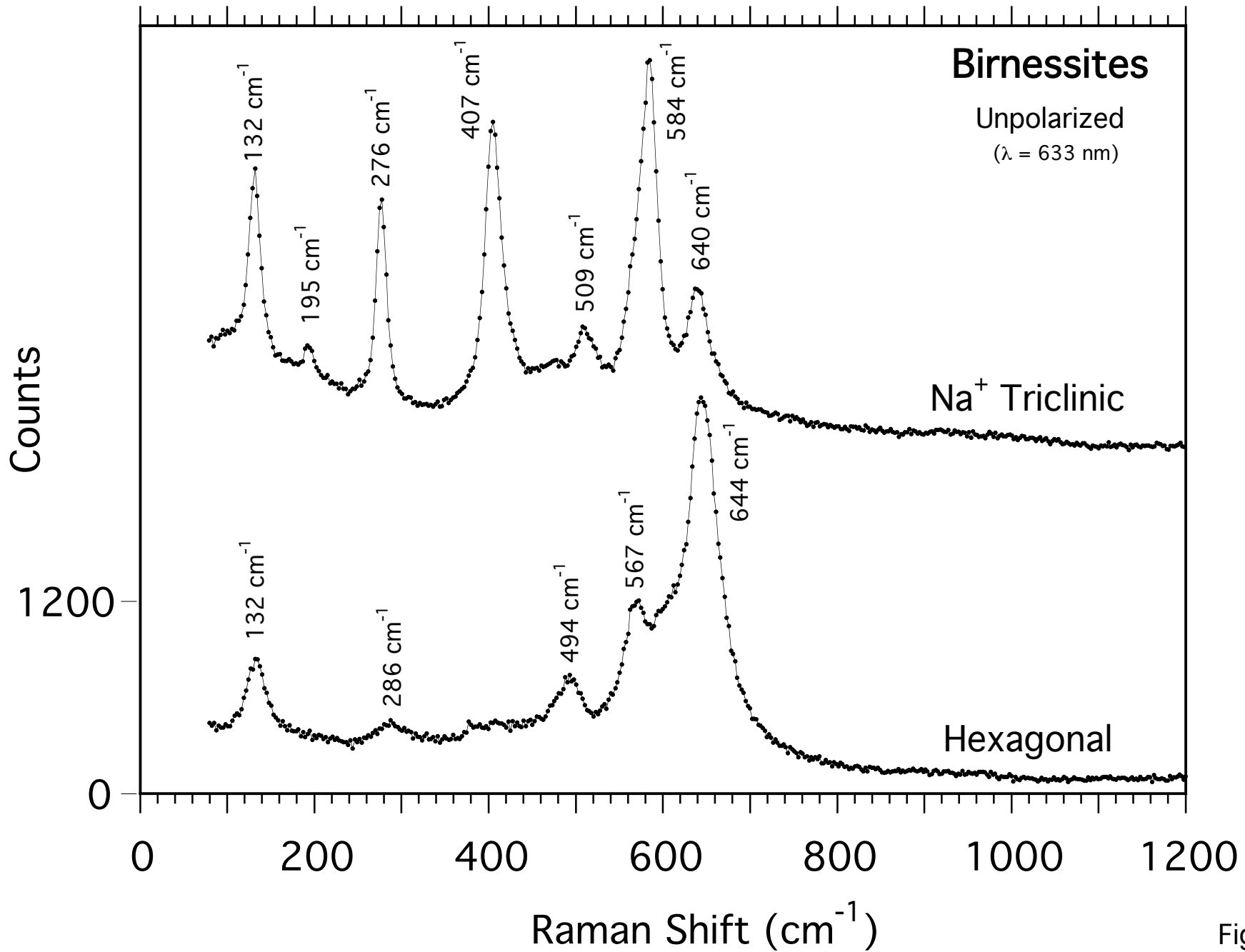