9 **Carlfrancisite: $Mn^{2+}_3(Mn^{2+},Mg,Fe^{3+},Al)_{42}(As^{3+}O_3)_2(As^{5+}O_4)_4[(Si,As^{5+})O_4]_6[(As^{5+},Si)O_4]_2(OH)_{42}$,**

10 **a new arseno-silicate mineral from the Kombat mine, Otavi Valley, Namibia**

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24   **ABSTRACT**

25   Carlfrancisite, $Mn^{2+}{}_3(Mn^{2+},Mg,Fe^{3+},Al)_{42}(As^{3+}O_3)_2(As^{5+}O_4)_4[(Si,As^{5+})O_4]_6[(As^{5+},Si)O_4]_2$

26    $(OH)_{42}$, is a new mineral from the Kombat mine, Otavi Valley, Namibia, and occurs as curved

27   platy aggregates ~2 cm across on a matrix of Mn arsenates and oxides. It is yellowy orange to

28   pale yellow with a very pale-yellow streak, translucent with a vitreous to opalescent lustre, and

29   does not fluoresce under ultraviolet light. Cleavage is micaceous on {001}, and no parting or

30   twinning were observed. Mohs hardness is 3, and carlfrancisite is brittle with a hackly fracture.

31   The calculated density is 3.620 g/cm^3. Optical properties were measured with a Bloss spindle

32   stage for the wavelength 590 nm using a gel filter. The indices of refraction are ε = 1.756, ω =

33   1.758, and it is non-pleochroic. Carlfrancisite is trigonal, space group $R\overline{3}c$, a 8.2238(2), c

34   205.113(6) Å, V 12,013.5(4) Å^3, Z = 6, c:a = 1:24.941. The seven strongest lines in the X-ray

35   powder-diffraction pattern are as follows: d (Å), I, ($h\,k\,l$): 2.826, 100, ($\overline{2}$ 2 44); 2.371, 88, ($\overline{2}$ 3

36   40, $\overline{1}$ 3 41); 1.552, 84, ($\overline{1}$ 5 0); 2.676, 63, ($\overline{2}$ 3 7); 3.243, 54, (0 1 56, $\overline{1}$ 2 39); 4.107, 48, ($\overline{1}$ 2

37   0); 2.918, 47, (0 2 40). Chemical analysis by electron microprobe and crystal-structure

38   refinement gave As_2O_5 13.07, As_2O_3 3.18, P_2O_5 0.50, V_2O_5 0.74, SiO_2 8.96, Al_2O_3 0.78, FeO

39   0.22, MnO 53.25, MgO 9.37, H_2O(calc) 8.42, sum 98.49 wt.%. The H_2O content and the valence

40   states of As were determined by crystal-structure analysis. The empirical formula is

41    $Mn^{2+}{}_{33.55}Mg_{10.39}Fe^{2+}{}_{0.14}Al_{0.68}As^{3+}{}_{1.44}(Si_{6.67}P_{0.32}V^{5+}{}_{0.37}As^{5+}{}_{5.08})O_{54}(OH)_{42}$ on the basis of 96 anions

42   with (OH) = 42 a.p.f.u. The structure of carlfrancisite is closely related to that of mcgovernite and

43   turtmannite.

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46   *Keywords:* Carlfrancisite, new mineral species, arseno-silicate, Tsumeb mine, Otavi Valley,

47   Namibia, electron microprobe analysis, optical properties, chemical analysis, mcgovernite,

48   turtmannite.

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INTRODUCTION

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51   The mineralization at the Kombat mine, Namibia, consists of epigenetic, hydrothermal

52   and metasomatic replacement deposits and fracture-fill Cu-Pb-(Ag) sulfides, and a strong

53   metamorphic overprint has given rise to lenses of Mn- and Fe-oxide and -silicate minerals

54   (Schneider 2004). Dunn et al. (1988) reported a mcgovernite-like mineral from this locality. As

55   part of our ongoing interest in the basic Mn arsenates (Cooper and Hawthorne 1999, 2001, in

56   prep., 2013), we have characterized the mineral described by Dunn et al. (1988) and report the

57   results here. This mineral is named carlfrancisite after Carl A. Francis (born October 21, 1949,

58   in Stafford Springs, Connecticut, USA), mineralogist and curator of the Harvard mineral

59   collection, who was involved in the discovery and initial characterization of the chemical

