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1 **Raman spectroscopic study of the uranyl titanate mineral holfertite**

2 **$\text{Ca}_x\text{U}_{2-x}\text{Ti}(\text{O}_{8-x}\text{OH}_{4x})\cdot 3\text{H}_2\text{O}$ and the lack of metamictization**

3
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8
9 **Abstract**

10
11 Raman spectra of the uranyl titanate mineral holfertite $\text{Ca}_x\text{U}_{2-x}\text{Ti}(\text{O}_{8-x}\text{OH}_{4x})\cdot 3\text{H}_2\text{O}$ were
12 analysed and related to the mineral structure. Observed bands are attributed to the TiO and
13 $(\text{UO}_2)^{2+}$ stretching and bending vibrations, U-OH bending vibrations, H₂O stretching,
14 bending. The mineral holfertite is metamict as is evidenced by order/disorder of the mineral.
15 Unexpectedly the Raman spectrum of holfertite does not show any metamictization. The
16 intensity of the UO stretching and bending modes show normal intensity and the bands are
17 sharp.

18
19 **KEYWORDS:** holfertite, uranyl, titanium, mineral, betafite, Raman spectroscopy, U-O bond
20 length

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23 INTRODUCTION

24
25 In the uranium processing industry, certain minerals are difficult to convert to yellow
26 cake because of their formulation. Among these uranium minerals are those which contain
27 titanium. These minerals include absite $\text{Ti}_7\text{U}_2\text{ThO}_{20}\cdot 5\text{H}_2\text{O}$, betafite $(\text{Ca,U})_2(\text{Ti,Nb})_2\text{O}_6(\text{OH})$,
28 brannerite $(\text{U}^{4+},\text{REE,Th,Ca})(\text{Ti,Fe}^{3+},\text{Nb})_2(\text{O,OH})_6$, davidite-(La)
29 $(\text{La,Ce})(\text{Y,U,Fe}^{2+})(\text{Ti,Fe}^{3+})_{20}(\text{O,OH})_{38}$ and holfertite $\text{Ca}_x\text{U}_{2-x}\text{Ti}(\text{O}_{8-x}\text{OH}_{4x})\cdot 3\text{H}_2\text{O}$ [1, 2]. The
30 presence of holfertite and related minerals is of particular importance at the Ranger Uranium
31 Mine, at Kakadu, Northern Territory, Australia. Holfertite is an hydrated calcium uranyl
32 hydroxy titanate with a trigonal structure and consists of small yellow rod-like needles [1, 2].
33 The mineral has probably been formed through Metamictization (sometimes called
34 metamiction). The exact formula of the mineral is imprecise because of disorder-order in
35 the structure [2]. According to Belakovskiy et al. the structure of holfertite is based upon
36 chains of U and Ti polyhedra linking through common vertices to form a framework with
37 channels along (001). The channels are $\sim 8 \text{ \AA}$ wide and are occupied by Ca and H_2O .

38
39 Belakovskiy et al. Reported an infrared spectrum of holfertite [1]. These authors
40 reported an infrared spectrum which they felt was ambiguous in relation to the presence of
41 OH units. Intense infrared bands at 3390 and 1621 cm^{-1} were attributed to H_2O stretching and
42 bending vibrations. Uranyl groups were identified by an infrared band at 892 cm^{-1} ,
43 presumably attributable to the antisymmetric stretching vibration. TiO was identified through
44 the infrared band at 622 cm^{-1} . No Raman spectrum of holfertite has been published, although
45 a Raman spectrum exists in the RRUFF data base
46 (<http://rruff.info/holfertite/display=default/>).

47 Raman spectroscopy has proven very useful for the study of minerals. Indeed Raman
48 spectroscopy has proven most useful for the study of diagenetically related minerals as often
49 occurs with minerals containing uranyl groups [3-7]. This paper is a part of systematic
50 studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone and
51 their synthetic analogs. In this work we attribute bands at various wavenumbers to vibrational
52 modes of holfertite using Raman spectroscopy and relate the spectra to the molecular
53 structure of the mineral.

57 **EXPERIMENTAL**

58 **Minerals**

59

60 The holfertite mineral used in this work was obtained from Museum Victoria. The
61 sample originated from the Holfertite pit, Stravation Canyon (Searles Canyon) Thomas
62 Range, Juab County, Utah, USA. The chemical composition of the mineral has been
63 published [1]. A Raman spectrum was also downloaded from the RRUFF data base
64 (<http://rruff.info/holfertite/display=default/>). The sample also originated from Searle Canyon,
65 Thomas Range, Juab County, Utah, USA

66

67 **Raman microprobe spectroscopy**

68

69 The crystals of holfertite were placed and orientated on the stage of an Olympus
70 BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000
71 Raman microscope system, which also includes a monochromator, a filter system and a
72 Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a
73 resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Repeated acquisition using the
74 highest magnification was accumulated to improve the signal to noise ratio. Spectra were
75 calibrated using the 520.5 cm^{-1} line of a silicon wafer. Previous studies by the authors provide
76 more details of the experimental technique.

