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## Raman spectroscopic study of the uranyl carbonate mineral zellerite

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### Abstract

Raman and infrared spectra of the uranyl mineral zellerite,  $\text{Ca}[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ , were measured and tentatively interpreted. U-O bond in uranyl and O-H...O hydrogen bonds were calculated from the vibrational spectra. The presence of structurally nonequivalent water molecules in the crystal structure of zellerite was inferred. Proposed chemical formula of zellerite is supported. Raman bands at 3514, 3375 and 2945  $\text{cm}^{-1}$  and broad infrared bands at 3513, 3396 and 3326  $\text{cm}^{-1}$  are related to the  $\nu$  OH stretching vibrations of hydrogen bonded water molecules. Observed wavenumbers of these vibrations prove that in fact hydrogen bonds participate in the crystal structure of zellerite. The presence of two bands at 1618 and 1681  $\text{cm}^{-1}$  proves structurally distinct and nonequivalent water molecules in the crystal structure of zellerite.

**Key words:** zellerite, uranyl diaquod carbonate, molecular water, Raman and infrared spectroscopy, U-O bond lengths, O-H...O bond lengths

### Introduction

Carbonate complexation of uranium(VI), i.e. of uranyl,  $(\text{UO}_2)^{2+}$ , is among the most important reactions of uranium under natural conditions. The most important uranyl carbonate complexes are  $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$ , however, the presence of  $[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2]^{2-}$  and  $[\text{UO}_2\text{CO}_3]^0$  was proved above all in solid state and also in solution<sup>1</sup>. Uranyl carbonate chemistry and mineralogy has been studied intensively [see e.g. references<sup>2-8</sup> and references therein]. Uranyl tricarbonate complex,  $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$ , is represented in nature and in the laboratory by a relatively large number of uranyl tricarbonate minerals and synthetic compounds containing especially monovalent alkali and divalent alkaline earth cations. Uranyl monocarbonate complex  $[\text{UO}_2\text{CO}_3]$  is represented by uranyl minerals rutherfordine, blatonite and joliotite, while the uranyl dicarbonate complex,  $[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2]^{2-}$  is known only as uranyl minerals zellerite,  $\text{Ca}[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ , and metazellerite,  $\text{Ca}[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  and some insufficiently described synthetic analogues<sup>6-8</sup>

Uranyl carbonate minerals may precipitate when evaporation is significant or when the fugacity of  $\text{CO}_2$  is greater than atmospheric<sup>9</sup>. Uranyl dicarbonates and

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tricarbonates tend to form only where evaporation is high and pH is favorable for the formation of a such complex anion, most of these minerals, however, are ephemeral, dissolving readily when re-exposed to fresh water<sup>9</sup>. Uranyl carbonate complexes in solution are quite stable and are probably the most important solution complexes responsible for uranium migration in oxidizing environments<sup>8,9</sup>. Uranyl carbonate complexes may be important in actinide-contaminated soils and certain high-level nuclear-waste repositories because they may be sinks for <sup>14</sup>C, transuranic actinides and possibly certain fission-products<sup>9</sup>

Zellerite and its partly dehydrated metazellerite,  $\text{Ca}[(\text{UO}_2)(\text{CO}_3)_2] \cdot x\text{H}_2\text{O}$ , are rare weathering products of uranium ores, formed at low pH in the presence of oxidizing pyrite<sup>10,11</sup>. For the dicarbonate species, hexagonally coordinated  $[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2]^{2-}$  with  $D_{2h}$  symmetry and two bidentately bonded carbonate groups and two water molecules in the uranyl equatorial plane is found as most probable structure<sup>1</sup>. Chemical formulas of zellerite and metazellerite should be therefore written as  $\text{Ca}[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$  and  $\text{Ca}[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ , respectively. Zellerite is orthorhombic, space group  $D_{2h}^1 - \text{Pmmm}$  or  $C_{2v}^7 - \text{Pmn}2_1$ ,  $a = 11.220(15)$ ,  $b = 19.252(16)$ ,  $c = 4.933(16)$  Å,  $Z = 4$ . The very rare metazellerite is also orthorhombic, space group  $C_{2v}^9 - \text{Pbn}2_1$  or  $D_{2h}^{16} - \text{Pbnm}$ ,  $a = 9.718(5)$ ,  $b = 18.226(9)$ ,  $c = 4.965(4)$  Å,  $Z = 4$ <sup>10,11</sup>. No other crystal structure data for both minerals are available. Infrared spectrum of zellerite was published, but without any interpretation<sup>12</sup> and reviewed by Čejka<sup>13</sup>.

