A vibrational spectroscopic study of planchéite $Cu_8Si_8O_{22}(OH)_4 \cdot H_2O$

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ABSTRACT

Planchéite $Cu_8Si_8O_{22}(OH)_4 \cdot H_2O$ is a hydrated copper hydroxy silicate. The objective of this work is to use Raman and infrared spectroscopy to determine the molecular structure of planchéite. Raman bands of planchéite at around 1048, 1081 and 1127 are described as the ν_1 $-SiO_3$ symmetric stretching vibrations; Raman bands at 828, 906 are attributed to the ν_3 – SiO_3 antisymmetric stretching vibrations. The Raman band at 699 cm^{-1} is assigned to the ν_4 bending modes of the $-SiO_3$ units. The intense Raman band at 3479 cm^{-1} is ascribed to the stretching vibration of the OH units. The Raman band at 3250 cm^{-1} is evidence for water in the structure. A comparison of the spectra of planchéite with that of shattuckite and chrysocolla.

Keywords: planchéite, shattuckite, silicate, Raman spectroscopy, hydroxyl, healing mineral

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Introduction

The mineral planchéite is a hydrated copper silicate mineral with formula $Cu_8Si_8O_{22}(OH)_4 \cdot H_2O$ [1]. The two minerals shattuckite $Cu_5(SiO_3)_4(OH)_2$ [2] and planchéite were first thought to be the same mineral [3]. However it was proven that the minerals were different [3, 4]. Shattuckite is closely allied to planchéite $Cu_8Si_8O_{22}(OH)_4 \cdot H_2O$ in structure and appearance [5-7]. The mineral planchéite is orthorhombic of point group *2/m 2/m 2/m.* The cell data is space group: Pcnb: a = 19.043(3), b = 20.129(5), c = 5.269(1), Z = 4. This is the most symmetrical class in the orthorhombic crystal class. Planchéite is a chain silicate with double chains of silica tetrahedra parallel to the *C* crystal axis. Planchéite occurs as sprays of acicular or fibrous radial clusters, with fibers extended parallel to the chains, i.e. along the *C* crystal axis. Planchéite is a secondary mineral formed in the oxidized zone of copper ore deposits. The mineral may be associated with other secondary copper minerals including chrysocolla, dioptase, conichalcite, malachite and tenorite.

Raman spectroscopy has proven very useful for the study of minerals [8, 9]. Indeed, Raman spectroscopy is most useful for the study of diagenetically related minerals as often occurs with minerals containing copper and silicate groups. Yet, there appear to be no Raman or spectroscopic studies of this mineral planchéite. Some infrared [10] and optical studies have been undertaken [11, 12]. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. The objective of this research is to report the Raman spectra of planchéite and to relate the spectra to the molecular structure of the mineral.

EXPERIMENTAL

Minerals

The planchéite minerals were supplied by the Mineralogical Research Company. The mineral sample studied in this work originated from Tsumeb, Guchab, Okatumba, about 80 km east of Windhoek, Namibia. The type locality of the mineral is the Sanda Mine, Mindouli, Pool Region, Republic of Congo. Details of the mineral have been published (page 651) [13]. Planchéite is also found at the Mt Isa Mines, Mt Isa, Queensland, Australia. Shattuckite from Bisbee, Cohise County, Arizona , was used for spectroscopic purposes in this work Details of the mineral shattuckite have been published (page 726) [13].

Raman spectroscopy

Crystals of planchéite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 200 and 4000 cm^{-1}. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique. Alignment of all crystals in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation.

Infrared spectroscopy

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

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

than 0.995.

RESULTS AND DISCUSSION

Background

The isolated tetrahedral SiO_4 unit has 9 internal modes of which four modes are vibrationally active due to degeneracy. These vibrations are labelled as the ν_1 symmetric stretching mode, the ν_2 doubly degenerate bend, the ν_3 triply degenerate stretching vibration and the ν_4 triply degenerate bending mode. Only the ν_3 and ν_4 modes are infrared active providing the symmetry of the SiO_4 unit is maintained. The values for zircon as an example are ν_1 974, ν_2 266 and 439, ν_3 885, 989 and 1008, and ν_4 430, 608 cm^{-1}. The fact that planchéite follows a pyroxene type structure means that the siloxane units for polymeric chains and thus the degeneracy of the vibrational modes above will be lifted. The result of this is that the spectra will show much greater complexity. Two types of oxygens may be distinguished, namely terminal and bridging oxygens. Additional bands should be observed related to the Si-O-Si bending vibrations.