77

78 Spectral manipulation such as baseline adjustment, smoothing and normalisation were
79 performed using the Spectracalc software package GRAMS (Galactic Industries Corporation,
80 NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software
81 package which enabled the type of fitting function to be selected and allows specific
82 parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss
83 cross-product function with the minimum number of component bands used for the fitting
84 process. The Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was
85 undertaken until reproducible results were obtained with squared correlations of r^2 greater
86 than 0.995.

87

88

89 RESULTS AND DISCUSSION

90

91 It is noted that the XRD patterns show a disordered structure. Yet quality Raman spectra may
92 be obtained indicating that the disorder does not occur at the molecular level. The Raman
93 spectrum of holfertite is displayed in Figure 1. An intense sharp band is observed at 828 cm^{-1}
94 and is assigned to the UO_2^{2+} symmetric stretching mode. In the infrared spectrum a broadish
95 band was observed at 892 cm^{-1} and is assigned to the UO_2^{2+} antisymmetric stretching mode.
96 The Raman spectrum of holfertite downloaded from the RRUFF data base is given in Figure
97 2. A sharp intense band is observed at 812 cm^{-1} and corresponds to the 828 cm^{-1} band
98 observed in this work.

99

100 The Raman spectrum displays a sharp band at 749 cm^{-1} . It is likely that this band is due to the
101 TiO stretching vibration of TiO_4 units in the holfertite structure. In the RRUFF spectrum a
102 Raman band at 733 cm^{-1} is observed. In the infrared spectrum of Belakovskiy et al. [1] A
103 quite broad band at 622 cm^{-1} was assigned to the TiO stretching vibrations. These authors
104 proposed that an infrared band at 3420 cm^{-1} was due to overtones of the TiO stretching
105 vibration. Such an assignment seems unlikely. A low intensity Raman band at 641 cm^{-1} is
106 observed. This band may be also associated with TiO vibrations. A Raman band at 628 cm^{-1}
107 was observed in the RRUFF spectrum. A very intense sharp band is observed at 389 cm^{-1}
108 (Figure 1) and at 384 cm^{-1} (Figure 2). This band is associated with OTiO bending vibrations.
109 Other low intensity bands are observed at $328, 257, 201$ and 144 cm^{-1} . The latter three bands
110 are associated with OUO bending vibrations. An intense band at 159 cm^{-1} was observed in
111 the RRUFF spectrum and is the bending mode of the OUO units.

112

113 The Raman spectrum in the 1000 to 3800 cm^{-1} region is reported in Figure 3. The spectrum
114 suffers a little from a lack of signal to noise, nevertheless Raman bands may be resolved as
115 shown. An intense sharp band is observed at 3500 cm^{-1} with a shoulder at 3406 cm^{-1} . There
116 are two possible assignemnts for these bands a) the bands are due to water stretching
117 vibrations and b) the bands are due to stretching vibrations iof the OH units. In the infrared
118 spectrum reported by Belakovskiy et al. The band at 3390 cm^{-1} was assigned to a water
119 stretching vibration. These authors also observed an infrared band at 3240 cm^{-1} . Two Raman
120 bands are observed at 2866 and 2925 cm^{-1} . These bands may be due to organic molecules on
121 the surface of the mineral. A Raman band at 1628 cm^{-1} is observed and is assigned to a water

122 bending vibration. A Raman band at 1128 cm^{-1} is also observed and the position of this band
123 suggests it may be assigned to a UOH bending mode.

124

125 **The effect of metamictization**

126

127 Metamictization is a natural process in which a mineral self destructs, usually through the
128 loss of an alpha particle. This process involves the random expansion of the unit cell with
129 consequent lengthening of the UO bonds. This results in a decrease in the expected intensity
130 of the Raman bands associated with UO_2^{2+} units and also a significant broadening of the
131 bands. Metamictization causes the disorder in the holfertite mineral. However in the Raman
132 spectra of holfertite the peaks are sharp and intense, suggesting at least at the molecular level
133 that metamictization has not affected the structure. Our studies have shown that uranyl
134 containing minerals including absite $\text{Ti}_7\text{U}_2\text{ThO}_{20}\cdot 5\text{H}_2\text{O}$, betafite $(\text{Ca,U})_2(\text{Ti,Nb})_2\text{O}_6(\text{OH})$,
135 brannerite $(\text{U}^{4+},\text{REE,Th,Ca})(\text{Ti,Fe}^{3+},\text{Nb})_2(\text{O,OH})_6$, davidite-(La)
136 $(\text{La,Ce})(\text{Y,U,Fe}^{2+})(\text{Ti,Fe}^{3+})_{20}(\text{O,OH})_{38}$ all show the effect of metamictization with a large
137 decrease in the intensity of bands associated with UO_2^{2+} units and broadening of the bands.

