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(2014)

Vibrational spectroscopic characterization of the phosphate mineral althausite $Mg_2(PO_4)(OH,F,O)$ – implications for the molecular structure.
Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy,
120, pp. 252-256.

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<http://doi.org/10.1016/j.saa.2013.10.018>

1 **Vibrational spectroscopic characterization of the phosphate mineral althausite**
2 **Mg₂(PO₄)(OH,F,O) – implications for the molecular structure**

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4
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10
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13
14 **Abstract:**

15 Natural single-crystal specimens of althausite from Brazil, with general formula
16 Mg₂(PO₄)(OH,F,O) were investigated by Raman and infrared spectroscopy. The mineral
17 occurs as a secondary product in granitic pegmatites. The Raman spectrum of althausite is
18 characterized by bands at 1020, 1033 and 1044 cm⁻¹, assigned to ν₁ symmetric stretching
19 modes of the HOPO₃³⁻ and PO₄³⁻ units. Raman bands at around 1067, 1083 and 1138 cm⁻¹ are
20 attributed to both the HOP and PO antisymmetric stretching vibrations. The set of Raman
21 bands observed at 575, 589 and 606 cm⁻¹ are assigned to the ν₄ out of plane bending modes of
22 the PO₄ and H₂PO₄ units. Raman bands at 439, 461, 475 and 503 cm⁻¹ are attributed to the ν₂
23 PO₄ and H₂PO₄ bending modes. Strong Raman bands observed at 312, 346 cm⁻¹ with
24 shoulder bands at 361, 381 and 398 cm⁻¹ are assigned to MgO stretching vibrations. No
25 bands which are attributable to water were found. Vibrational spectroscopy enables aspects of
26 the molecular structure of althausite to be assessed.

27
28 **Keywords:** althausite, phosphate, Raman, infrared, pegmatite

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31 1. **Introduction**

32 Althausite $Mg_2(PO_4)(OH,F,O)$ is a hydroxy phosphate of magnesium. The mineral is found in
33 complex granitic pegmatites, formed by oxidation and hydration of primary minerals. The
34 mineral originates from Minas Gerais [1], at the Sapucaia pegmatite mine, about 50 km east-
35 southeast of Governador Valdares, and in good crystals from the Criminoso pegmatite mine,
36 about 35 km north. The mineral varies in colour from dark blue-green to black. The mineral
37 is found at many sites worldwide [1-9] including at Olary, South Australia [9], and is found
38 in magnetite-serpentinite deposits. The name of the mineral honors Professor Egon Althaus
39 (1933–), Karlsruhe University, Karlsruhe, Germany.

40

41 The mineral is orthorhombic [10], pseudotetragonal with point group: $2/m$. The cell data is
42 *Space Group: $P2_1/c$, with $a = 8.258$, $b = 6.054$, $c = 14.383$, $\beta = 120.150$ and $Z = 4$.*

43 According to Roemming and Raade, magnesium atoms occur in both five- and six-fold
44 coordination, and the coordination polyhedra are highly distorted [10]. The Mg octahedra
45 form chains along D by edge-sharing. Hydroxyl and fluorine occur in a largely ordered
46 distribution among two different structural sites and occupy alternating positions along
47 'channels' parallel to D. The mineral is related to the mineral wagnerite Mg_2PO_4F [11-14].
48 Wagnerite may be considered the fluorine end-member and althausite, the hydroxyl end
49 member. Another mineral, which is chemically closely related to althausite, is holtedahlite
50 Mg_2PO_4OH [15]. Althausite has some formal structural features in common with the
51 minerals libethenite-olivenite-adamite-eveite-andalusite, in that they contain similar cation
52 polyhedra with 5- and 6-coordination and the same kind of edge-sharing octahedral chains
53 [12, 16]. Complex phase relationships exist in the $MgO-P_2O_5-H_2O$ system [11].

54

55 Raman spectroscopy has proven most useful for the study of mineral structures. The objective
56 of this research is to report the Raman and infrared spectra of althausite and to relate the
57 spectra to the molecular structure of the mineral. This is the first report of a systematic study
58 of the mineral althausite from Brazil.

59

60 2. Experimental

61 2.1 Samples description and preparation

62 The althausite sample studied in this work was collected from Minas Gerais [1], at the
63 Sapucaia pegmatite mine, about 50 km east-southeast of Governador Valdares. The sample
64 was incorporated to the collection of the Geology Department of the Federal University of
65 Ouro Preto, Minas Gerais, Brazil, with sample code SAC-024.

66

67 2.2 Scanning electron microscopy (SEM)

68 Experiments and analyses involving electron microscopy were performed in the Center of
69 Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais,
70 Brazil (<http://www.microscopia.ufmg.br>). Althausite crystal cleavage fragment was coated
71 with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron images
72 were obtained using a JEOL JSM-6360LV equipment.