Raman spectroscopy

The Raman spectrum over the 100 to 4000 cm^{-1} region is displayed in Figure 1. It is obvious that there are wide spectral regions where no bands are found. Therefore, the spectra are divided into regions based upon the type of vibration being observed. For example, the OH stretching region is observed in the 2700 to 3600 cm^{-1} region. The infrared spectrum of planchéite over the 500 to 4000 cm^{-1} region is displayed in Figure 2. Comparison of the spectra enables the relative intensities of both the Raman and infrared bands to be observed.

Dowty [14-16] showed the relationship between crystal structure of silicate minerals and their vibrational spectra. Dowty calculated the band positions for the different ideal silicate units. Importantly, the type of structure of silicate minerals can be predicted from the position of the Raman and infrared bands. Dowty showed that the $-SiO_3$ units had a unique band position of 980 cm^{-1} [16] (see Figures 2 and 4 of this reference). Dowty also showed that Si_2O_5 units had a Raman peak at around 1100 cm^{-1}. The Raman spectrum in the 600 to 1400 cm^{-1} region is shown in Figure 3. This spectral region is where the Si-O stretching vibrations are found. The intense sharp band at 1081 cm^{-1} is assigned to the SiO symmetrical stretching vibration. This band according to Dowty is associated with the vibrations of Si_2O_5 units . The shoulder

band at 1048 cm^{-1} is also attributed to the SiO symmetrical stretching vibration. The sharp Raman band at around 668 cm^{-1} is assigned to the ν_4 bending mode. The three bands at 828, 863 and 906 cm^{-1} are attributed to the ν_3 $-SiO_3$ antisymmetric stretching vibrations. In comparison, for the mineral shattuckite, a band at around 980 cm^{-1} is observed and attributed to the ν_1 $-SiO_3$ symmetric stretching vibration. The bands for shattuckite at around 890, 1058 and 1102 are described as the ν_3 $-SiO_3$ antisymmetric stretching vibrations. The fact that shattuckite follows a pyroxene type structure means that the siloxane units for polymeric chains and thus the degeneracy of the vibrational modes above will be lifted. The result of this is that the spectra will show much greater complexity. Two types of oxygens may be distinguished, namely terminal and bridging oxygens. Additional bands should be observed related to the Si-O-Si bending vibrations. The Raman spectrum of shattuckite displays a band at 1043 cm^{-1} with a shoulder band at 1048 cm^{-1}. Dowty's calculations predicted the band at 1081 cm^{-1} is attributable to a Si_2O_5 silicate unit [16]. Chrysocolla (Cu, $Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O$ is another hydrated copper hydroxy silicate, the spectra of which may also be sued for comparative purposes. The Raman spectrum of chrysocolla displays a Raman band at around 1042 cm^{-1}. This band is attributed to a SiO_3 stretching vibration of silicate. The 1043 cm^{-1} band of shattuckite is in a similar position to the 1042 cm^{-1} of chrysocolla.

The infrared spectrum of planchéite in the 600 to 1200 cm^{-1} region is reported in Figure 4. Much greater complexity is observed in the infrared spectrum compared with the Raman spectrum. Bands in the Raman spectra are sharp compared with the bands in the infrared spectrum. The sharp bands at 1051 and 1097 cm^{-1} with shoulders at 1037 and 1105 cm^{-1} are assigned to the SiO stretching vibrations. The intense infrared bands in the 740 to 900 cm^{-1} are attributed to the ν_3 antisymmetric –Si-O stretching modes. In comparison, the Raman band for shattuckite at around 670 cm^{-1} is assigned to the ν_4 bending modes of the $-SiO_3$ units. Another shattuckite band is around 785 cm^{-1}. This band is considered to be a Si-O-Si chain stretching mode.

The Raman spectrum of planchéite in the 100 to 600 cm^{-1} region is reported in Figure 5. The Raman bands at around 384, 403 and 421 cm^{-1} are attributed to the ν_2 –O-Si-O bending modes. For shattuckite, Raman bands at around 395 and 441 cm^{-1} are attributed to the ν_2 bending modes. The Raman bands at 476 and 505 cm^{-1} may be assigned to the ν_4 –O-Si-O bending modes. The Raman bands at 302 and 328 cm^{-1} are associated with CuO stretching

vibrations. The Raman bands in the 100 to 245 cm^{-1} may be described as lattice vibrations. The sharp bands at 139 and 186 cm^{-1} may be described as lattice vibrations.