60   composition and unit cell of this mineral, and who has made many significant contributions to

61   scientific mineralogy, mineral curation and to the mineral-collecting community. The new mineral

62   and mineral name have been approved by the Commission on New Minerals, Nomenclature

63   and Classification, International Mineralogical Association (IMA 2012-033). The holotype

64   specimen of carlfrancisite has been deposited in the mineral collection of the Department of

65   Natural History, Royal Ontario Museum, catalogue number M56375.

66

67   OCCURRENCE

68   Carlfrancisite was found in 1982 in the E15-11 south stope, 11 level, at the 1241-m

69   elevation, in the Asis West sector of the Kombat mine (Dunn et al. 1988), Otavi Valley, Namibia,

70   latitude 19°45′ S, longitude 17°45′ E, associated with alleghanyite, chlorite, pyrochroite, spinels

71   and ribbeite. Carlfrancisite and associated Mn silicates and oxides occur as metamorphosed

72   lenses associated with Cu-Pb-Ag sulphide ores in feldspathic sandstone that have subsequently

73   been reworked by late hydrothermal solutions (Innes and Chaplin 1986).

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PHYSICAL PROPERTIES

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77   Carlfrancisite occurs as curved platy aggregates ~2 cm across on a matrix of Mn

78   arsenates and oxides (Fig. 1a). It is pale yellow to yellowy orange (Fig. 1b) with a very pale

79   yellow streak, is translucent with a vitreous to opalescent lustre, and does not fluoresce under

80   ultraviolet light. Cleavage is micaceous on {001}, and no parting or twinning were observed.

81   Mohs hardness is 3, and carlfrancisite is brittle with a hackly fracture. The calculated density is

82   3.620 g/cm^3. Optical properties were measured with a Bloss spindle stage for the wavelength

83   590 nm using a gel filter. Carlfrancisite is non-pleochroic, uniaxial positive with indices of

84   refraction ω = 1.756, ε = 1.758, both ±0.002.

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VIBRATIONAL SPECTROSCOPY

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87   The Raman spectrum of carlfrancisite was collected in back-scattered mode with a

88   HORIBA Jobin Yvon-LabRAM ARAMIS integrated confocal micro-Raman system equipped with

89   a 460 mm focal-length spectrograph and a multichannel air-cooled (-70°C) CCD detector. A

90   magnification of 100x was used with an estimated spot size of 1 μm, a 1800 gr/mm grating, an

91   excitation radiation of 532 nm, and a laser power between 5 and 12.5 mW. Calibration was

92   done using the 520.7 cm^{-1} line of Si metal, data were collected over the range 4000-100 cm^{-1} for

93   20 s, and the final spectrum is the average of 2 scans. The FTIR spectrum was collected using

94   a Bruker Hyperion IR microscopy equipped with a liquid-nitrogen-cooled detector on a thin film

95   produced with a diamond anvil. Spectra over the range 4000-400 cm^{-1} were obtained by

96   averaging 100 scans with a resolution of 4 cm^{-1}. Base-line correction was done using the OPUS

97   spectroscopic software (Bruker Optic GmbH).

98   Both infrared and Raman spectra have an intense envelope of absorption centered on

99   ~3550 cm^{-1} (Figs. 2 and 3) and showing extensive fine structure with numerous sharp bands

100   characteristic of O-H stretching modes, in accord with the presence of numerous (OH) groups in

101   the structure. The IR spectrum (Fig. 4) shows a strong absorption centered at ~890 cm^{-1} with

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102   two shoulders at 952 and 932, an intense peak at 802 cm^{-1} and weaker peaks at 1024, 741 and

103   670 cm^{-1}, whereas the Raman spectrum shows a strong band at ~790 cm^{-1} with shoulders at

104   822 and 843 cm^{-1} and separate weak peaks at 897 and 732 cm^{-1} (Fig. 2). In carlfrancisite, there

105   are three groups, $(SiO_4)^{4-}$, $(AsO_4)^{3-}$ and $(AsO_3)^{3-}$ that will each have a symmetric stretch and an

106   asymmetric stretch. However, the frequency separations between the bands due to the

107   asymmetric and the symmetric stretches vary strongly from one structure to another, and cannot

108   be assigned with conviction. The Raman spectrum of the much simpler mineral dixenite,

109    $Cu^+Mn^{2+}_{14}(As^{3+}O_3)_5(SiO_4)_2(As^{5+}O_4)$ (OH)$_6$, has been assigned by Bahfenne and Frost (2009), but

110   some features of the assignment are not compatible with the known structure of dixenite. Any

111   assignment of the vibrational spectra of carlfrancisite at the present time would be speculative at

112   best.