The Gibbs free energy of formation for zellerite was calculated by Finch and Murakami<sup>9,14</sup>. EXAFS spectroscopy of zellerite was presented by Catalano and Brown<sup>15</sup>. According to the  $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$  cluster in the crystal structure of uranyl tricarbonates, the  $[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2]^{2-}$  cluster may be expected in the crystal structure of uranyl diaquodicarbonates. Crystal structure of zellerite may be understood as an example of such an arrangement. Participation of water molecules from the uranyl diaquod carbonate cluster in O-H...O bond formation and stabilization of the zellerite crystal structure may be expected. Remaining hydrogen bonded water molecules may be coordinated by  $\text{Ca}^{2+}$  cations. According to Coleman et al.<sup>11</sup>, a mineralogical series calcite,  $\text{CaCO}_3$  - liebigite,  $\text{Ca}_2[(\text{UO}_2)(\text{CO}_3)_3] \cdot 11\text{H}_2\text{O}$  - zellerite,  $\text{Ca}[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2]$  - rutherfordine,  $\text{UO}_2\text{CO}_3$  may be established. However, Catalano and Brown<sup>15</sup> assume that a structural relation between zellerite and rutherfordine may exist.

Raman spectroscopy has proven very useful for the study of minerals<sup>16-26</sup>. Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with uranium containing minerals<sup>17,19,24,25,27</sup>. Some previous studies have been undertaken by the authors using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated solutions<sup>16-21,23-25,27-34</sup>. Very few spectroscopic studies of the uranyl phosphates have been forthcoming and what studies that are available are not new. Few Raman studies of any note are available<sup>16,17,22,26,35-38</sup>. The aim of this paper is to present Raman and infrared spectra of the uranyl mineral carbonate zellerite and to relate the Raman spectra to the structure of the mineral. The paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone and their synthetic analogs.

## Experimental

### *The Mineral zellerite*

The mineral zellerite  $\text{CaUO}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$  was supplied by the Mineralogical Research Company. The mineral originated from the White Canyon No1 Mine, Frey Point, Utah, USA<sup>11,39</sup>. A second sample was obtained from Lucky Mc Mine, Wyoming, USA<sup>10</sup>. Another district of origin is Jáchymov, the Krušné Hory Mts., Czech Republic<sup>40</sup>. The analysis of zellerite is given as CaO 10.3 %,  $\text{UO}_3$  53.9 % and  $\text{CO}_3$  16.9%<sup>10</sup>.

### *Raman microprobe spectroscopy*

The crystals of zellerite were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of  $2 \text{ cm}^{-1}$  in the range between 100 and  $4000 \text{ cm}^{-1}$ . Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the  $520.5 \text{ cm}^{-1}$  line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique.<sup>16,17,19,25,27,32,28,41-46</sup>

### *Infrared absorption spectroscopy*

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the  $4000\text{--}525 \text{ cm}^{-1}$  range were obtained by the co-addition of 64 scans with a resolution of  $4 \text{ cm}^{-1}$  and a mirror velocity of  $0.6329 \text{ cm/s}$ . Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz 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

### *Raman and infrared uranyl, (UO<sub>2</sub>)<sup>2+</sup>, vibrations*

The linear uranyl group, (UO<sub>2</sub>)<sup>2+</sup>, has four normal vibrations but three fundamental bands only:  $\nu_1$  symmetric stretching fundamental, Raman active,  $\nu_2$  ( $\delta$ ) doubly degenerate bending fundamental, infrared active, and  $\nu_3$  antisymmetric stretching fundamental, infrared active. Distorsion of the uranyl group or change in the local symmetry can result in the removal of degeneracy of the  $\nu_2$  mode and Raman and infrared activation of all modes.<sup>47</sup>

