

Thermal decomposition of peisleyite: a thermogravimetry and hot stage Raman spectroscopic study

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Abstract

High resolution thermogravimetric analysis (HRTG) coupled with a gas evolution mass spectrometer was used to study the decomposition of peisleyite $\text{Na}_3\text{Al}_{16}(\text{SO}_4)(\text{PO}_4)_{10}(\text{OH})_{17}\cdot 20\text{H}_2\text{O}$. Peisleyite, a hydrated hydroxylated multianion mineral, shows thermal decomposition in five stages, indicative of a loss of water, hydroxyl units and sulphate. Thermal analysis shows the loss of water and hydroxyl units occurs in three distinct stages; at 36, 105 and 162 °C. The high resolution thermogravimetry was complimented with hot stage Raman spectroscopy, which follows the dehydration of peisleyite. This dehydration can be followed by the decrease in intensity of the OH stretching vibrations which occur between 4000 and 2500 cm^{-1} and by the shift in the sulphate and phosphate peaks which occur due to changes in the mineral structure. © 2004 Elsevier B.V. All rights reserved.

Keywords: Peisleyite; Sulphate; Phosphate; High resolution thermogravimetric analysis; Hot stage Raman spectroscopy; Tom's phosphate quarry

1. Introduction

Peisleyite is an interesting hydrated hydroxylated multianion mineral with the formula $\text{Na}_3\text{Al}_{16}(\text{SO}_4)_2(\text{PO}_4)_{10}(\text{OH})_{17}\cdot 20\text{H}_2\text{O}$ and was described from Toms phosphate quarry, South Australia [1,2]. Few studies of the mineral have been undertaken; no doubt because of the rarity of the mineral. No single crystal X-ray diffraction (XRD) studies have been undertaken. Peisleyite is a sodium aluminium sulphate phosphate hydroxide. It's powder X-ray diffraction pattern has been published (JCPDS No. 35-0674). The Raman and infrared spectroscopy of peisleyite is being investigated by the authors and nothing is known about the stability of the mineral. Certainly no thermal analytical studies have been undertaken.

Peisleyite contains both water molecules and hydroxyl units and the presence of these units lend themselves to thermal analysis. The sulphate will also be lost through thermal

treatment. The technique of thermal analysis (HRTG) combined with evolved gas mass spectrometry (MS) is ideal for the study of such a mineral [3–5]. Minerals which contain significant amounts of water such as hydrotalcite, vivianite and autunite lend themselves to this type of analysis [6–9]. The advantage of HRTG-MS is that the thermal analysis reveals the temperature of the mass loss steps and the mass spectrometry identifies the nature of the gases and the temperature at which these gases are evolved. MS of the breakdown products can be used to distinguish between the evolution of ammonia ($M = 17$) and hydroxyl units ($M = 17$). The OH units will condense to produce H_2O measured as evolved water vapour and oxygen will be retained generally as a metal oxide. The loss of carbonate can be followed by the mass gain of CO_2 ($M = 44$) and the loss of sulphate by the evolution of SO_2 ($M = 64$) [10]. The advantage of the MS system is that specific evolved gases can be observed simultaneously. Whilst these techniques can determine the temperature of the mass losses and the chemical reactions which produce these mass losses, no structural information is obtained. Crystal structural changes can be followed using temperature dependent X-ray diffraction. Another

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useful technique is to use hot stage Raman spectroscopy and/or infrared emission spectroscopy. The advantage of these latter techniques is that the changes in molecular structure can be followed in situ and at the elevated temperatures. No information about changes in the crystal structure can be obtained using these vibrational spectroscopic techniques. In this work we undertake the HRTG-MS of peisleyite and compliment the results of the thermal analysis with hot stage Raman spectroscopy.