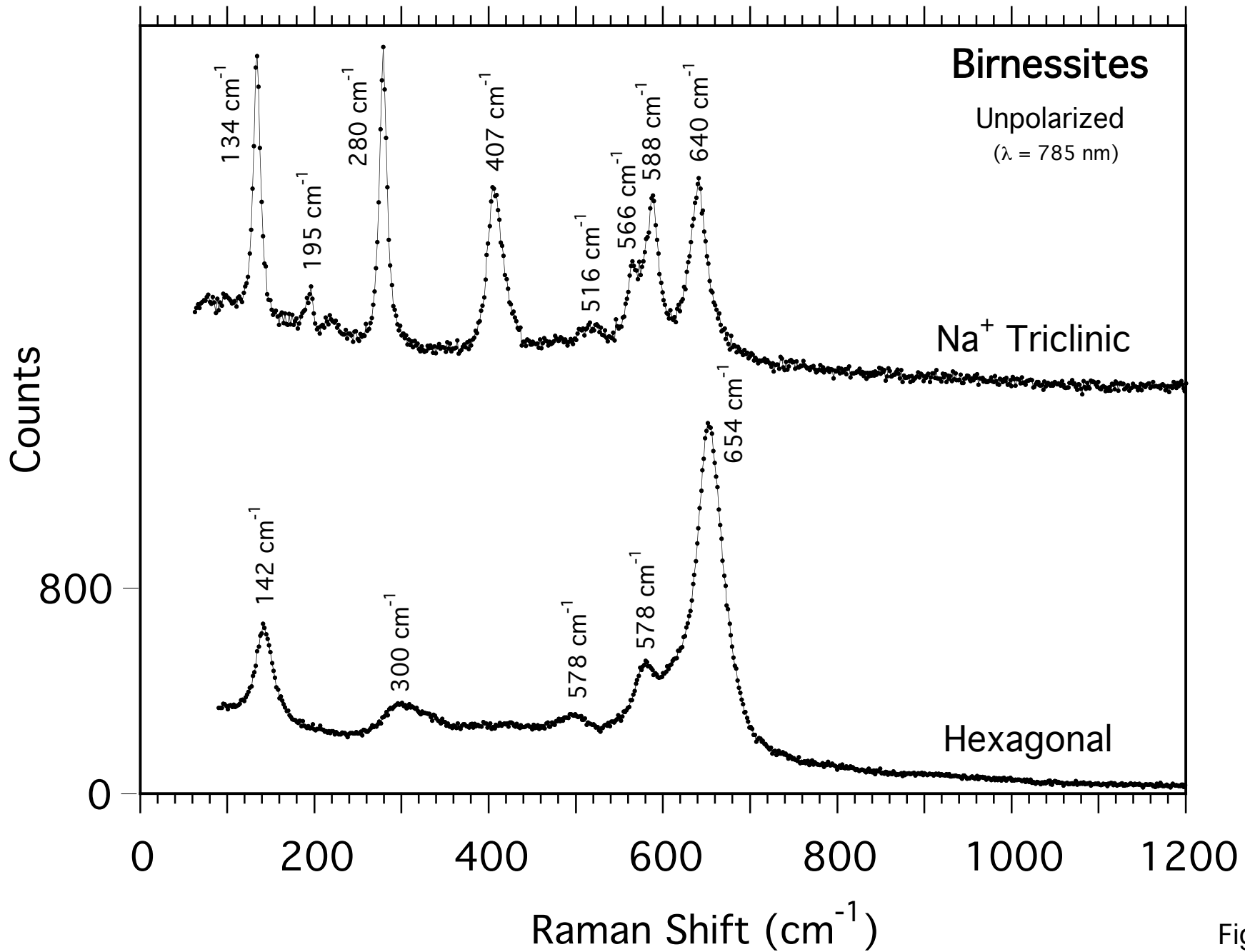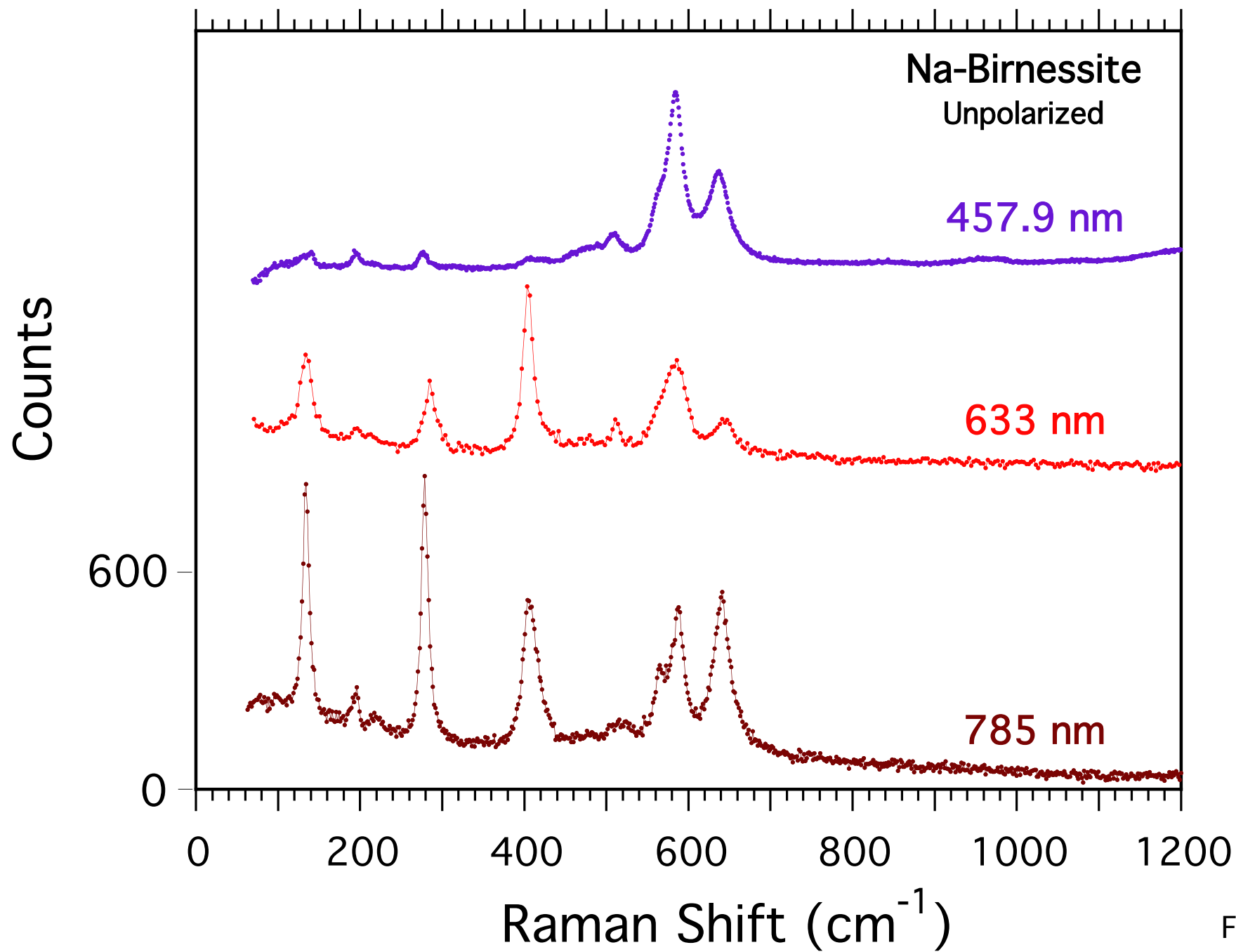