The Raman spectrum and the infrared spectrum of zellerite in the 100 to 1600 cm<sup>-1</sup> region is shown in Figures 1 and 2 respectively. Raman band at 834 cm<sup>-1</sup> is attributed to the  $\nu_1$  (UO<sub>2</sub>)<sup>2+</sup> symmetric stretching vibration. Infrared band at 899 cm<sup>-1</sup> is assigned to the  $\nu_3$  antisymmetric stretching vibration. A coincidence of these two vibrations with the  $\nu_2$  (CO<sub>3</sub>)<sup>2-</sup> bending vibration is expected<sup>48</sup>. The  $\nu_2$  (CO<sub>3</sub>)<sup>2-</sup> is infrared active and may be activated also in Raman spectrum because of D<sub>3h</sub>  $\Rightarrow$  C<sub>2v</sub> or C<sub>s</sub> symmetry lowering. U-O bond lengths in uranyl are calculated with two empirical relations  $R_{U-O} = 106.5[\nu_1(\text{UO}_2)^{2+}]^{-2/3} + 0.575 \text{ \AA}$  and  $R_{U-O} = 91.41[(\nu_3(\text{UO}_2)^{2+})^{-2/3} + 0.804 \text{ \AA}]$ <sup>49</sup>. Obtained U-O bond lengths, 1.777 and 1.785 Å, respectively, are in good agreement with the values inferred by Burns<sup>50-52</sup> for hexagonal dipyramidal uranyl coordination polyhedra, close to uranyl tricarbonate minerals and their synthetic analogues, and 1.781(5) Å inferred from EXAFS spectrum for zellerite by Catalano and Brown<sup>15</sup>. Raman band at 233 cm<sup>-1</sup> is assigned to the  $\nu_2$  ( $\delta$ ) (UO<sub>2</sub>)<sup>2+</sup> bending vibration, while the bands at 363 cm<sup>-1</sup> (Raman) and 565 and 594 cm<sup>-1</sup> (infrared) may be attributed to the U-O<sub>ligand</sub> vibrations<sup>53</sup>. However, bands at 565 and 594 cm<sup>-1</sup> may be also connected with water libration modes.

### *Raman and infrared carbonate, (CO<sub>3</sub>)<sup>2-</sup>, vibrations*

Vibrations of a free carbonate, (CO<sub>3</sub>)<sup>2-</sup>, group give rise to four fundamentals,  $\nu_1$  symmetric stretching vibration,  $\nu_2$  out-of-plane bending vibration,  $\nu_3$  doubly degenerate antisymmetric stretching vibration, and  $\nu_4$  doubly degenerate in-plane bending vibration. So far as planar (CO<sub>3</sub>)<sup>2-</sup> is not affected by the force field, it possesses the point symmetry D<sub>3h</sub>. The  $\nu_1$  fundamental is Raman active,  $\nu_2$  is infrared active,  $\nu_3$  and  $\nu_4$  are both infrared and Raman active. The number of the bands increases if the carbonate ion is embedded in a crystal lattice site of lower symmetry or if bonding forces between the carbonate oxygen atoms and other atoms in the crystal operate. If the resultant space symmetry group becomes isomorphous with some of the point groups C<sub>2v</sub>, C<sub>s</sub>, or C<sub>1</sub>, the degeneracy of the vibrational modes  $\nu_3$  and  $\nu_4$  is removed and all vibrations are then both infrared and Raman active. The number of Raman and infrared bands thus rises to the total of six. If in addition several crystallographically nonequivalent carbonate groups are present in the unit cell, the number of the active frequencies is accordingly multiplied. The (CO<sub>3</sub>)<sup>2-</sup> ion behaves as a monodentate (symmetry C<sub>s</sub> or C<sub>2v</sub>) or a bidentate (symmetry C<sub>2v</sub>) ligand<sup>47</sup>.

Raman band at 1091 cm<sup>-1</sup> and infrared bands at 1022 and 1101 cm<sup>-1</sup> are connected with the  $\nu_1$  (CO<sub>3</sub>)<sup>2-</sup> symmetric stretching vibrations. Raman band at 834

$\text{cm}^{-1}$  may be assigned to the  $\nu_2 (\text{CO}_3)^{2-}$  out-of-plane bending vibration coinciding with the  $\nu_1 (\text{UO}_2)^{2+}$  symmetric stretching vibration. In infrared, there may be at  $899 \text{ cm}^{-1}$  a coincidence of the  $\nu_2 (\text{CO}_3)^{2-}$  out-of-plane bending vibration and the  $\nu_3 (\text{UO}_2)^{2+}$  antisymmetric stretching vibration. An observed Raman band at  $1374$  and three split infrared bands at  $1411$ ,  $1511$  and  $1567 \text{ cm}^{-1}$  are assigned to the  $\nu_3 (\text{CO}_3)^{2-}$  antisymmetric stretching vibrations. Infrared splitting of the  $\nu_3 (\text{CO}_3)^{2-}$  vibrations ( $100\text{-}156 \text{ cm}^{-1}$ ) proves that only bidentately bonded carbonate groups are present in the crystal structure of zellerite<sup>13,54</sup>. Raman and infrared bands at  $758$  and  $667 \text{ cm}^{-1}$ , respectively, are attributed to the  $\nu_4 (\text{CO}_3)^{2-}$  in-plane bending vibrations.