The Raman spectrum of planchéite in the OH stretching region is reported in Figure 6. The spectrum is dominated by two bands at 3250 and 3479 cm^{-1}. These bands are assigned to the OH stretching vibration of the OH units in the planchéite structure. Other Raman bands are observed at 2864, 2901, 2923 cm^{-1} attributed to strongly hydrogen bonded water molecules. Another Raman band at 3061 cm^{-1} is assigned to water stretching bands. In comparison, the intense sharp band for shattuckite at around 3604 cm^{-1} is assigned to the OH stretching vibration of the OH units in the shattuckite structure. The infrared spectrum of planchéite in the 2400 to 3800 cm^{-1} region is shown in Figure 7. The sharp infrared band at 3498 cm^{-1} is assigned to the OH stretching vibration. A series of bands in the 2400 to 3400 cm^{-1} region are attributed to water stretching vibrations. Strong infrared bands are observed at 3188 and 3248 cm^{-1}.

The Raman spectrum in the 1400 to 1800 cm^{-1} region is displayed in Figure 8. An intense band at 1510 cm^{-1} with a shoulder at 1538 cm^{-1}, is observed and assigned to the hydroxyl deformation vibration. Other bands are observed at 1438, 1452 and 1597 cm^{-1}. The infrared spectrum in this spectral region is shown in Figure 9. Intense bands are observed at 1387 and 1514 cm^{-1} with shoulder bands at 1331, 1423 and 1538 cm^{-1}.

Conclusions

Vibrational spectroscopy has been used to characterise the copper silicate mineral planchéite. Planchéite is one of a number of copper based silicate minerals. There are a significant number of silicate minerals which have copper as one of the main cations. These include kinoite $Ca_2Cu_2Si_3O_{10}(OH)_4$, chrysocolla $(Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O$, dioptase $CuSiO_3 \cdot H_2O$, planchéite $Cu_8Si_8O_{22}(OH)_4 \cdot H_2O$, shattuckite $Cu_5(SiO_3)_4(OH)_2$,whelanite $Ca_5Cu_2(OH)_2CO_3,Si_6O_{17} \cdot 4H_2O$, ajoite $(K,Na)Cu_7AlSi_9O_{24}(OH)_6 \cdot 3H_2O$, apachite $Cu_9Si_{10}O_{29} \cdot 11H_2O$, papagoite $CaCuAlSi_2O_6(OH)_3$.

The mineral is a hydrated copper hydroxy silicate $Cu_8Si_8O_{22}(OH)_4 \cdot H_2O$. Based upon the vibrational spectroscopy of the hydroxyl stretching region, water is involved in very strong hydrogen bonding in planchéite.

Bands attributed to SiO stretching and bending vibrations are identified. The Raman and infrared spectra can be sued to distinguish the mineral planchéite from the other copper silicate minerals.

Acknowledgments

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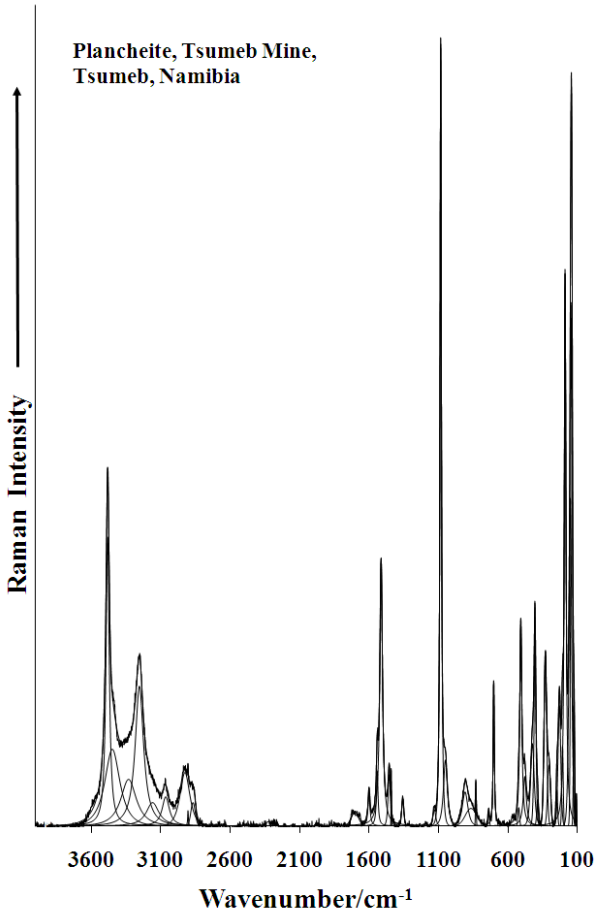
List of Figures