138

139 **CONCLUSIONS**

140

141 The minerals containing the uranyl group and titanium as an oxide are of interest
142 because of their difficulty in mineral processing. These minerals include holfertite, davidite,
143 bannerite, betafite. Observed Raman bands are attributed to the $(\text{UO}_2)^{2+}$ and TiO stretching
144 and bending vibrations, U-OH and OTiO bending vibrations. Minerals such as holfertite
145 undergo a process of metamictization, a process of crystal self destruction. This process
146 involves the expansion of the unit cell in a random manner. This expansion causes a
147 lengthening in the UO bond length. This effect is probably responsible for the disorder/ order
148 in the mineral holfertite and the lack of a precise formula for the mineral. At the molecular
149 level the effect of metamictization is not observed. The Raman spectra of holfertite do not
150 appear to show the effects of metamictization. No decrease in intensity of bands associated
151 with $(\text{UO}_2)^{2+}$ units is observed.

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163

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165

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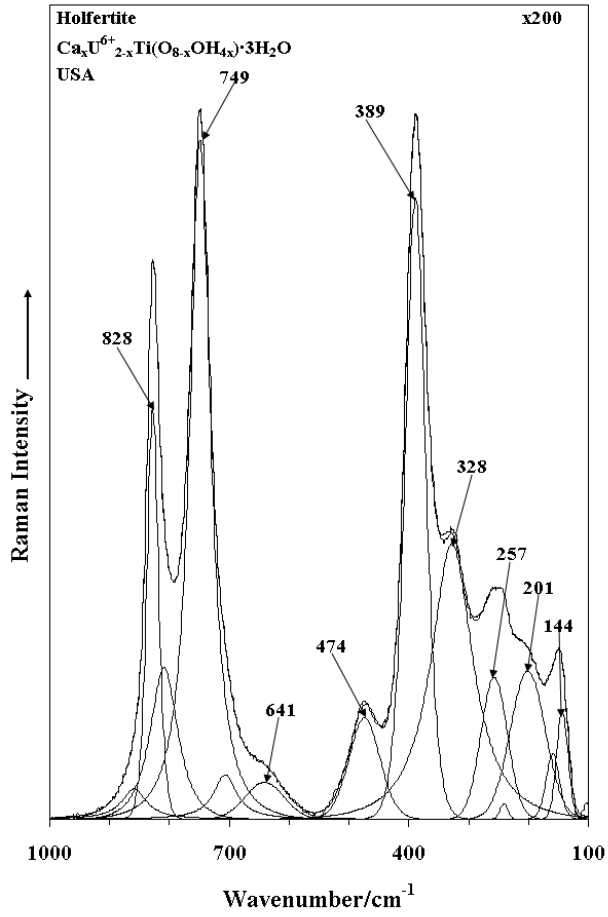
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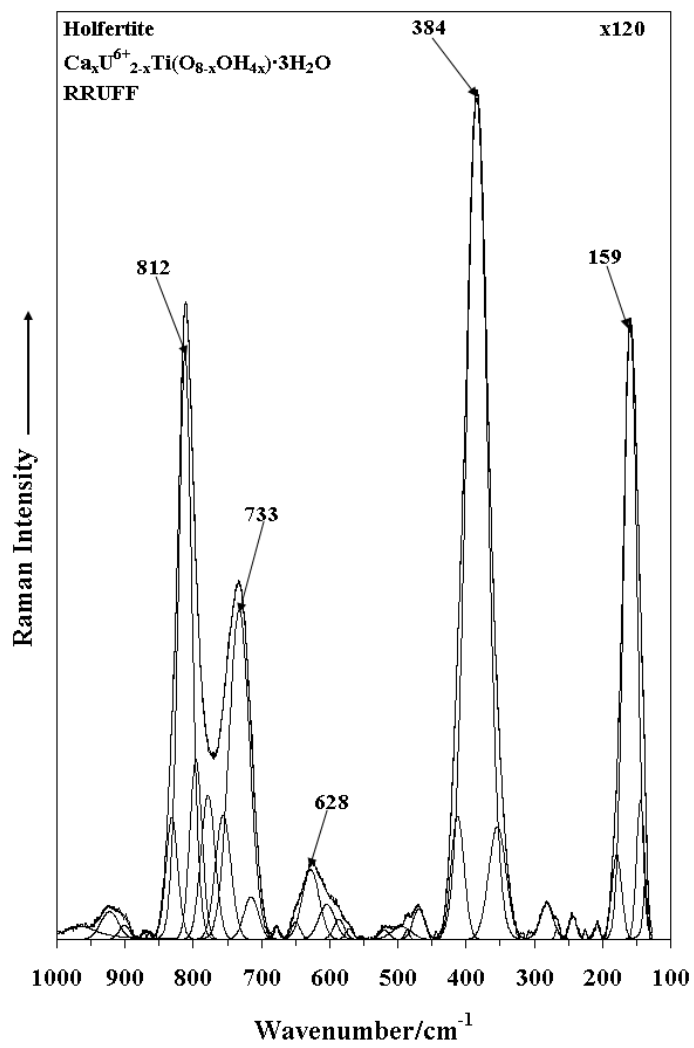