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114   CHEMICAL COMPOSITION

115   Carlfrancisite (not the crystal used for its structure determination) was analyzed with a

116   Cameca SX-100 electron microprobe operating in wavelength-dispersion mode with an

117   accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 10 μm. The

118   following standards were used: cobaltite: As; apatite: P; synthetic VP_2O_7: V; diopside: Si;

119   andalusite: Al; fayalite: Fe; spessartine: Mn; forsterite: Mg. The data were reduced and

120   corrected by the *PAP* method of Pouchou and Pichoir (1985) and are given in Table 1. The

121   As_2O_5 and As_2O_3 contents were derived from the corresponding site-occupancies from the

122   crystal-structure refinement and the As content determined by electron-microprobe analysis.

123   The presence and quantity of (OH) groups were established by crystal-structure solution and

124   refinement. In addition, both Raman and infrared spectroscopy (Fig. 3) show the presence of

125   numerous sharp peaks assigned to O-H stretching modes. Table 1 gives the chemical

126   composition (mean of ten determinations). The empirical formula was calculated on the basis of

127   96 anions with (OH) = 42 a.p.f.u. (anions per formula unit) as indicated by crystal-structure

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128   solution and refinement, giving $Mn^{2+}_{33.55}Mg_{10.39}Fe^{2+}_{0.14}Al_{0.68}As^{3+}_{1.44}(Si_{6.67}P_{0.32}V^{5+}_{0.37}As^{5+}_{5.08})O_{54}$

129    $(OH)_{42}$. The general structural formula is ideally $Mn^{2+}_3(Mn^{2+},Mg,Fe^{3+},Al)_{42}(As^{3+}O_3)_2(As^{5+}O_4)_4$

130    $[(Si,As^{5+})O_4]_6[(As^{5+},Si)O_4]_2(OH)_{42}$.

131

132   **X-RAY POWDER DIFFRACTION**

133   X-ray powder-diffraction data were obtained as indicated in Table 2. We indexed the

134   powder pattern from intensities calculated with the routine XPOW embedded in the Bruker

135   system of programs, and used this indexing to refine the unit-cell dimensions using the program

136   CELREF (Appleman and Evans 1973). However, this resulted in lines that could not be indexed

137   on the resulting unit-cell of carlfrancisite. However, detailed examination of the single-crystal

138   diffraction frames did not show the presence of any reflections that could not be indexed on the

139   carlfrancisite cell. Eventually, we realized that the routines we were using to calculate reflection

140   intensities did not assign *hkl* indices greater than 50. Normally this is not an issue, but for

141   carlfrancisite with its *c* dimension of ~205 Å, indices for *l* can considerably exceed this value.

142   Where the pattern was directly indexed from single-crystal data (rather than calculating the

143   resultant powder-pattern intensities), all lines could be indexed. Data (in Å for Cu*K*α) are listed

144   in Table 2. Unit-cell parameters refined from the powder data are as follows: *a* = 8.2148(2), *c* =

145   204.54(4) Å, *V* = 11,953(1) Å^3, close to the values obtained by single-crystal diffraction (see

146   below).

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148   **SINGLE-CRYSTAL DIFFRACTION**

149   A crystal was attached to a tapered glass fibre and mounted on a Bruker D8 three-circle

150   diffractometer equipped with a rotating-anode generator (Mo*K*α), multilayer optics and an

151   APEX-II detector. A total of 111,042 intensities was collected to 60° 2θ using 10 s per 0.2°

152   frames with a crystal-to-detector distance of 5 cm. The following unit-cell dimensions were

153   obtained by least-squares refinement of the positions of 9,631 reflections with *I* > 10σ*I*: *a* =

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154   8.2238(2), c = 205.113(6) Å, V = 12,013.5(4) Å^3, Z = 6, c:a = 1:24.941. Systematic extinctions

155   are in accord with the space group $R\bar{3}c$. The crystal structure is extremely complicated and will

156   be described in detail elsewhere, together with the structure of mcgovernite.