2. Occurrence

Peisleyite has only been recorded from Tom's phosphate quarry (34°21'S, 138°55'E), which is located approximately 8 km ESE of the town of Kapunda, in the Mt. Lofty Ranges, South Australia [1,11]. Here peisleyite occurs as brittle, white, chalky material which is commonly massive. Toms phosphate quarry occurs in a region of phosphate concentration (Upper Precambrian Brighton limestone) which encompasses the southern portion of the Adelaide Geosyncline [1]. In this region several pits and quarries have been intermittently worked since 1903. These workings include the St. Kitts and St. Johns phosphate quarries SE of Kapunda and the Moculta [2,12] and Penrice phosphate deposits [11] N and NE of Angaston. Toms quarry was run and operated by BHP especially for pig iron requirements during the 1941–1944 period, and produced some 40,000 t at 20% P₂O₅ and 15% Fe₂O₃ [14]. This deposit is still being worked at a production rate of 1250 t per year. At Tom's quarry extensive weathering has taken place, acting as a reservoir of P, Fe and Al for secondary mineral phases.

The mineralogy of Toms phosphate quarry has not been described in detail, whilst various publications have mentioned occurrences of various species. The main phosphate minerals that occur at the quarry are: apatite (largely hydroxylapatite), wavellite, minyulite, fluellite, cacoxenite, leucophosphite [1,13] and perhamite [2]. Variscite, strengite, dufrénite, crandallite, kingite and cyrilovite have also been recorded from the quarry, as specimens exist in the Museum of Victoria collections. Other minerals associated with these phosphates include: quartz, jasper and massive goethite.

3. Experimental

3.1. Thermal analysis

Thermal decomposition of peisleyite was carried out in a TA[®] Instruments Incorporated high resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm³/min). Approximately 10 mg of sample was heated in an open platinum crucible at 1.0 °C/min up to 800 °C. The TGA instrument was coupled to a Balzers

(Pfeiffer) mass spectrometer for gas analysis. Only selected gases were analyzed.

3.2. Raman microprobe spectroscopy

Samples of peisleyite from the Museum Victoria collection (M45908 and M40338) were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10× and 50× objective lenses, as part of a Renishaw 1000 Raman microscope system. This system also includes a monochromator, filter system and a CCD detector. Raman spectra were recorded at a resolution of 2 cm⁻¹ in the range between 100 and 4000 cm⁻¹ using a HeNe laser operating at 633 nm. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio [14–16]. Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. In order to ensure that the correct spectra were obtained, the incident excitation radiation was scrambled, while spectra at controlled temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

Spectroscopic 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 Gauss–Lorentz 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 correlations of *R*² greater than 0.995.

4. Results and discussion

4.1. Thermal analysis

The mineral peisleyite has the formula Na₃Al₁₆(SO₄)₂(PO₄)₁₀(OH)₁₇·20H₂O with a molecular mass of Mr = 2291.3 g/mol. Thus there should be a theoretical loss of water of 15.7%. The high resolution thermogravimetric analysis combined with the differential thermogravimetric curve is shown in Fig. 1. There are three mass loss steps which involve the loss of water. These are as follows:

| | | |
|---------|----------------------------|-----------------------------------|
| Step 1: | 11.2% ~ 14H ₂ O | at 36 °C |
| Step 2: | 7.1% ~ 9H ₂ O | at 105 °C |
| Step 3: | 6.5% ~ 8.5H ₂ O | at 162 °C (theoretical loss 7.0%) |

The mass loss step at 162 °C is attributed to the condensation of hydroxyl units and the formation of H₂O.

In the first step 14 mol of water are lost, in the second 9 mol of water, making a total of 23 mol of water which is 3 mol more than the molecular formula. This difference may