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254 **Figure 1**

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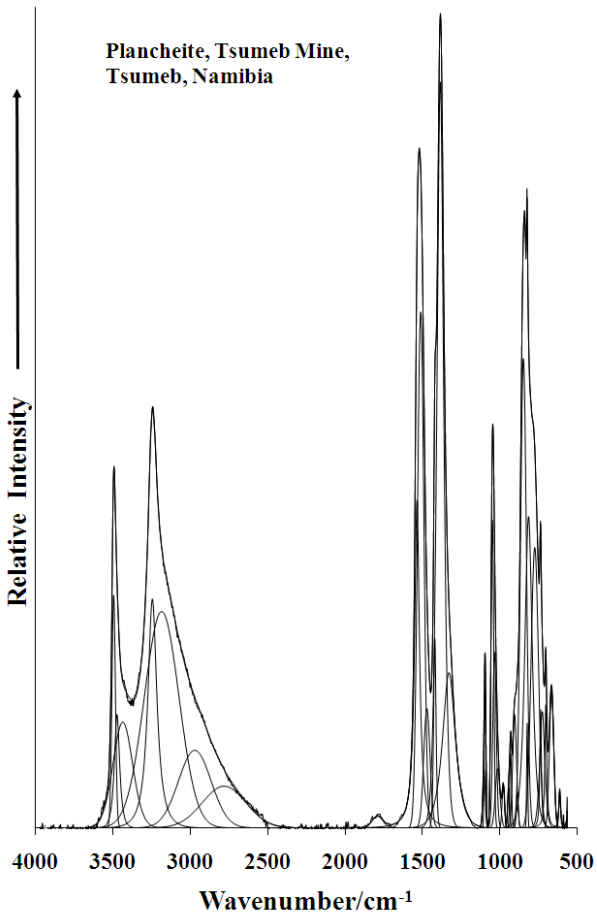