73

74 2.3 Raman microprobe spectroscopy

75 Crystals of althausite were placed on a polished metal surface on the stage of an Olympus
76 BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is
77 part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a
78 filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a
79 Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and
80 collected at a nominal resolution of 2 cm^{-1} and a precision of $\pm 1 \text{ cm}^{-1}$ in the range between
81 200 and 4000 cm^{-1} . Repeated acquisitions on the crystals using the highest magnification
82 (50x) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra
83 were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The Raman spectrum of at least
84 10 crystals was collected to ensure the consistency of the spectra.

85

86 2.4 Infrared spectroscopy

87 Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart
88 endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were
89 obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of
90 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

91

92 Spectral manipulation such as baseline correction/adjustment and smoothing were performed
93 using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH,
94 USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package
95 that enabled the type of fitting function to be selected and allows specific parameters to be
96 fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product
97 function with the minimum number of component bands used for the fitting process. The
98 Gaussian-Lorentzian ratio was maintained at values greater than 0.7 and fitting was
99 undertaken until reproducible results were obtained with squared correlations of r^2 greater
100 than 0.995.

101

102 3. Results and discussion

103

104 3.1 *Vibrational Spectroscopy Background*

105 In aqueous systems, the Raman spectra of phosphate oxyanions show a symmetric stretching
106 mode (ν_1) at 938 cm^{-1} , an antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , a symmetric
107 bending mode (ν_2) at 420 cm^{-1} and a ν_4 bending mode at 567 cm^{-1} [17-19]. S.D. Ross in
108 Farmer listed some well-known minerals containing phosphate which were either hydrated or
109 hydroxylated or both [20]. The vibrational spectrum of the dihydrogen phosphate anion has
110 been reported by Farmer [20]. The PO_2 symmetric stretching mode occurs at 1072 cm^{-1} and
111 the POH symmetric stretching mode at $\sim 878\text{ cm}^{-1}$. The POH antisymmetric stretching mode
112 was found at 947 cm^{-1} and the $\text{P}(\text{OH})_2$ bending mode at 380 cm^{-1} . The band at 1150 cm^{-1} was
113 assigned to the PO_2 antisymmetric stretching mode. The position of these bands will shift
114 according to the crystal structure of the mineral.

115

116 The vibrational spectra of phosphate minerals have been published by Farmer's treatise
117 Chapter 17 [20]. The Table 17.III in ref. [20] reports the band positions of a wide range of
118 phosphates and arsenates. The band positions for the monohydrogen phosphate anion of
119 disodium hydrogen phosphate dihydrate is given as ν_1 at 820 and 866 cm^{-1} , ν_2 at around 460
120 cm^{-1} , ν_3 as $953, 993, 1055, 1070, 1120$ and 1135 cm^{-1} , ν_4 at $520, 539, 558, 575\text{ cm}^{-1}$. The
121 POH unit has vibrations associated with the OH specie. The stretching vibration of the POH
122 units was tabulated as 2430 and 2870 cm^{-1} , and bending modes at 766 and 1256 cm^{-1} . Water
123 stretching vibrations were found at 3050 and 3350 cm^{-1} . The position of the bands for the
124 disodium hydrogen phosphate is very dependent on the waters of hydration. There have been

125 several Raman spectroscopic studies of the monosodium dihydrogen phosphate chemicals
126 [21-25].

127

128 **3.2 Vibrational Spectroscopy**

129 The Raman spectrum of althausite over the 100 to 4000 cm^{-1} spectral range is illustrated in
130 **Figure 1a**. This figure shows the peak position and the relative intensities of the Raman
131 bands. It is noted there are large parts of the spectrum where no intensity is observed and
132 therefore, the spectrum is subdivided into sections based upon the types of vibration being
133 studied. The infrared spectrum of althausite over the 500 to 4000 cm^{-1} spectral range is
134 reported in **Figure 1b**. This figure shows the position and relative intensities of the infrared
135 bands. There are large parts of the infrared spectrum where little or no intensity is observed.
136 Hence, the spectrum is subdivided into sections based on which bands are being studied.

137

138 The Raman spectrum of althausite over the 800 to 1200 cm^{-1} spectral range are reported in
139 **Figure 2a**. The Raman spectrum of althausite in this spectral region shows complexity with a
140 series of overlapping bands. The chemistry of althausite is such that it is expected to have
141 interactions between the phosphate and hydroxyl units. This means that HOPO_3^{3-} units will
142 form. Raman bands are observed at 964, 986 and 993 cm^{-1} . It is proposed that these three
143 bands are attributed to the PO stretching vibrations of HOPO_3^{3-} , PO_4^{3-} and H_2PO_4^- units.
144 According to Roemming and Raade [10], the phosphate units in the crystal structure of
145 althausite are not equivalent and the interaction with the hydroxyl or fluorine units will be
146 different, so it is not unexpected that a number of phosphate stretching vibrations would be
147 observed.