157

158   **RELATED MINERALS**

159   Carlfrancisite, ideally $Mn^{2+}_3(Mn^{2+},Mg,Fe^{3+},Al)_{42}(As^{3+}O_3)_2(As^{5+}O_4)_4[(Si,As^{5+})O_4]_6$

160     $[(As^{5+},Si)O_4]_2(OH)_{42}$, is related to mcgovernite (Palache and Bauer 1927; Wuensch 1960, 1968;

161   Cooper and Hawthorne 2001), ideally $(Zn,Mn^{2+})_3(Mn^{2+},Mg,Fe^{3+},Al)_{42}[(As^{3+},Zn)O_3]_2(As^{5+}O_4)_4$

162     $[(Si,As^{5+})O_4]_8(OH)_{42}$, and turtmannite (Brugger et al. 2001), ideally $(Mn,Mg)_{22.5}Mg_{3-3x}(VO_4)_3$

163     $(SiO_4)_3(AsO_3)_xO_{5-5x}(OH)_{20+x}$. All three structures have the same space group $R\bar{3}c$ and similar

164   unit-cell dimensions, and consist of close-packed and not-so-close-packed layers of octahedra

165   and tetrahedra stacked along the c direction. Comparative data are given in Table 3. These

166   structures are the most complicated of a family of minerals based on dominantly close-packed

167   layers (Wuensch 1968), including arakiite (Cooper and Hawthorne 1999), dixenite (Araki and

168   Moore 1981), franciscanite (Pertlik 1986), hematolite (Moore and Araki 1978), kraissilite (Moore

169   and Ito 1978; Cooper and Hawthorne 2013), örebroite (Dunn et al. 1986) and welinite (Moore

170   1967).

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172   **ACKNOWLEDGEMENTS**

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9

227   **Figure captions**

228

229   **Figure 1.** Images of carlfrancisite: (a) platy aggregates on a matrix of Mn arsenates and oxides;

230   (b) yellow-orange platy aggregate of carlfrancisite.

231

232   **Figure 2.** The Raman spectrum of carlfrancisite.

233

234   **Figure 3.** The Raman (top) and infrared (bottom) spectra of carlfrancisite in the principal OH-

235   stretching region.

236

237   **Figure 4.** The infrared spectrum of carlfrancisite from 1200 to 650 cm^{-1}.

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TABLE 1. Chemical composition of carlfrancisite.

Constituent	wt.%	Range
As_2O_5 *	13.07	–
As_2O_3 *	3.18	–
P_2O_5	0.50(5)	0.41-0.57
SiO_2	8.96(8)	8.86-9.10
Al_2O_3	0.78(3)	0.73-0.83
V_2O_3	0.61(4)	0.54-0.67
FeO	0.22(3)	0.18-0.26
MnO	53.25(26)	52.88-53.65
MgO	9.37(11)	9.20-9.52
H_2O	8.58	—
Total	98.52	

F, Cu, Zn: below detection limits.