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258 **Figure 2**

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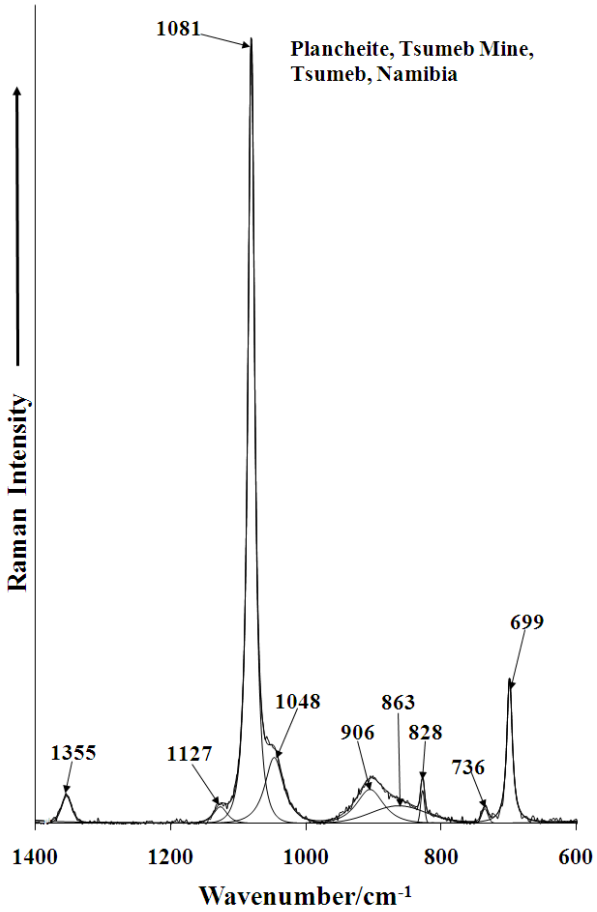
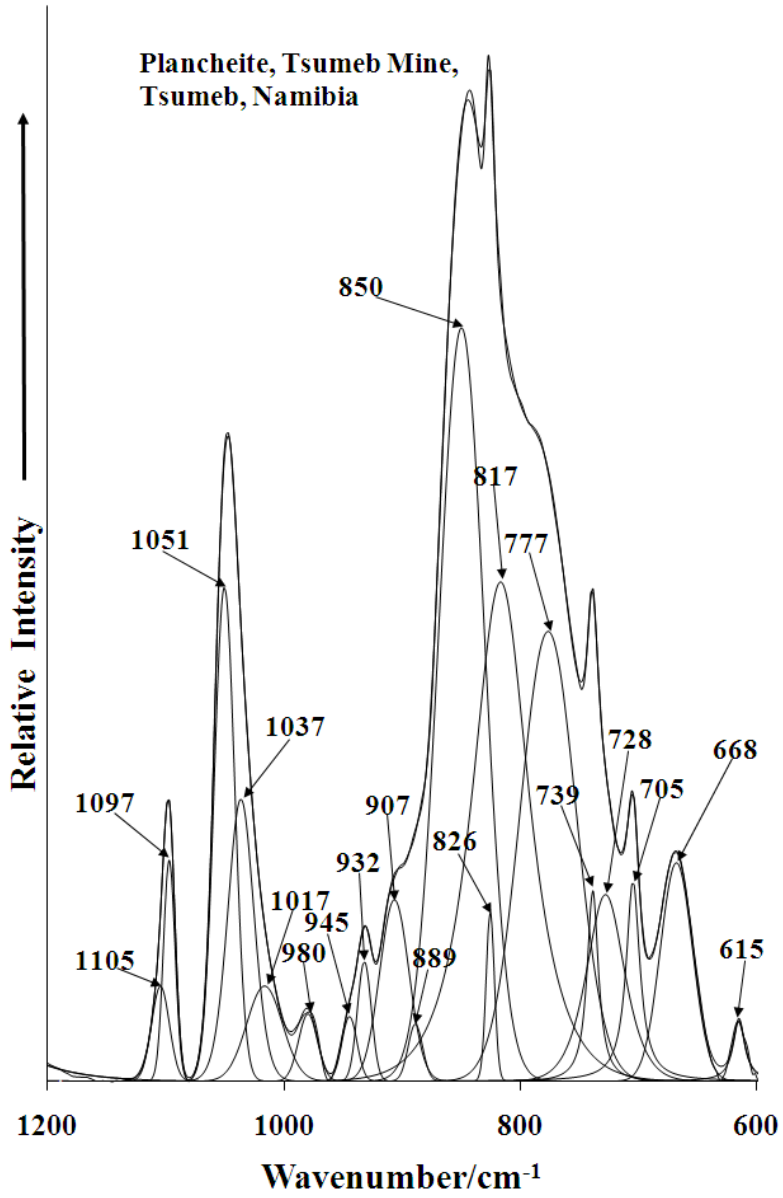

1081
Plancheite, Tsumeb Mine,
Tsumeb, Namibia
Raman Intensity
699
1048
863
906
828
1355
1127
736
1400
1200
1000
800
600
Wavenumber/cm-1