148

149

150 Galy [23] first studied the polarized Raman spectra of the H_2PO_4^- anion. Choi *et al.* reported
151 the polarization spectra of NaH_2PO_4 crystals. Casciani and Condrate [26] published spectra
152 on brushite and monetite together with synthetic anhydrous monocalcium phosphate
153 ($\text{Ca}(\text{H}_2\text{PO}_4)_2$), monocalcium dihydrogen phosphate hydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) and
154 octacalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$). These authors determined band assignments for
155 $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and reported bands at 1012 and 1085 cm^{-1} as POH and PO stretching vibrations,
156 respectively. The three Raman bands at 1033, 1049 and 1062 cm^{-1} are attributed to both the
157 HOP and PO antisymmetric stretching vibrations. Casciani and Condrate [26] tabulated
158 Raman bands at 1132 and 1155 cm^{-1} and assigned these bands to P-O symmetric and the P-O

159 antisymmetric stretching vibrations. It is proposed that the proton on the hydroxyl units is
160 very liable and can oscillate between the OH units and the phosphate units. In this way the
161 hydrogen phosphate units are formed. The low intensity Raman bands at 968 and 988 cm^{-1}
162 are ascribed to the hydroxyl deformation modes of the OH units in the althausite structure.

163

164 The infrared spectrum of althausite is shown in **Figure 2b**. This infrared spectrum shows even
165 greater complexity than the Raman spectrum (**Figure 2a**). The infrared spectrum may be band
166 component analyzed into component bands. The infrared bands at 932, 976 and 1002 cm^{-1}
167 are assigned to the PO stretching vibrations of the HOPO_3^{3-} , PO_4^{3-} and H_2PO_4^- units. The
168 three infrared bands at 1031, 1066 and 1135 cm^{-1} are assigned to the antisymmetric stretching
169 vibrations of these units.

170

171 The Raman spectra of althausite in the 400 to 700 cm^{-1} and 100 to 400 cm^{-1} spectral range are
172 displayed in **Figure 3**. The spectrum in **Figure 3a** may be subdivided into sections. (a) the
173 bands at around 589 cm^{-1} (b) the bands in the 439 to 503 cm^{-1} spectral range and (c) bands in
174 the 312 to 398 cm^{-1} . In addition, there is a low intensity band at 702 cm^{-1} . The Raman bands
175 observed at 575, 589 and 606 cm^{-1} are assigned to the ν_4 out of plane bending modes of the
176 PO_4 and H_2PO_4 units. The Raman spectrum of NaH_2PO_4 shows bands at 526, 546 and 618
177 cm^{-1} . The observation of multiple bands in this spectral region supports the concept of
178 symmetry reduction of both the phosphate and hydrogen phosphate units. Raman bands at
179 439, 461, 475 and 503 cm^{-1} are attributed to the ν_2 PO_4 and H_2PO_4 bending modes. The
180 Raman spectrum of NaH_2PO_4 shows two Raman bands at 460 and 482 cm^{-1} . The observation
181 of multiple Raman bands in this spectral region for the althausite mineral supports the
182 concept of symmetry reduction of the phosphate anion. Strong Raman bands are observed at
183 312, 346 cm^{-1} with shoulder bands at 361, 381 and 398 cm^{-1} . These bands are assigned to
184 MgO stretching vibrations. Again, the observation of multiple bands in this spectral region
185 supports the concept of the non-equivalence of phosphate units in the structure of althausite.
186 There are a number of bands in the Raman spectrum of the far low wavenumber region.
187 These bands are ascribed to lattice vibrations.

188

189 The Raman spectrum in the 3300 to 3800 cm^{-1} spectral region is displayed in **Figure 4a**. The
190 spectral profile is complex with multiple overlapping bands. Raman bands are observed at
191 3472, 3488, 3500, 3511 and 3523 cm^{-1} . These bands are assigned to the OH stretching
192 vibrations of the OH units in the althausite structure. From these values, a hydrogen bond

193 distance may be calculated of around 2.94 Å, which is in good agreement with that obtained
194 from XRD data of 2.39 Å [10]. The Raman spectrum over the 1100 to 1400 cm⁻¹ spectral
195 range is shown in Figure 5a. No Raman bands at around 1630 cm⁻¹ were observed, thus
196 confirming the absence of water in the structure of althausite. A broad Raman peak was
197 found at around 1320 cm⁻¹ and a sharper peak at 1130 cm⁻¹ was observed.