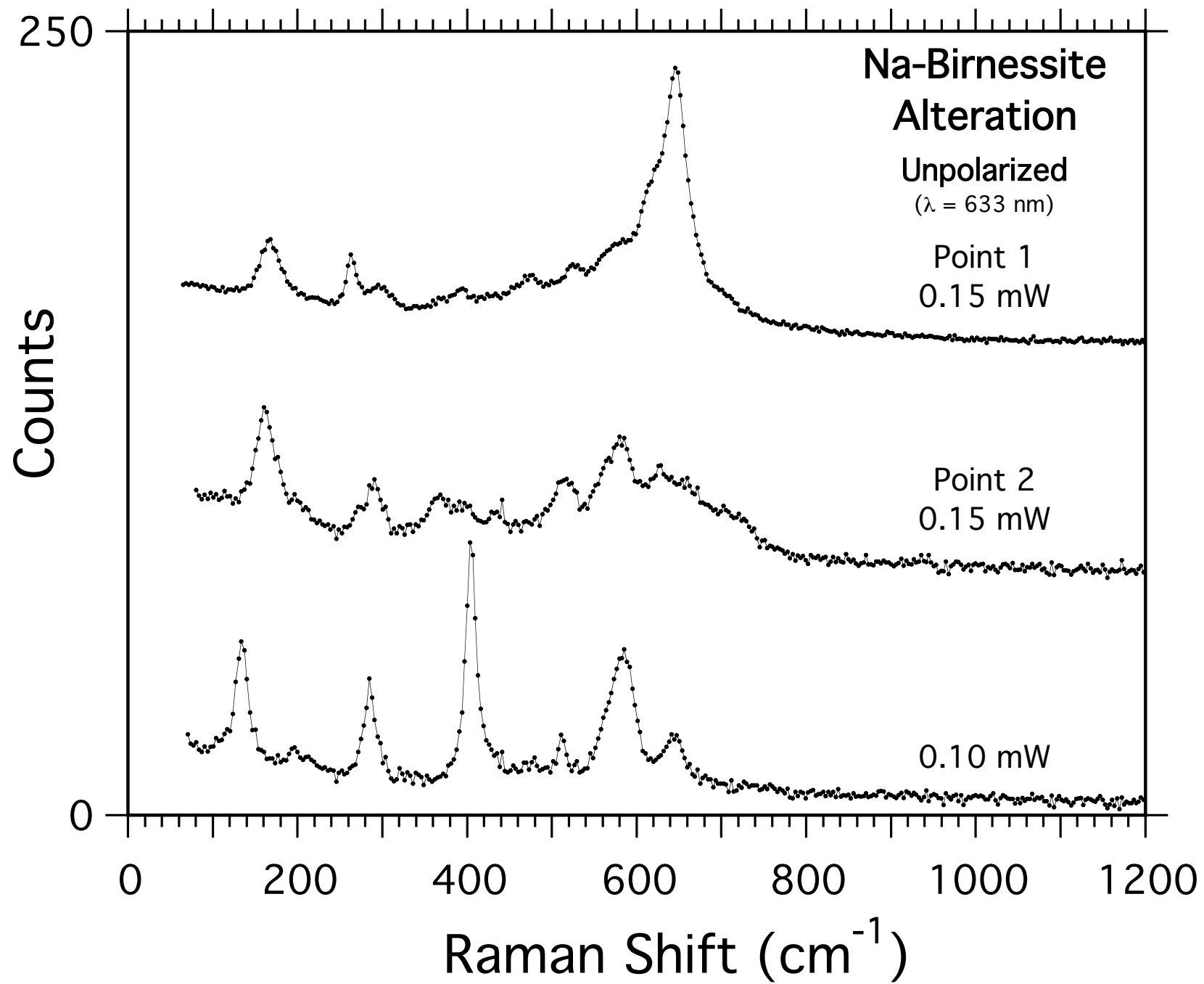
Fig. 12a