*As_2O_5 16.76(28), range = 16.34-17.25 wt.%

TABLE 2. X-ray powder-diffraction pattern for carlfrancisite

$I_{obs.}$	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	h	k	l	$I_{obs.}$	$d_{obs.}$ (Å)	d_{calc} (Å)	h	k	l
25	17.086	17.055	0	0	12	88 B	2.371 *	2.371	3	0	0
27	11.386	11.370	0	0	18	"	2.371 *	2.369	3	0	3
9	6.837	6.853	0	1	8	18	2.341	2.341	$\bar{2}$	3	43
14	6.221	6.216	$\bar{1}$	1	16	11	2.287	2.287	$\bar{1}$	3	47
36	5.689	5.685	0	0	36	16	2.276	2.274	0	0	90
"	5.689	5.650	$\bar{1}$	1	22	15 B	2.245	2.247	$\bar{1}$	3	50
15	5.275	5.277	0	1	26	19	2.209	2.211	$\bar{1}$	2	78
11	5.091	5.097	$\bar{1}$	1	28	"	2.209	2.206	$\bar{1}$	3	53
11	4.880	4.873	0	0	42	9	2.180	2.179	$\bar{2}$	3	55
8	4.754	4.756	0	1	32	12 B	2.128	2.132	0	3	42
8	4.593	4.595	$\bar{1}$	1	34	"	2.128	2.125	$\bar{1}$	3	59
21 B	4.286	4.294	0	1	38	13	2.044	2.044	$\bar{1}$	3	65
48	4.107	4.106	$\bar{1}$	2	0	14	2.018	2.018	$\bar{2}$	3	67
15	3.925	3.932	$\bar{1}$	2	15	14	2.009	2.005	$\bar{1}$	3	68
11	3.889	3.893	0	1	44	13	1.968	1.967	$\bar{1}$	1	100
17	3.783	3.784	$\bar{1}$	2	21	8 B	1.939	1.940	$\bar{2}$	3	73
15	3.616	3.611	$\bar{1}$	2	27	24	1.890	1.890	$\bar{1}$	3	77
8 B	3.522	3.522	$\bar{2}$	2	8	9	1.857	1.858	$\bar{1}$	4	37
"	3.522	3.518	$\bar{1}$	2	30	18	1.817	1.817	$\bar{1}$	3	83
43	3.430	3.444	$\bar{1}$	1	52	12	1.795	1.794	$\bar{2}$	3	85
"	3.430	3.424	$\bar{1}$	2	33	7 B	1.776 *	1.774	0	2	100
11	3.329	3.329	$\bar{1}$	2	36	"	1.776 *	1.774	0	4	8
54 B	3.243	3.251	0	1	56	11 B	1.761 *	1.761	1	1	105
"	3.243	3.234	$\bar{1}$	2	39	"	1.761 *	1.761	2	0	101
10	3.194	3.198	0	2	28	31	1.725	1.725	$\bar{2}$	3	91
37	3.139	3.140	$\bar{1}$	2	42	30 B	1.698	1.699	$\bar{3}$	3	84
43 B	3.051	3.062	0	2	34	"	1.698	1.699	0	3	84
"	3.051	3.048	$\bar{1}$	2	45	11 B	1.682	1.681	$\bar{1}$	3	95
10	2.996	2.994	0	1	62	5	1.660	1.661	0	4	44
10	2.967	2.968	$\bar{2}$	2	38	"	1.660	1.660	$\bar{2}$	3	97
47	2.918	2.920	0	2	40	16	1.649	1.649	$\bar{1}$	3	98
86	2.869	2.870	$\bar{1}$	2	51	27	1.629	1.628	$\bar{2}$	3	100
100	2.826	2.825	$\bar{2}$	2	44	"	1.629	1.629	$\bar{3}$	5	7
32	2.778	2.778	0	2	46	19	1.619	1.618	$\bar{1}$	3	101
14	2.706	2.704	$\bar{1}$	1	70	9 B	1.606	1.608	$\bar{1}$	1	124
"	2.706	2.703	$\bar{1}$	2	57	"	1.606	1.606	$\bar{3}$	4	74
63	2.676	2.677	$\bar{2}$	3	7	10 B	1.598	1.599	0	4	56
13	2.645	2.644	$\bar{1}$	3	14	"	1.598	1.598	$\bar{2}$	3	103
23	2.622	2.624	$\bar{1}$	3	17	6 B	1.586	1.588	$\bar{1}$	3	104
15	2.579	2.578	0	1	74	"	1.586	1.584	$\bar{3}$	5	31
28	2.545	2.544	$\bar{1}$	3	26	12 B	1.565	1.568	$\bar{2}$	3	106
9	2.524	2.523	$\bar{2}$	3	28	"	1.565	1.565	$\bar{3}$	5	37
19	2.435	2.436	0	0	84	84	1.552	1.552	$\bar{1}$	5	0
30	2.418	2.418	$\bar{2}$	3	37	15	1.540	1.540	$\bar{2}$	5	44
39	2.408	2.405	$\bar{1}$	3	38						

Powder data collected on Siemens D5000 powder diffractometer from 4 - 62° 2θ; step width = 0.020°; step time = 20 s; divergence and anti-scatter slits = 1.0 mm; Cu$K\alpha$ radiation (λ = 1.54178Å); 40 V / 40 mA; no internal standard used. Indexed on a = 8.2128(14), c = 204.66(5) Å, V = 11,955.2(3.5) Å^3.