198

199 The infrared spectrum of althausite in the 2800 to 3800 cm⁻¹ spectral range is reported in
200 Figure 4b. The spectrum is broad with the main peak observed at 3500 cm⁻¹. There is a long
201 tail on the low wavenumber side and additional bands may be resolved. These bands may be
202 attributed to the stretching vibrations of the OH units. An additional infrared band at 3679
203 cm⁻¹ is observed. The infrared spectrum of althausite showed no bands at around 1630 cm⁻¹.
204 This indicates that no water was present (Figure 5b). Raade and Tysseland reported the
205 infrared spectrum of althausite in their paper of 1975. They showed a stretching wavenumber
206 for althausite at 3510 cm⁻¹ [27]. These workers also synthesised the mineral analogue of
207 althausite for which some splitting of the infrared bands occurred' thus indicating the non-
208 equivalence of the OH units in the structure of althausite. Such a concept is strongly
209 supported by our Raman spectra where multiple OH stretching vibrations are observed.

210

211 4. Conclusions

212 Althausite is one of many phosphate minerals found in granitic pegmatites. However, this
213 particular phosphate mineral of formula Mg₂(PO₄)(OH,F,O) is an anhydrous mineral in which
214 no water is present in the mineral formula. Whilst the colour of the mineral varies and is
215 probably a function of the mineral origin, the mineral is often black or bluish black. Thus, it
216 might be expected that the mineral might be difficult to measure its Raman spectrum; however
217 this is not the case and the Raman spectra are readily obtained.

218

219 The mineral is a typical phosphate and Raman and infrared bands are attributed to HOP and
220 PO bending and stretching vibrations of the HOPO₃³⁻ and PO₄³⁻ units. The Raman spectrum
221 of althausite shows multiple bands attributable to the OH units. At least four bands are
222 observed, thus indicating the non-equivalence of the OH units in the althausite structure. The
223 infrared spectrum displays a broad band centred upon 3500 cm⁻¹. Vibrational spectroscopy
224 enables aspects of the molecular structure of althausite to be assessed.

225

226

227

228 **Acknowledgments**

229 The financial and infra-structure support of the Discipline of Nanotechnology and Molecular
230 Science, Science and Engineering Faculty of the Queensland University of Technology, is
231 gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the
232 instrumentation. The authors would like to acknowledge the Center of Microscopy at the
233 Universidade Federal de Minas Gerais (<http://www.microscopia.ufmg.br>) for providing the
234 equipment and technical support for experiments involving electron microscopy. R. Scholz
235 thanks to CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico (grant
236 No. 306287/2012-9).

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240

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- 308
- 309

310 **List of Figures**

311

312 **Figure 1 (a) Raman spectrum of althausite over the 100 to 4000 cm^{-1} spectral range (b)**

313 **Infrared spectrum of althausite over the 500 to 4000 cm^{-1} spectral range**

314

315 **Figure 2 (a) Raman spectrum of althausite over the 800 to 1400 cm^{-1} spectral range (b)**

316 **Infrared spectrum of althausite over the 500 to 1300 cm^{-1} spectral range**

317

318 **Figure 3 (a) Raman spectrum of althausite over the 400 to 700 cm^{-1} spectral range (b)**

319 **Raman spectrum of althausite over the 100 to 400 cm^{-1} spectral range**

320

321 **Figure 4 (a) Raman spectrum of althausite over the 3300 to 3800 cm^{-1} spectral range (b)**

322 **Infrared spectrum of althausite over the 2800 to 3800 cm^{-1} spectral range**

323

324 **Figure 5 (a) Raman spectrum of althausite (upper spectrum) in the 1100 to 1400 cm^{-1}**