Figure 3



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267 **Figure 4**

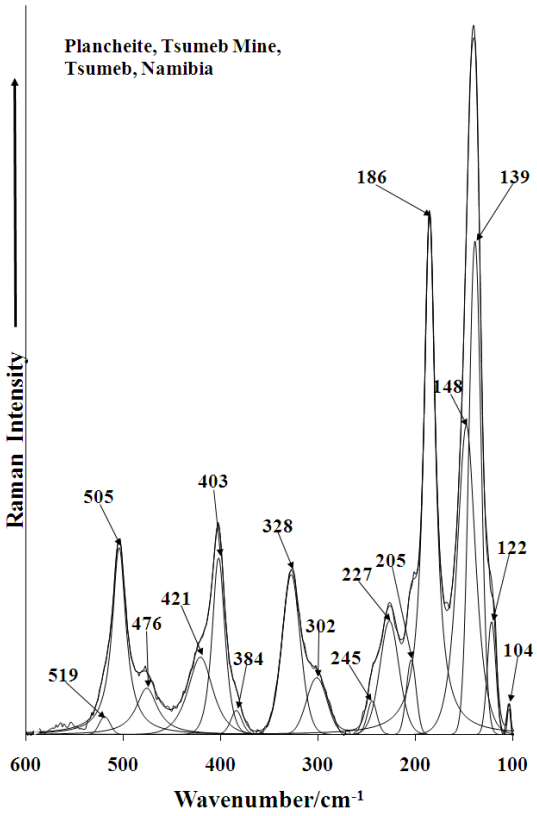

Plancheite, Tsumeb Mine,
Tsumeb, Namibia
Raman Intensity
186
139
148
505
403
328
122
227
205
421
476
302
384
245
519
104
600
500
400
300
200
100
Wavenumber/cm-1

Figure 5

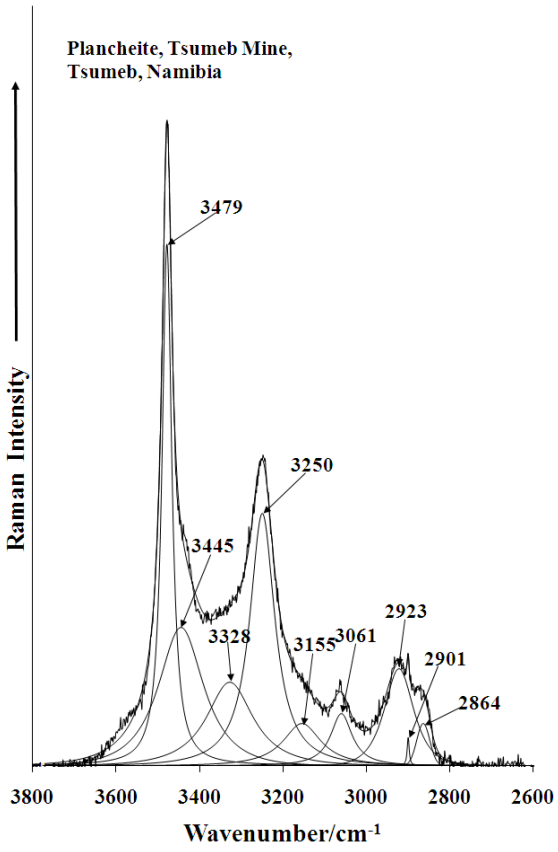

Plancheite, Tsumeb Mine,
Tsumeb, Namibia
Raman Intensity
3479
3250
3445
3328
3155
3061
2923
2901
2864
3800
3600
3400
3200
3000
2800
2600
Wavenumber/cm-1

Figure 6

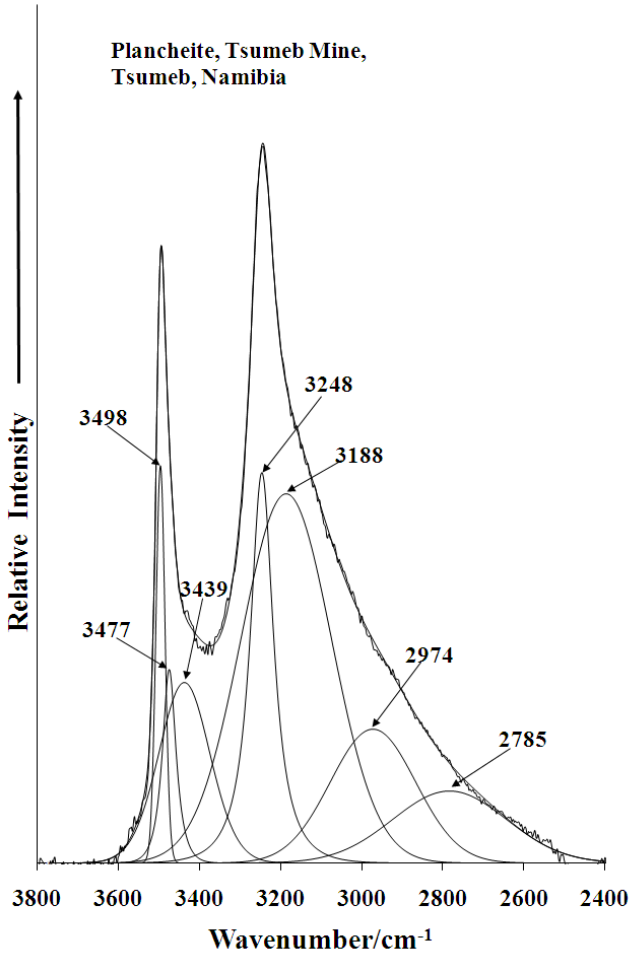

Plancheite, Tsumeb Mine,
Tsumeb, Namibia
Relative Intensity
3498
3248
3188
3439
3477
2974
2785
3800
3600
3400
3200
3000
2800
2600
2400
Wavenumber/cm-1