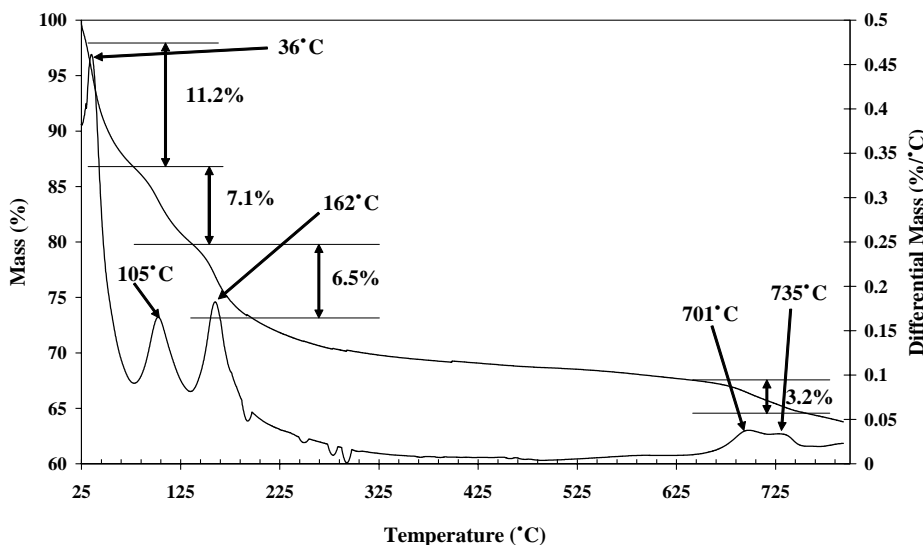


Fig. 1. High resolution TGA–dTGA analysis of peisleyite from 25 to 800 °C.

be accounted in two ways: firstly the moles of water in the mineral formula are incorrect and secondly the large number of moles of water in excess is attributed to adsorbed water on the mineral. These techniques are unable to determine which of these scenarios is the case for peisleyite. The mass loss step at 162 °C is attributed to the loss of hydroxyl units from the mineral. The mass loss of OH units is 6.5% which accounts for 17 mol of OH units. Two higher temperature mass losses at 701 and 735 °C are observed and are assigned to the decomposition of sulphate group under the formation of SO₂. It is suggested that the phosphate is retained to temperatures exceeding 800 °C.

The temperature dependent evolution of water together with the DTG curve is shown in Fig. 2. The maxima of

water evolution occur at precisely the same temperatures at which the mass losses in the HRTG curve. A small mass gain of water is observed at 140 °C and a further mass gain at 460 °C. The evolved water vapour at 140 and 162 °C suggests that the condensation of the hydroxyl units occur in two steps. The mass spectrum of SO₂ shows that the two mass losses at 701 and 735 °C are associated with the loss of sulphate.

The following mechanism for the decomposition of peisleyite is proposed.

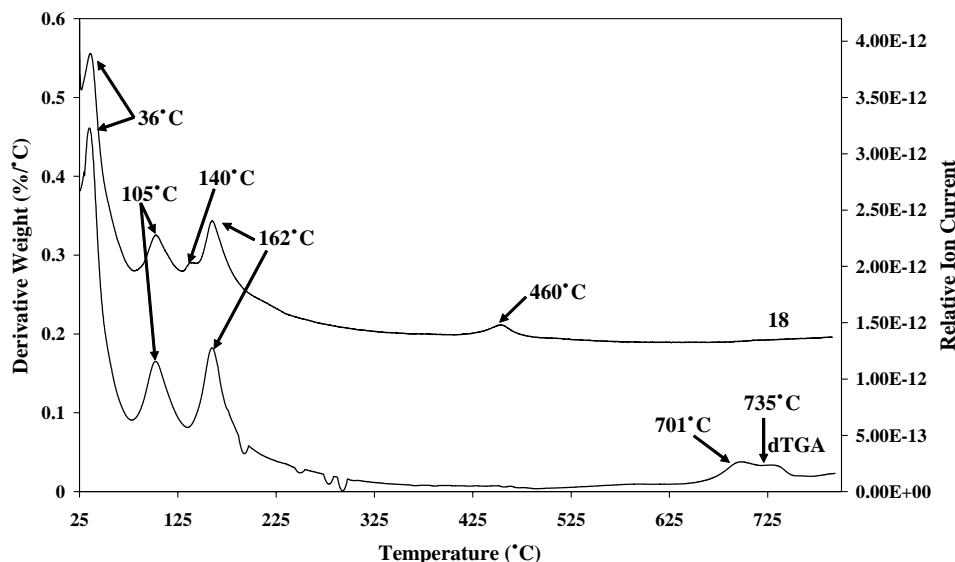
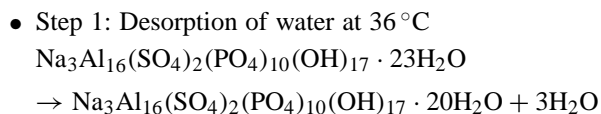
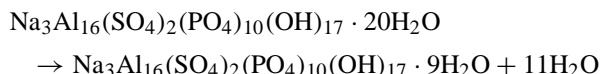
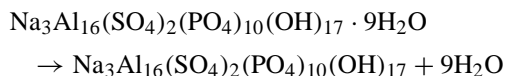