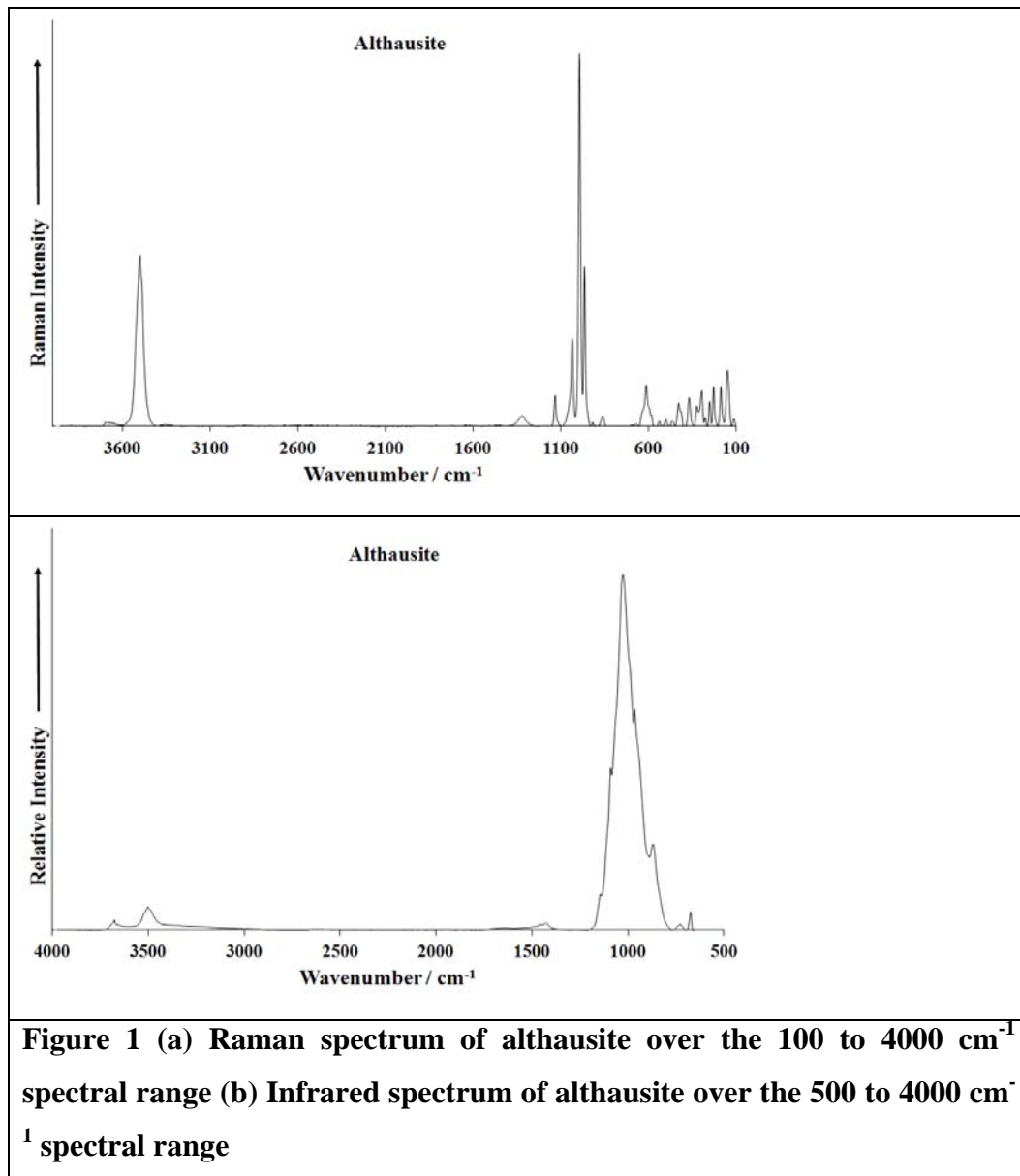
325 **spectral range (b) infrared spectrum of althausite (lower spectrum) in the 1300 to 1700**