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188 **Figure 1**

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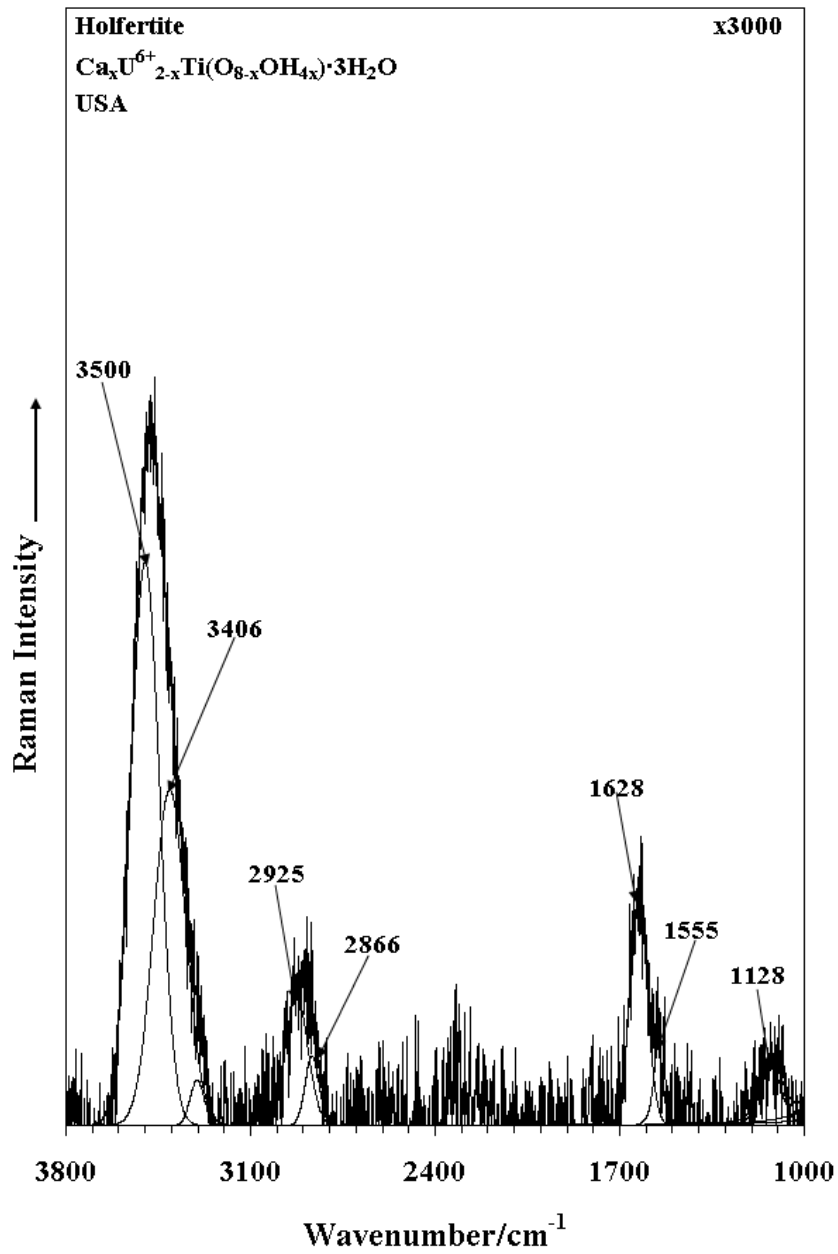


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193 **Figure 2 RRUFF**

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196

197 **Figure 3**

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