Fig. 2. The dTGA and mass spectrum of molar mass 18 of peisleyite from 25 to 800 °C.

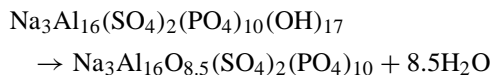
- Step 2: Loss of water at 36 °C—formation of metapeisleyite



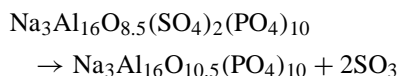
- Step 3: Formation of anhydrous metapeisleyite



- Step 4: Dehydroxylation—loss of hydroxyl units



- Step 5: Loss of sulphate



Thus it is suggested that the thermal decomposition of peisleyite results in the formation of either a sodium aluminium phosphate or a mixture of sodium and aluminium phosphate. The single crystal XRD patterns of the mineral peisleyite are not known. Preliminary X-ray diffraction results suggest that a single phase is formed which is not a mixture of the phosphates/sulphates. It should be noted that in this work we are dealing with very small amounts of sample as supplied by Museum Victoria. The sample may have adsorbed water during storage at the museum.

4.2. Raman spectroscopy

The decomposition of peisleyite can be followed using a Raman microscope and a thermal stage. The fitted spectra

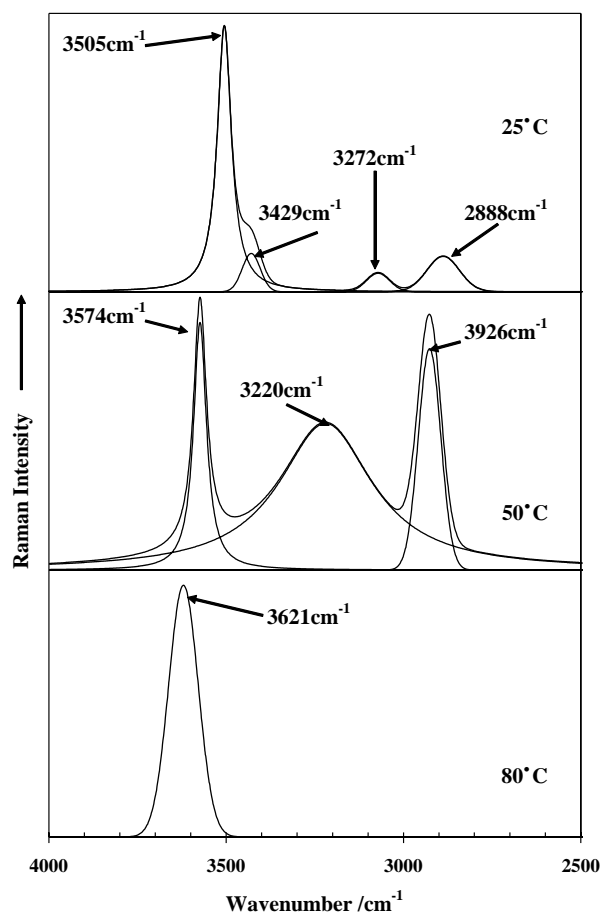


Fig. 3. Raman spectra of peisleyite in the 4000–2500 cm^{-1} region.

are shown in Figs. 3–6. The results of the band component analyses are reported in Table 1. Fig. 3 shows that changes to the spectra occur between 25 and 50 °C, due to a loss of water at 36 °C. The adsorbed water causes strong OH