326 **cm^{-1} spectral range**

327

328

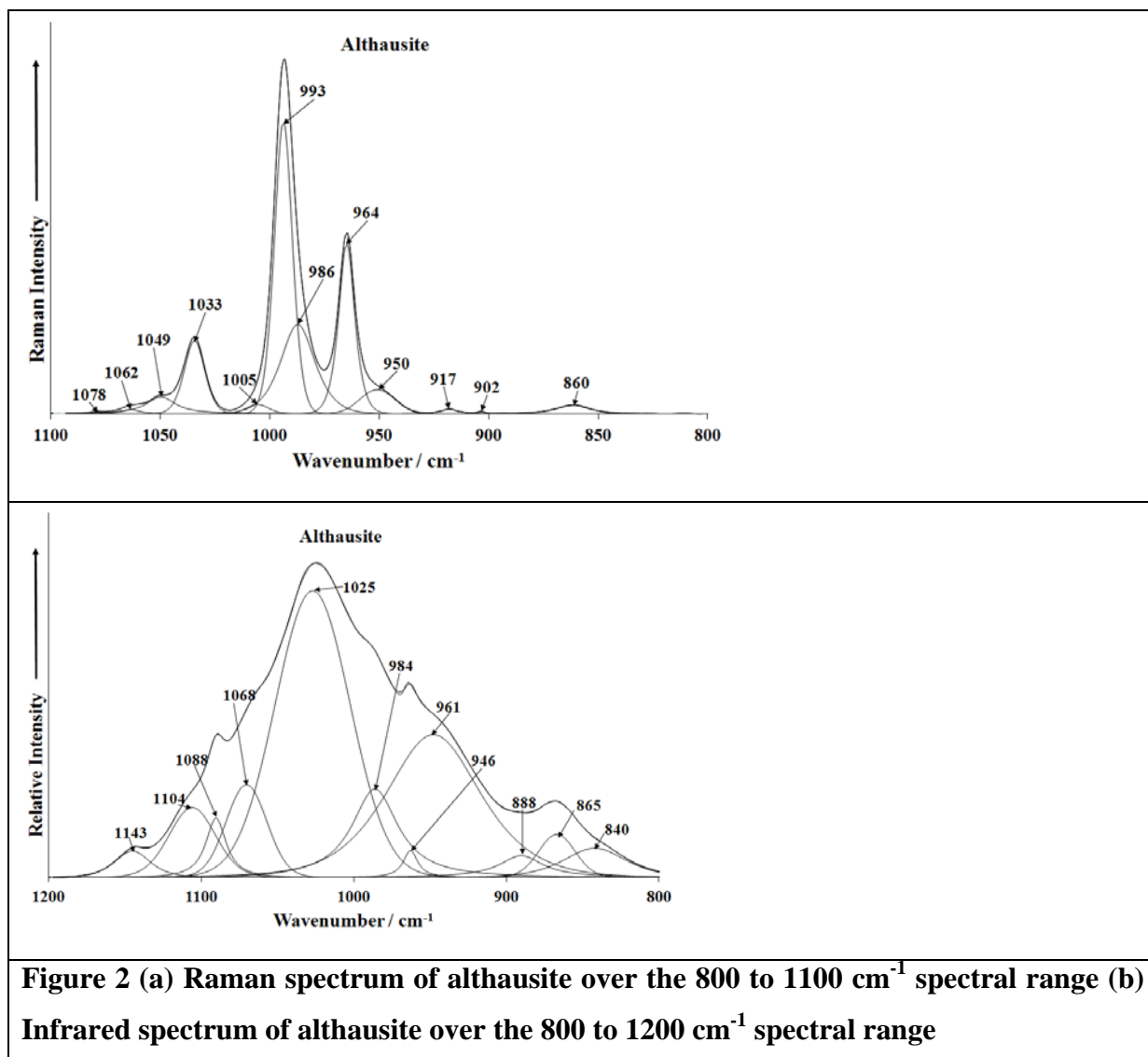