B = broad reflection, * = not used in refinement

TABLE 3.   Comparison of the properties of carlfrancisite, mcgovernite and turtmannite

	Carlfrancisite[*,1]	Mcgovernite[2]	Turtmannite[3]
Formula	see below*	see below	see below
Symmetry	Rhombohedral	Rhombohedral	Rhombohedral
Space group	$R\bar{3}c$	$R\bar{3}c$	$R\bar{3}c$
a (Å)	8.2238	8.2061	8.259
c	205.113	204.118	204.3
Z	6	6	6
V (Å^3)	12,013.5	11,851.3	12,068.5
Colour	shades of yellow	shades of brown-orange	bright yellow
Cleavage	{001} perfect	{001} perfect	{001} perfect
Hardness	3	3	–
Occurrence	Mn deposit	Mn-Zn deposit	Mn deposit

*Carlfrancisite: $Mn^{2+}_3(Mn^{2+},Mg)_{34}(Mg, Fe,Al)_8[(As^{3+}O_3),(Mn^{2+}O_6)]_2(As^{5+}O_4)_4 [(Si,As^{5+})O_4]_6[(As^{5+},Si)O_4]_2(OH)_{42}$;

mcgovernite:$(Zn,Mn^{2+})_3(Mn^{2+},Mg,Fe^{3+},Al)_{42}[(^{[3]}As^{3+},^{[5]}Zn)O_3]_2(As^{5+}O_4)_4 [(Si,As^{5+})O_4]_8(OH)_{42}$;

turtmannite: $(Mn,Mg)_{45}Mg_{6(1-x)}(VO_4)_6(SiO_4)_6(AsO_3)_xO_{10(1-x)}(OH)_{40+x}$.

The characteristic differences between carlfrancisite and mcgovernite are as follows. Essential [5]-coordinated Zn in mcgovernite is replaced by Mn in carlfrancisite. In addition, in mcgovernite, there are two tetrahedrally coordinated sites fully occupied by As^{5+} and four tetrahedrally coordinated sites occupied by Si and As^{5+} with Si dominant at all four sites; in carlfrancisite, there are two tetrahedrally coordinated sites fully occupied by As^{5+} and four tetrahedrally coordinated sites occupied by Si and As^{5+} with Si dominant at only three of these four sites. Turtmannite is distinct from both carlfrancisite and mcgovernite by having essential tetrahedrally coordinated V^{5+}.