### ***Raman and infrared water, H<sub>2</sub>O, molecules vibrations***

The Raman spectrum and the infrared spectrum of zellerite in the  $2800$  to  $3800 \text{ cm}^{-1}$  region is shown in Figures 3 and 4 respectively. The presence of water is manifested in the spectrum by the  $\nu_1 \text{ H}_2\text{O}$  symmetric and  $\nu_3 \text{ H}_2\text{O}$  antisymmetric stretching vibration bands and by the band of the  $\nu_2 (\delta)$  bending vibration. The weak bands at relatively low wavenumbers are due to libration modes of water molecules, if water molecules are hydrogen bonded<sup>47</sup>. Raman bands at  $3514$ ,  $3375$  and  $2945 \text{ cm}^{-1}$  and broad infrared bands at  $3513$ ,  $3396$  and  $3326 \text{ cm}^{-1}$  are related to the  $\nu \text{ OH}$  stretching vibrations of hydrogen bonded water molecules. Observed wavenumbers of these vibrations prove that in fact hydrogen bonds participate in the crystal structure of zellerite. According to Hawthorne<sup>55</sup>, this may stabilize the zellerite structure. Inferred O-H...O bonds<sup>56</sup> are ( $\text{\AA}/\text{cm}^{-1}$ )  $2.92/3514$ ,  $2.79/3375$  and  $2.65/2945$  (Raman) and  $2.92/3513$ ,  $2.76/3396$  and  $2.76/3326$ . The  $\nu_2 (\delta) \text{ H}_2\text{O}$  bending vibration is characterized by two infrared absorption bands at  $1618$  and  $1681 \text{ cm}^{-1}$ . The presence of two bands proves structurally distinct and nonequivalent water molecules in the crystal structure of zellerite. This is in agreement with the proposed formula for zellerite,  $\text{Ca}[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2].3\text{H}_2\text{O}$ . Infrared bands observed at  $565$  and  $594 \text{ cm}^{-1}$  may be related to the libration modes of water molecules of  $\text{U-O}_{\text{ligand}}$  vibrations.

### **Conclusions**

- (1) Raman and infrared spectra of secondary uranyl mineral zellerite were measured and interpreted.
- (2) The presence of hydrogen bonded water molecules and their nonequivalency in zellerite were inferred.
- (3) U-O bond lengths in uranyl and O-H...O hydrogen bonds in the crystal structure of zellerite were calculated.
- (4) Chemical formula  $\text{Ca}[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2].3\text{H}_2\text{O}$  for zellerite is supported.

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Figure 2 Infrared spectra of zellerite in the 500 to 1700  $\text{cm}^{-1}$  region.

Figure 3 Raman spectra of zellerite in the 2800 to 3800  $\text{cm}^{-1}$  region.

Figure 4 Infrared spectra of zellerite in the 3400 to 3700  $\text{cm}^{-1}$  region.