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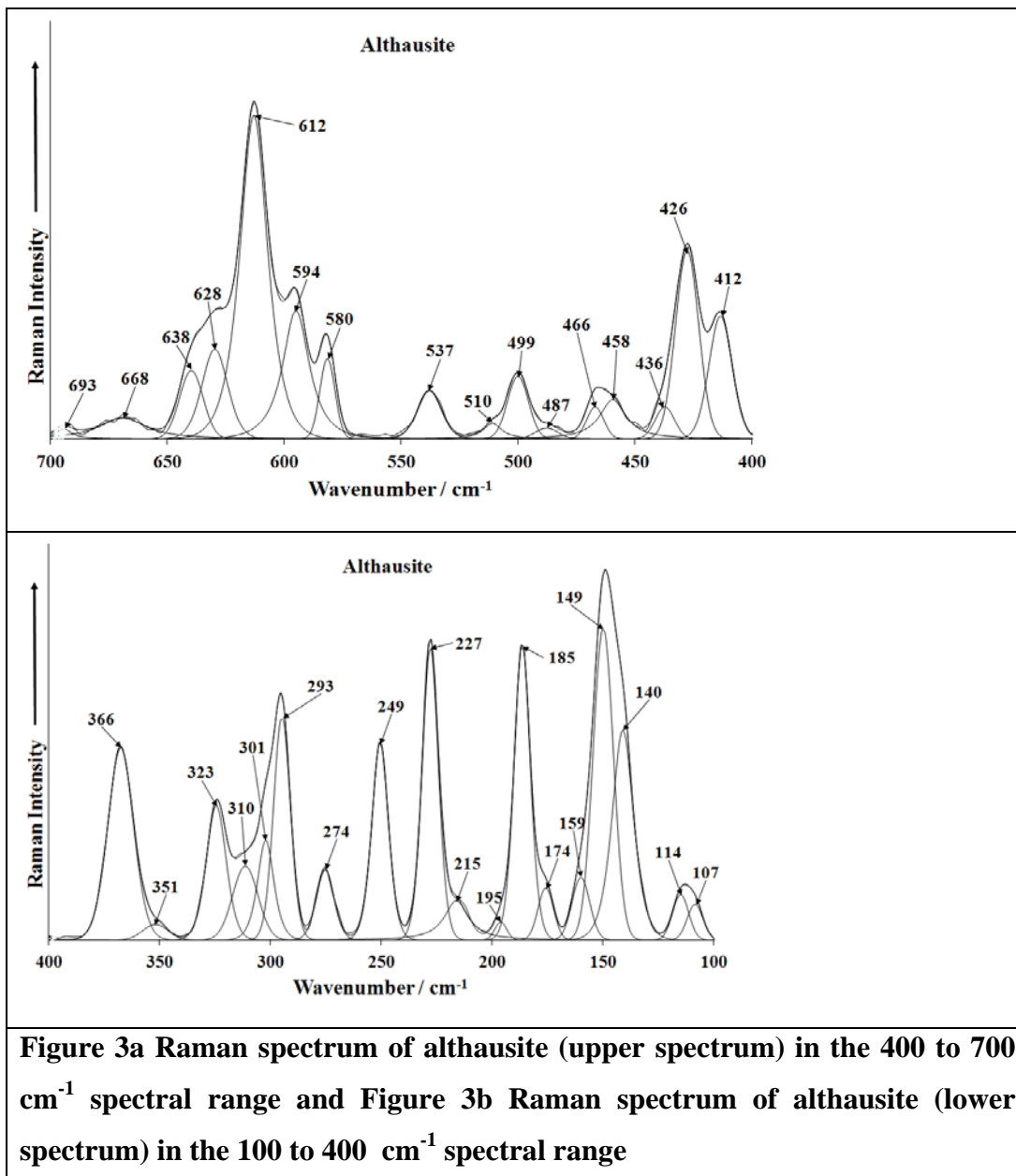