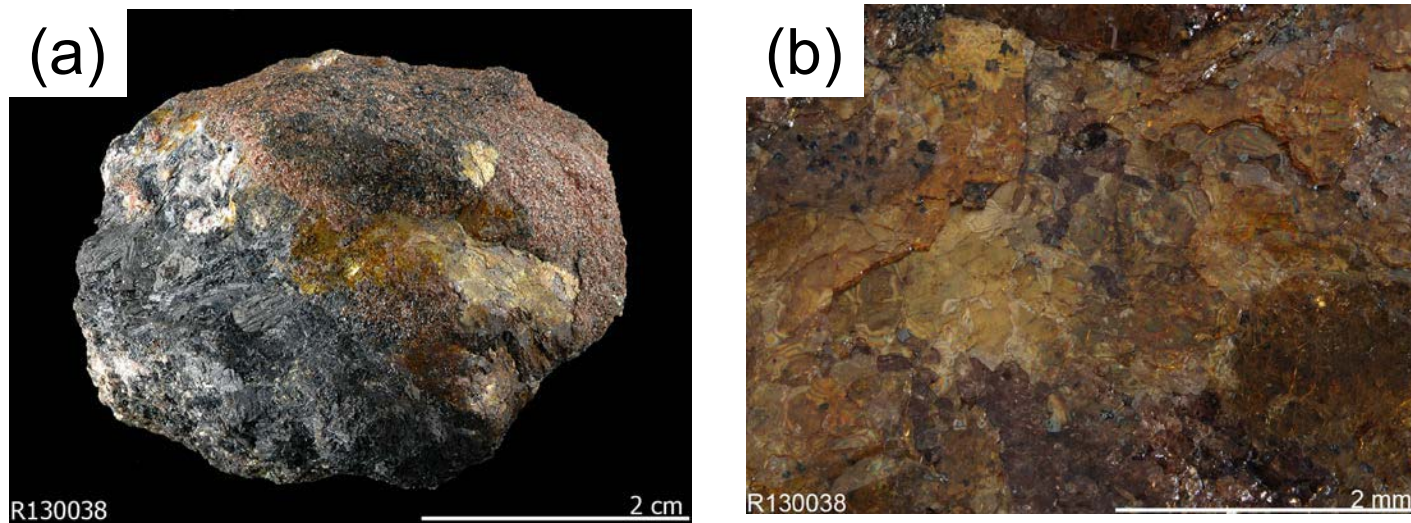[1] This study; [2] Cooper and Hawthorne (2001); [3] Brugger et al. (2001).
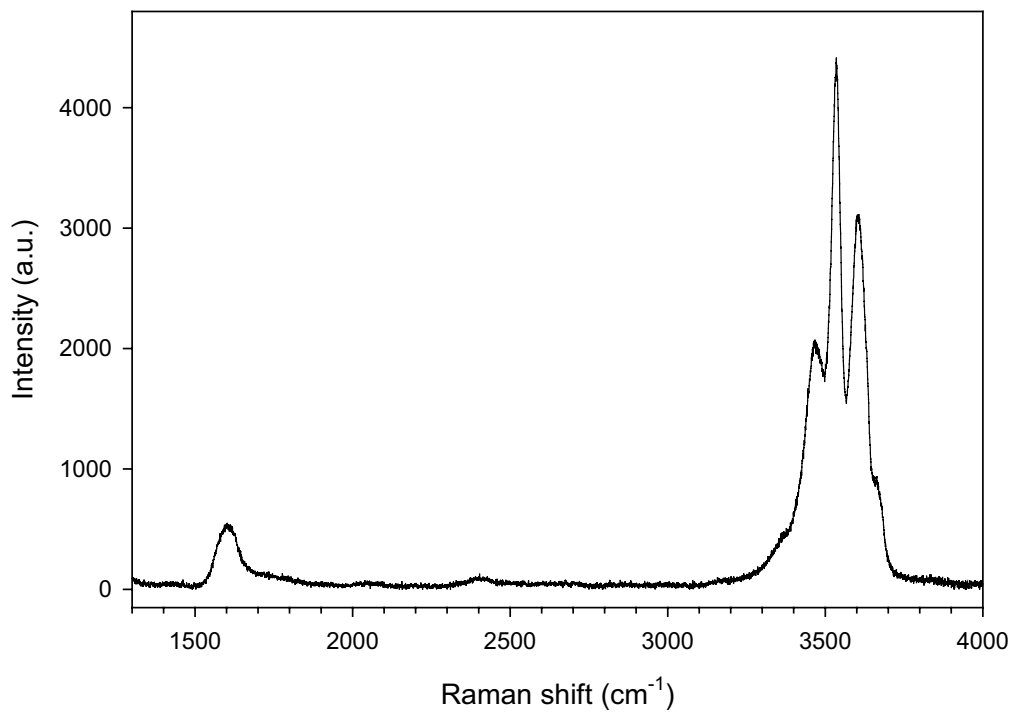