Table 1
Raman spectral analysis of peisleyite at elevated temperatures

| Band centre (cm^{-1})/intensity (%) | | | | | Suggested Assignment |
|--|-------------------------------------|---|--|--|--|
| 25 °C | 50 °C | 80 °C | 100 °C | 140 °C | |
| 3505/33.81 3072/2.57 1358/1.48 | 3429/4.17 2888/6.93 1289/1.37 | 3220/7.25 2926/1.88 | 3621/3.09 | | OH stretching modes |
| 1247/1.64 1023/9.48 | 1144/4.15 989/0.97 | 1140/2.64 1077/6.34 1020/18.04 | 1161/4.18 1033/5.42 1007/14.35 | 1121/11.92 1029/6.64 1005/5.28 | ν_3 antisymmetric stretching modes of SO_4 and PO_4 ν_3 antisymmetric stretching modes of SO_4 and PO_4 ν_1 symmetric stretching modes of SO_4 ν_1 symmetric stretching modes of PO_4 |
| 634/7.77 410/12.05 | 547/5.35 314/1.15 | 606/2.60 542/3.99 420/12.48 364/3.14 | 663/4.41 608/1.69 545/2.95 526/0.87 404/0.81 340/1.34 | 478/1.15 429/23.98 399/0.55 | ν_4 and ν_2 bending modes of SO_4 and PO_4 |
| 276/3.19 188/0.76 | 207/2.25 159/0.69 | 237/3.40 213/9.93 200/15.75 | 204/55.15 175/5.07 | 264/7.73 212/9.19 200/22.71 166/2.94 | Lattice modes |
| | | | | 930/7.05 1016/16.51 920/11.29 | |
| | | | | 1188/1.5 1121/8.77 | |
| | | | | 262/8.62 213/11.28 202/30.42 187/7.91 168/5.19 | |

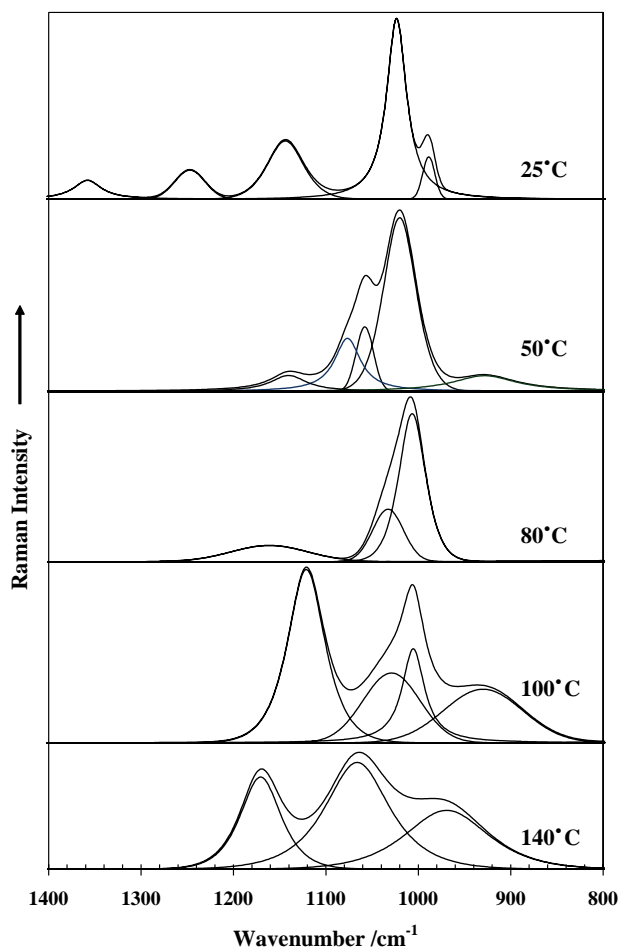


Fig. 4. Raman spectra of peisleyite in the 1400–800 cm^{-1} region.

stretching peaks at 25 °C. These bands show a loss of intensity at 50 °C as metapeisleyite is formed and a further loss of intensity at 80 °C as anhydrous metapeisleyite is formed. At 100 and 140 °C there is some intensity of the hydroxyl units remaining, the intensity of these bands is weak. At 25 °C the main OH stretching band occurs at 3505 cm^{-1} , which is likely to be due to the adsorbed water, with three other bands at 3429, 3072 and 2888 cm^{-1} . These bands shift significantly to 3574, 3220 and 2926 cm^{-1} at 50 °C. At 80 °C only one band remains which occurs at 3621 cm^{-1} (=3574 and 3429 cm^{-1}). The shift in the OH stretching bands is due to changes in the structure of the mineral as water is lost. The importance of this is that Raman spectroscopy can be used to identify peisleyite based on the positions of the OH stretching bands.