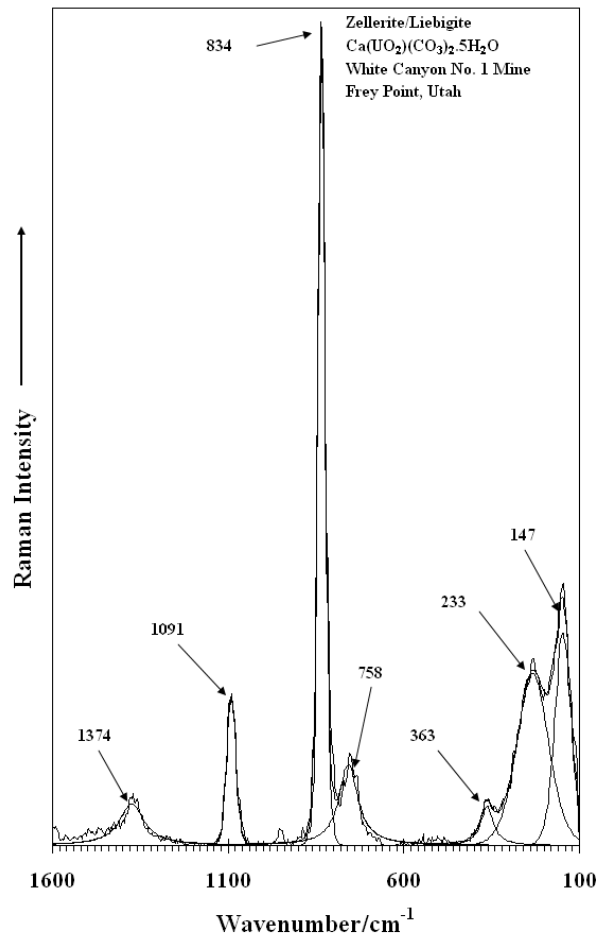


Figure 1

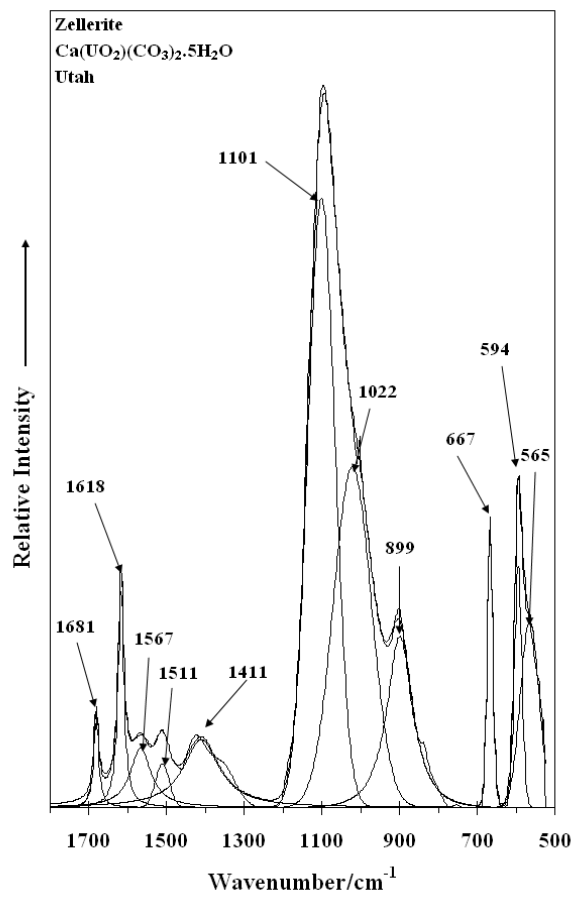
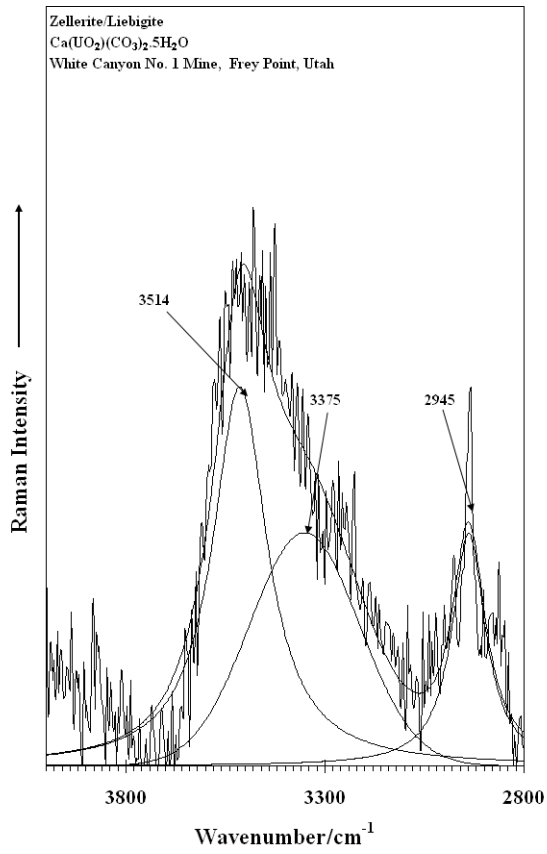


Figure 2



**Figure 3**

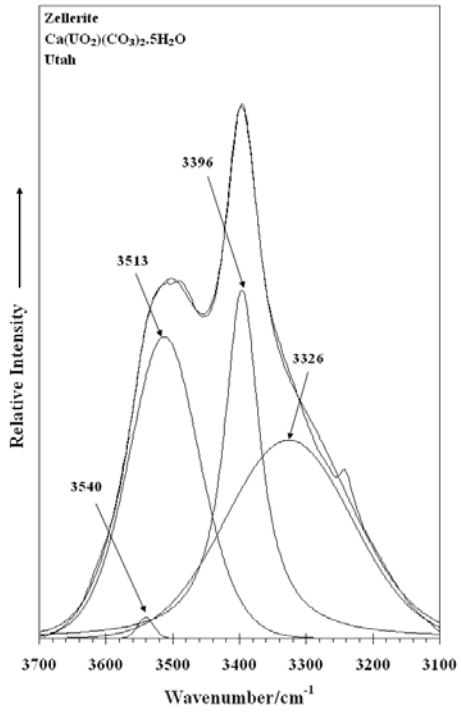


Figure 4