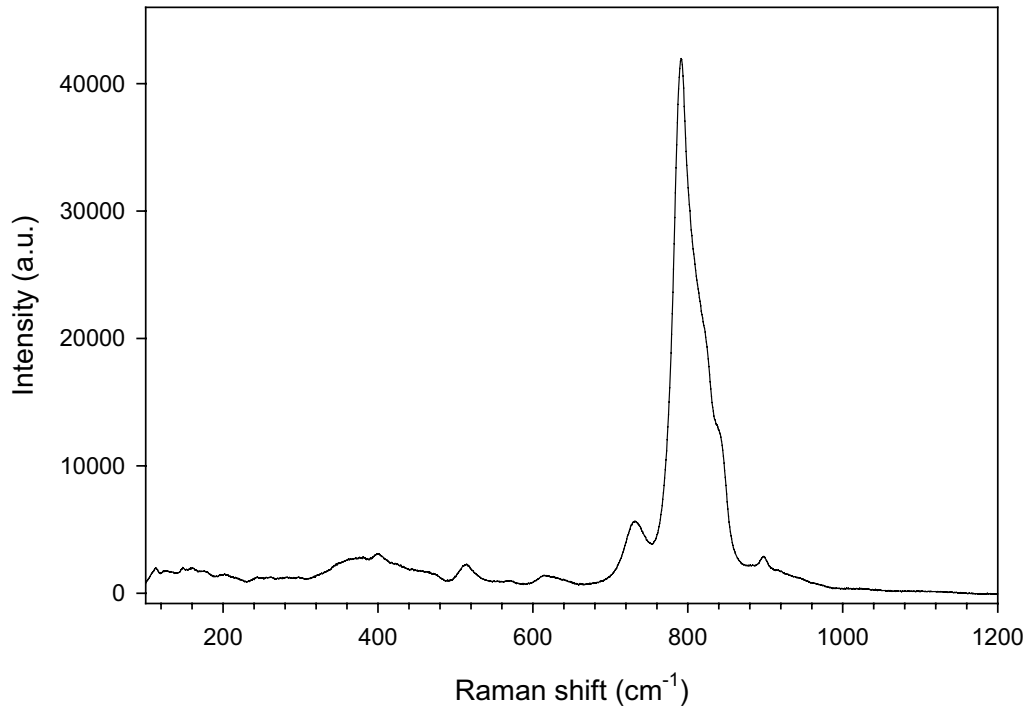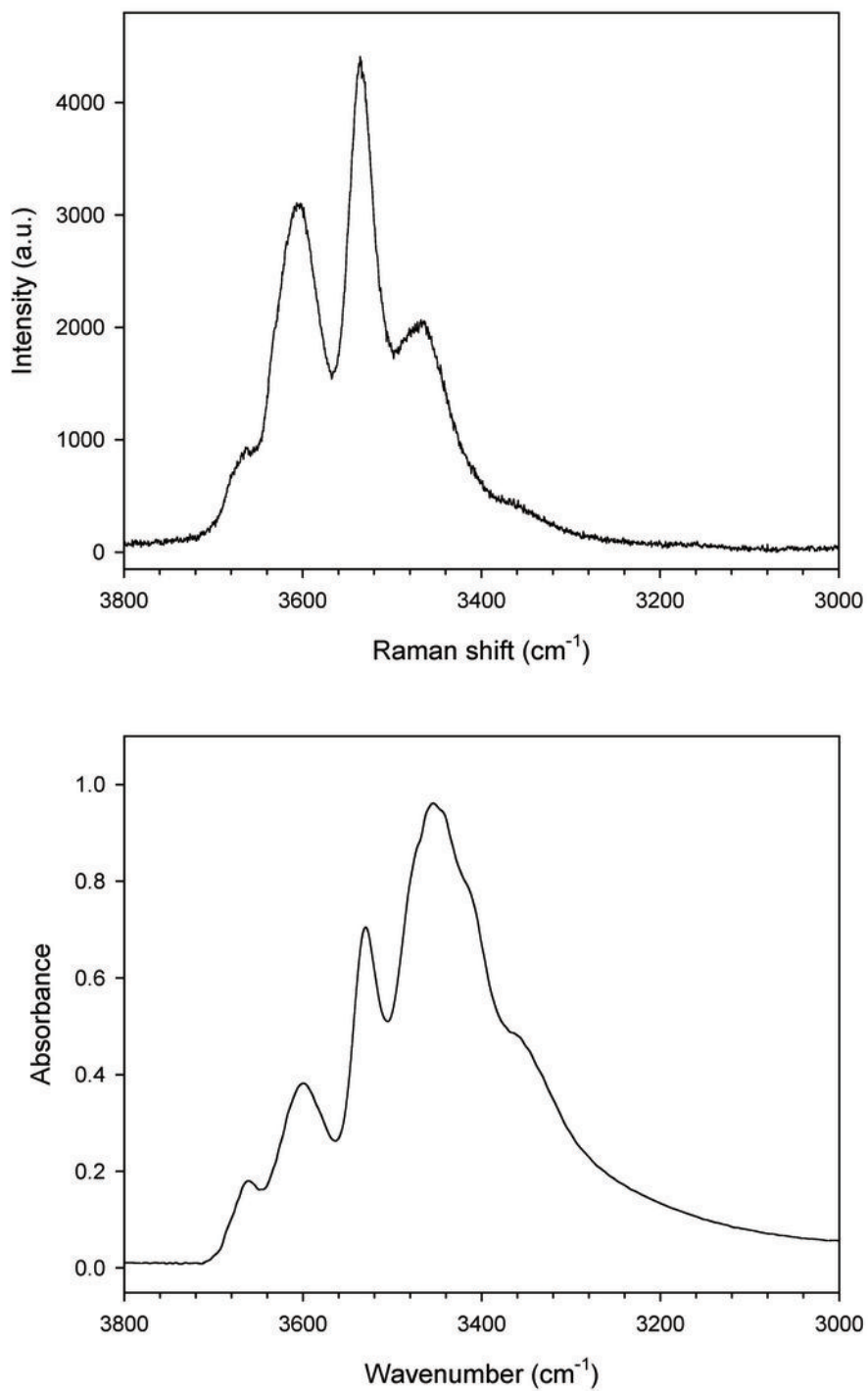
FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4