At 25 °C in the 800–1400 cm^{-1} bands are observed at 989, 1023, 1144, 1247, 1289 and 1358 cm^{-1} (Fig. 4). The band at 989 cm^{-1} is assigned to the SO_4 ν_1 symmetric stretching mode. The crystal structure of peisleyite is not known but it is probable that more than one crystallographic independent phosphate unit is present. Thus more than the four vibrations for the PO_4 units could be expected. The phos-

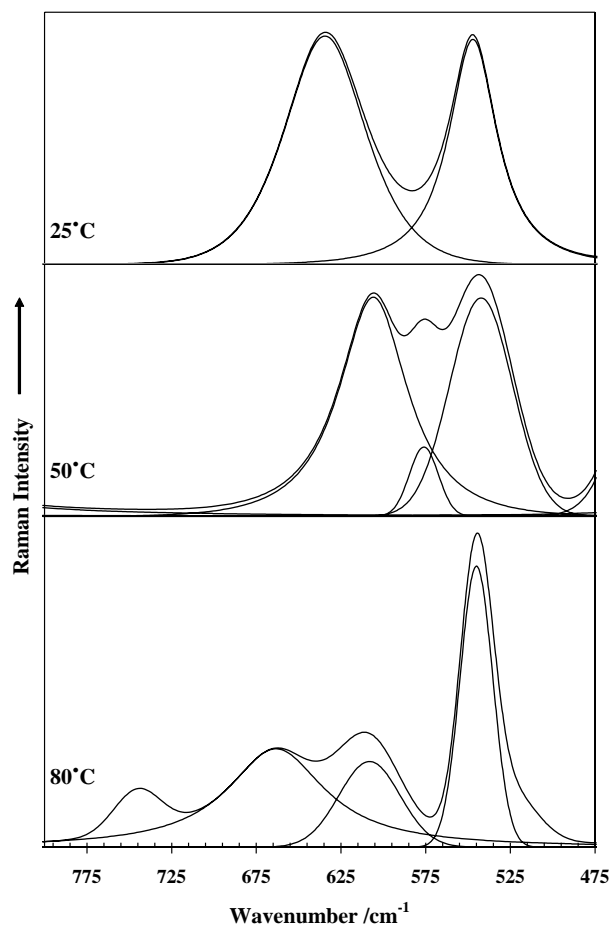


Fig. 5. Raman spectra of peisleyite in the 800–475 cm^{-1} region.

phate PO_4 symmetric stretching mode is not observed at this temperature. The position of this band would be expected at around 930 cm^{-1} . The other bands are assigned to a combination of the ν_3 antisymmetric stretching modes of the PO_4 and SO_4 units. At 50 °C, the higher wave number bands at 1289 and 1358 cm^{-1} are not observed. The two bands at 928 and 1020 cm^{-1} are assigned to the ν_1 symmetric stretching modes of the PO_4 and SO_4 units, respectively. It is noted that at 50 °C, the symmetric stretching mode of PO_4 is observed and that a significant shift in the position of the ν_1 symmetric stretching mode of SO_4 is observed. Bands are observed around these positions at 80, 100 and 140 °C. Three bands are observed at 1058, 1077 and 1140 cm^{-1} assigned to the antisymmetric stretching modes of SO_4 . At 80 °C, these bands are observed at 1033 and 1161 cm^{-1} , whilst at 100 and 140 °C they are observed at 1029 and 1121 cm^{-1} and 1188 and 1121 cm^{-1} , respectively.