Fig. 12b

Fig. 13

Fig. 14

Fig. 15

Fig. 16

Lithiophorite
(162391 S. Africa)

Unpolarized

532 nm

633 nm

785 nm
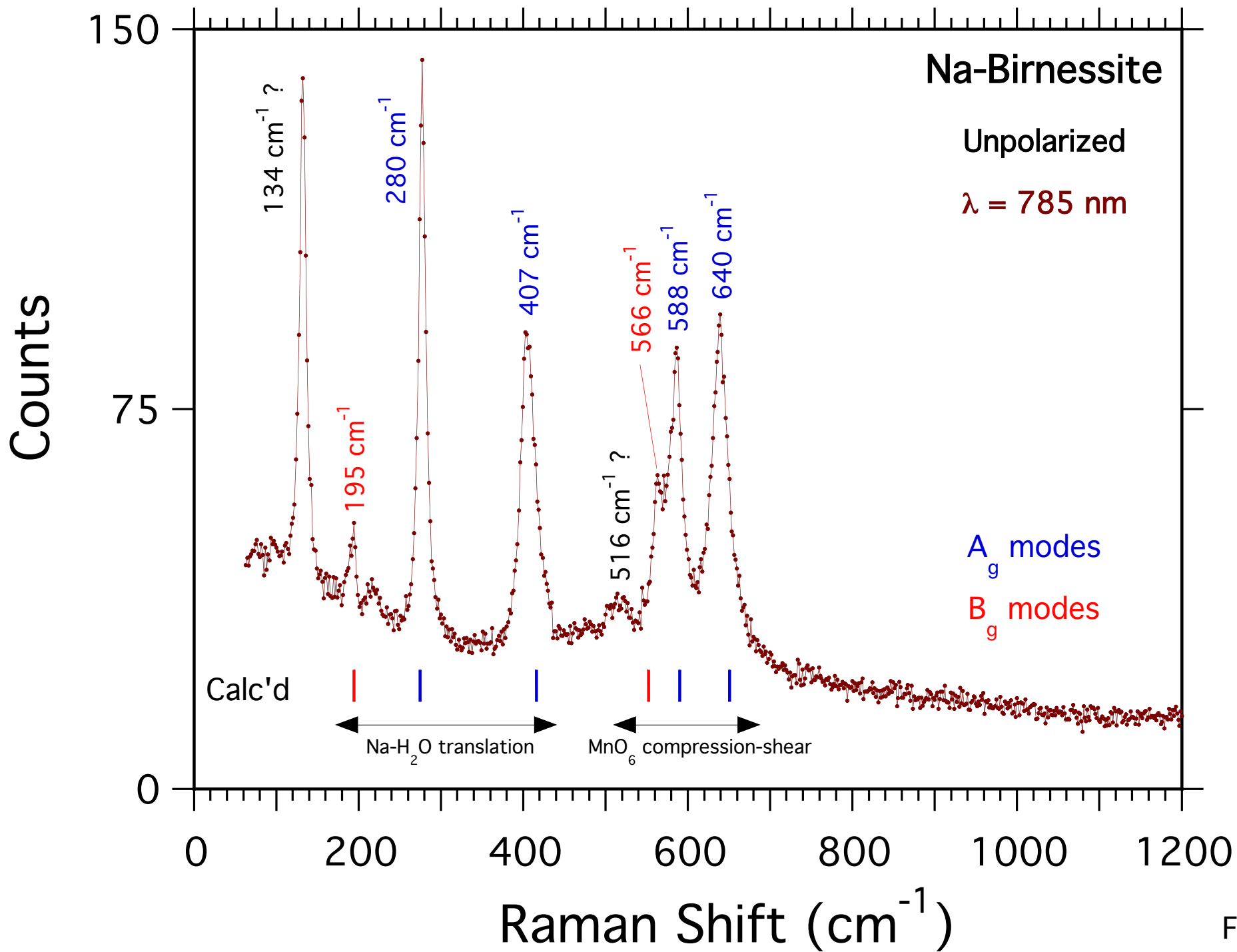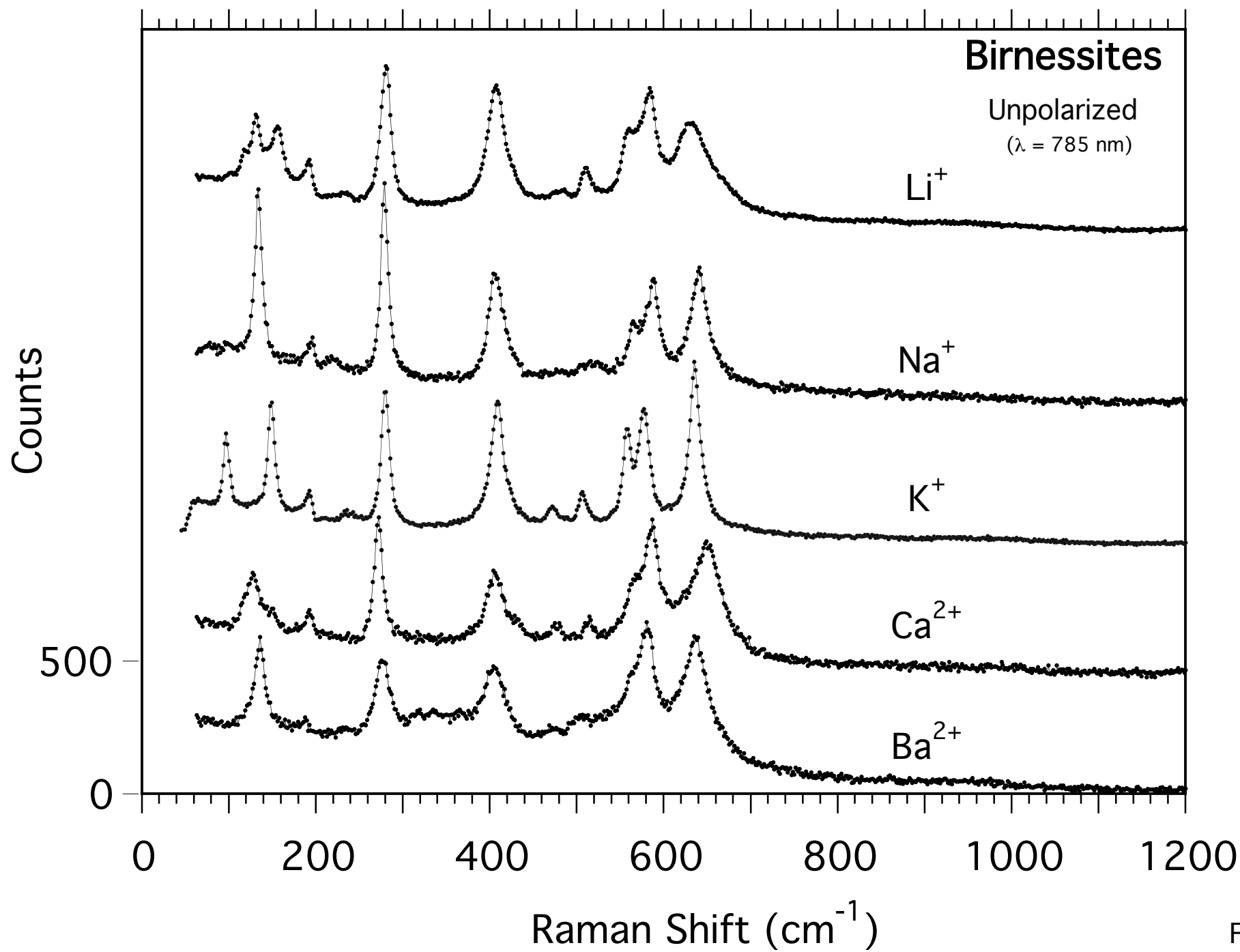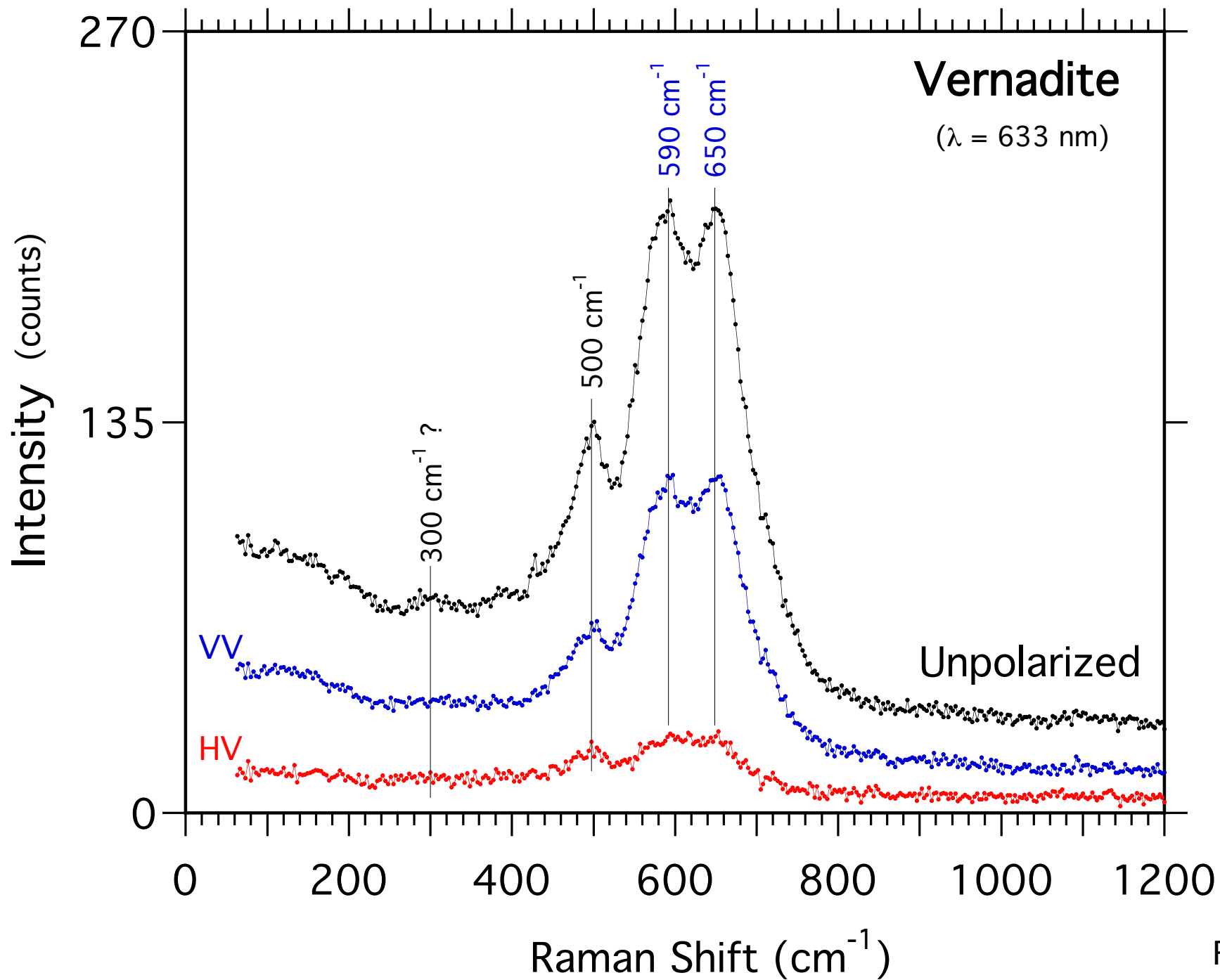