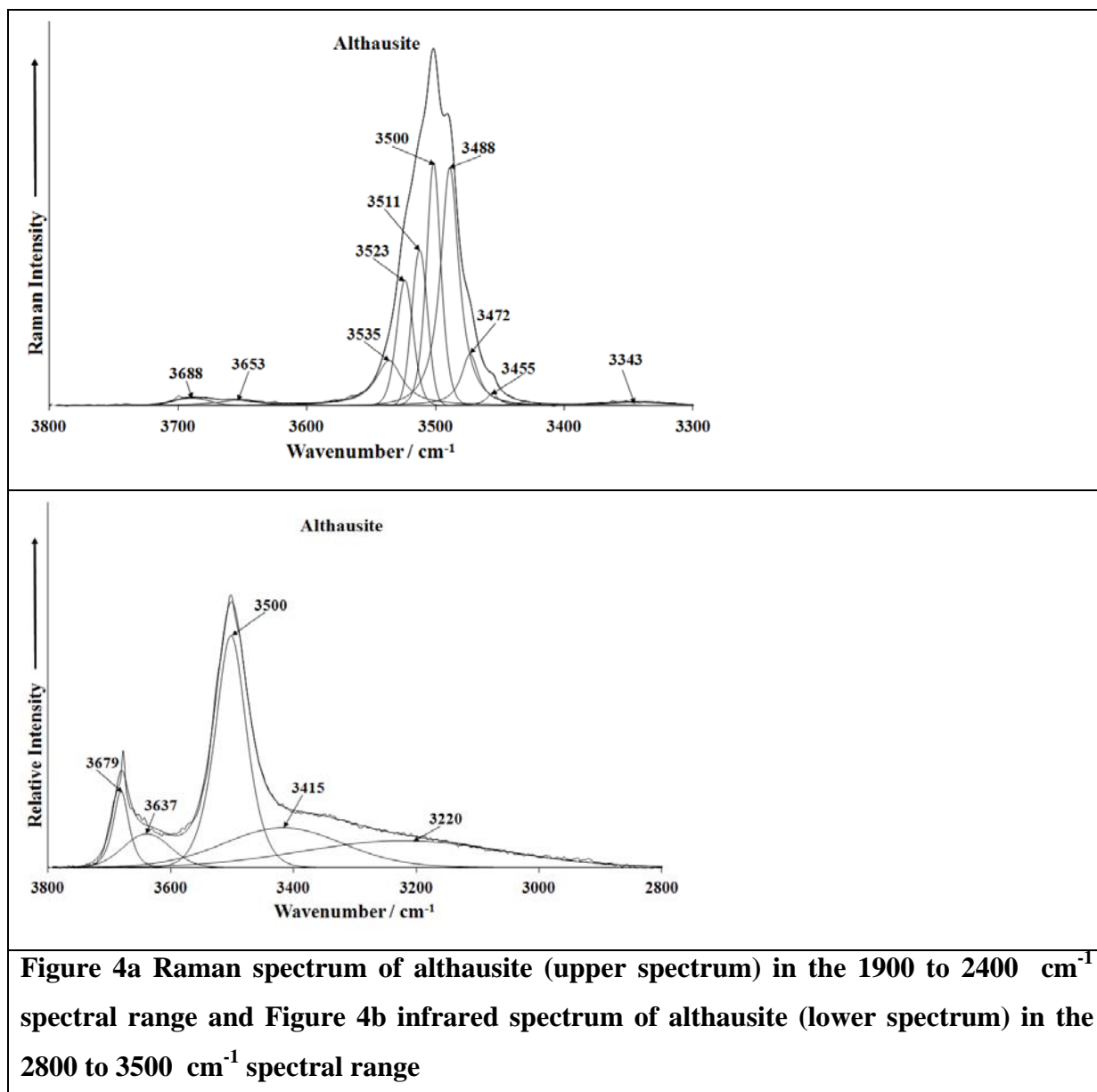
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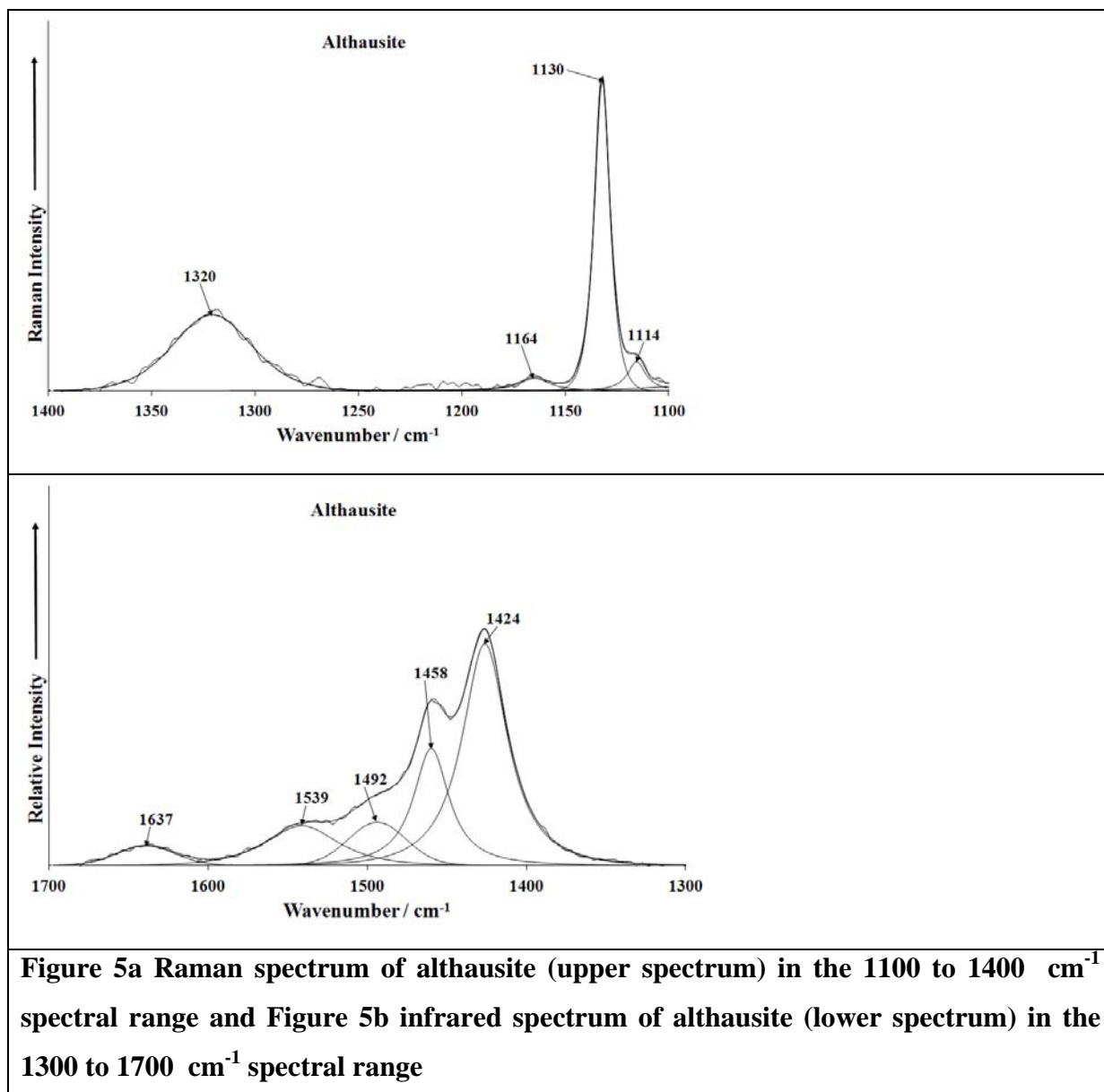
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