Figure 7

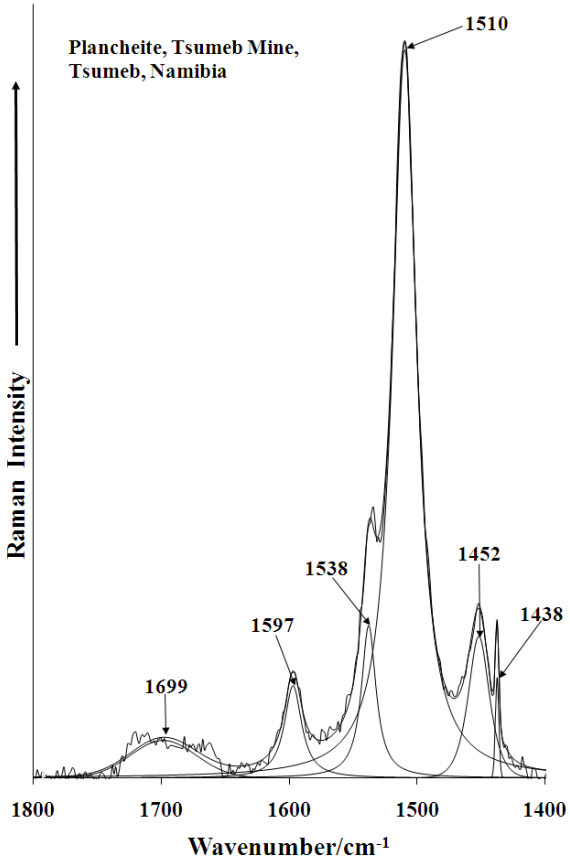
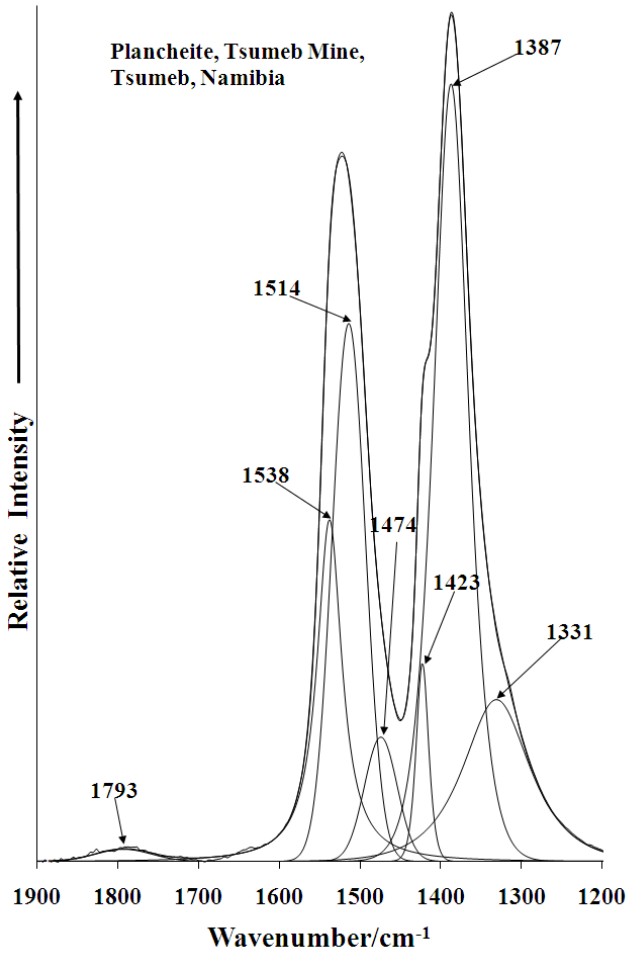

Plancheite, Tsumeb Mine,
Tsumeb, Namibia
1510
1452
1538
1438
1597
1699
Raman Intensity
1800
1700
1600
1500
1400
Wavenumber/cm-1

Figure 8



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290

291 **Figure 9**