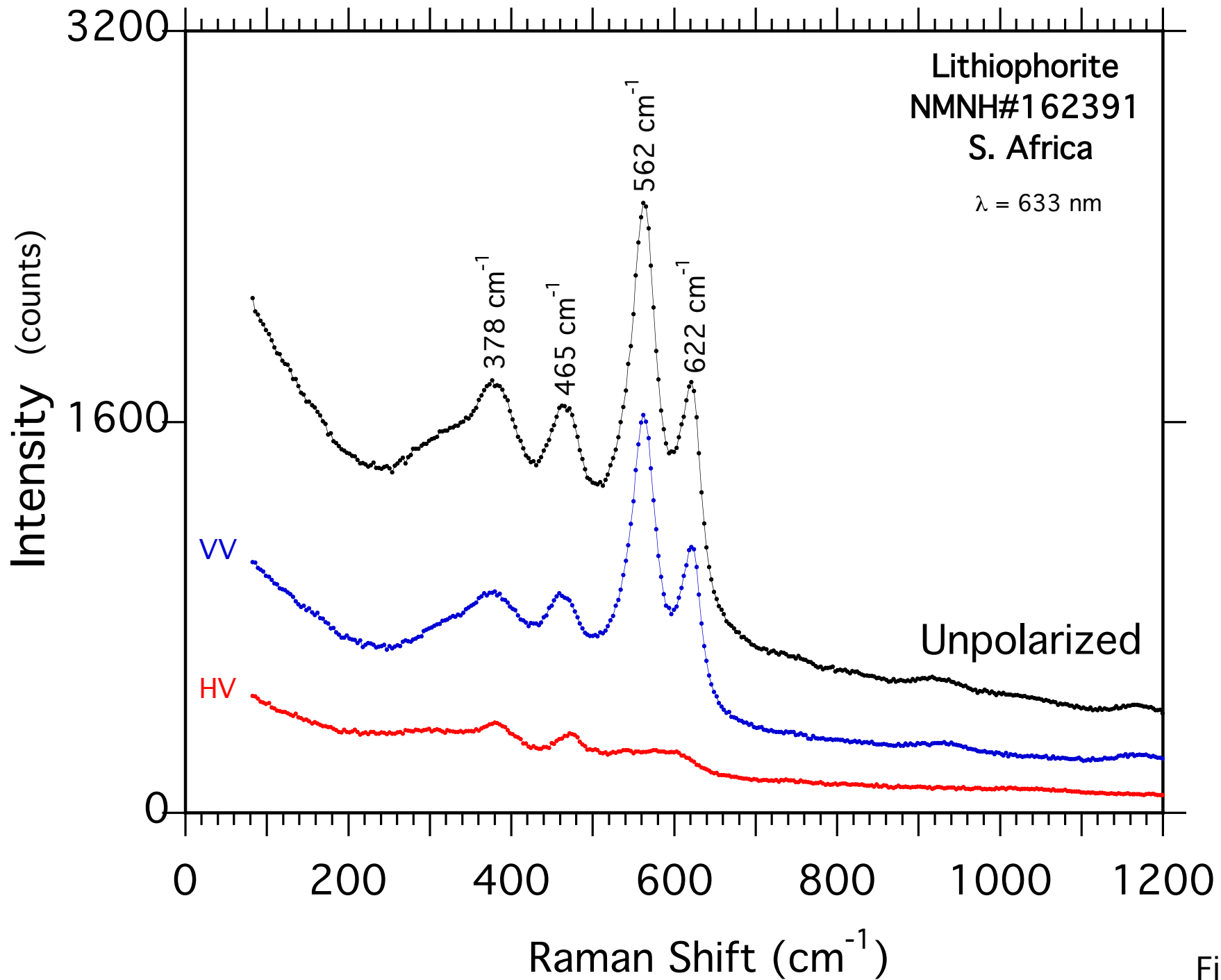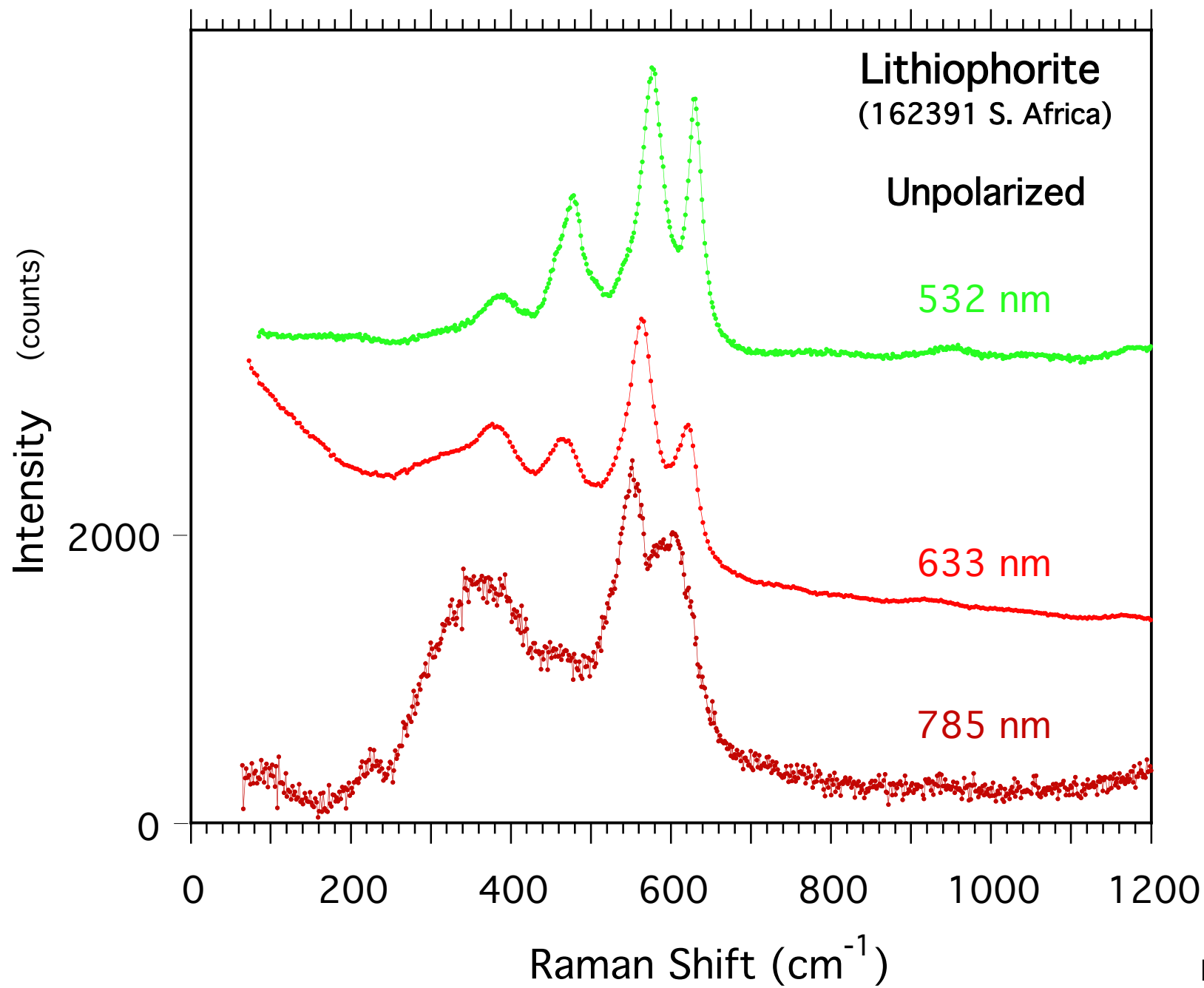
Fig. 17
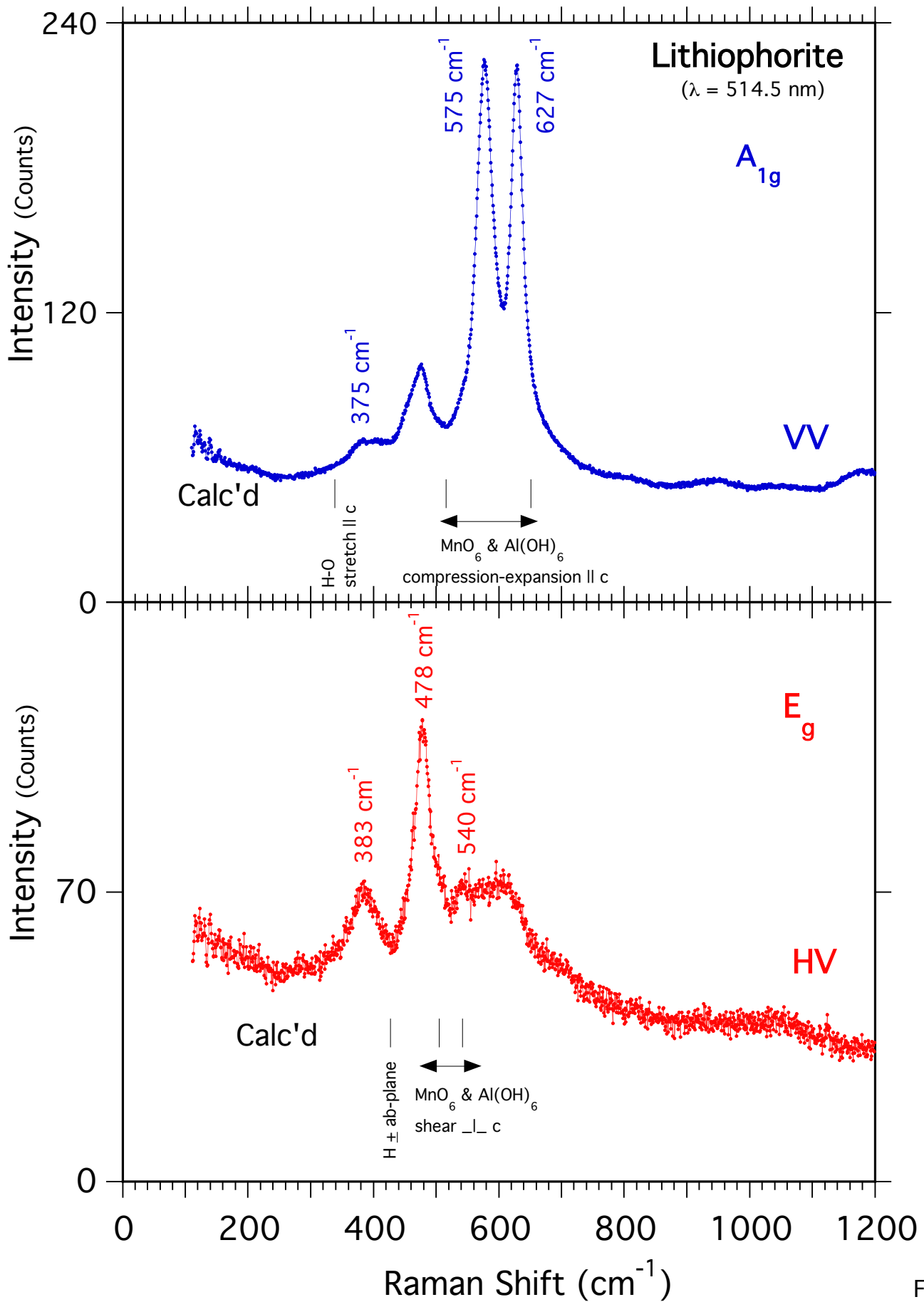
Fig. 18

Fig. 19

Fig. 20

Fig. 21

Phyllomanganates

Unpolarized
(λ = 785 nm)

Lithiophorite

Na-Birnessite

H-Birnessite

Rancieite

Chalcophanite

Intensity (counts)

Raman Shift (cm^{-1})

Fig. 22

Fig. 23

Fig. 24

Fig. 25