Fig. 5 displays the spectra of peisleyite at the elevated temperatures in the 475–775 cm^{-1} region. Two bands are observed at 25 °C at 634 and 547 cm^{-1} and one probable assignment is to the ν_4 bending modes of the SO_4 and PO_4 units. At 50 °C, three bands are observed at 606, 576 and 542 cm^{-1} . At 80 °C an intense band is observed at 526 cm^{-1} with three lower intensity bands at 545, 608 and 663 cm^{-1} .

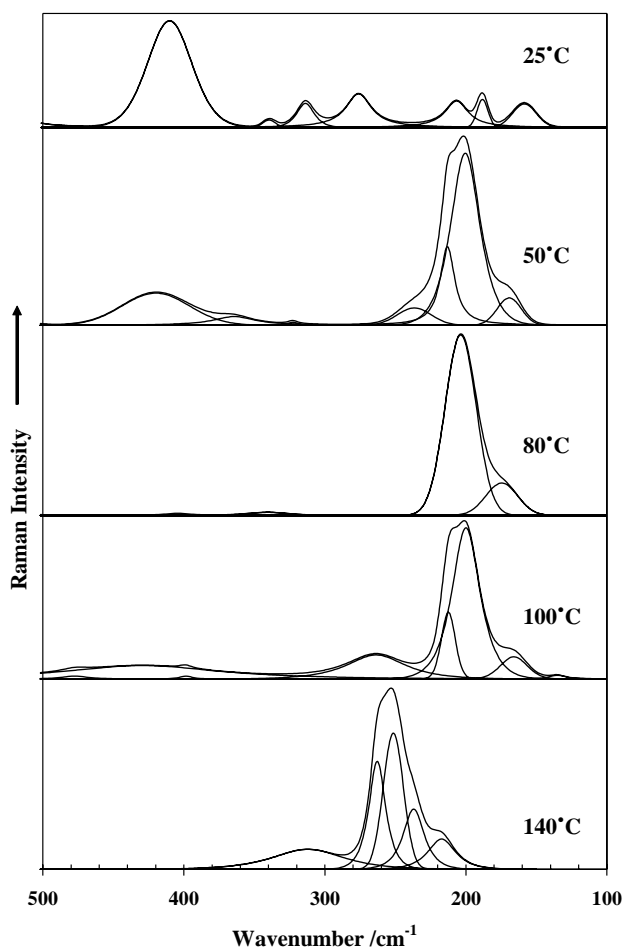


Fig. 6. Raman spectra of peisleyite in the 500–100 cm^{-1} region.

These bands are attributed to water librational modes. No bands are observed in these positions at elevated temperatures. In the region 100–500 cm^{-1} , two bands are observed at 410 and 314 cm^{-1} and are assigned to the ν_2 bending modes of the SO_4 and PO_4 units (Fig. 6). Significant changes are observed in the position of these bands at 50 °C. At 140 °C the bands are observed at 399 and 429 cm^{-1} , a total shift of 85 and 19 cm^{-1} . After this temperature no intensity can be determined in these bands. The mineral has lost crystallinity at this temperature. Bands below 276 cm^{-1} are assigned to lattice modes.

5. Conclusions

The thermal decomposition of the unusual multianion mineral peisleyite $\text{Na}_3\text{Al}_{16}(\text{SO}_4)_2(\text{PO}_4)_{10}(\text{OH})_{17}\cdot 20\text{H}_2\text{O}$ has been studied by a combination of high resolution thermogravimetry coupled to evolved gas mass spectrometry.

The HRTG shows that thermal decomposition occurs in five steps. Dehydration was found to occur at quite low temperatures at 36 °C. Other dehydration occurred at 105 °C and condensation of the OH units with the consequential formation of water at 162 °C. Higher temperature mass losses are due to the loss of sulphate whereas phosphate appears to be retained to elevated temperatures. Importantly the combination of HRTG with evolved gas mass spectrometry enabled the determination of the mass loss steps and the identification of the chemical evolved at the temperature of these mass loss steps. The changes in the structure of the peisleyite can be followed by the changes in the Raman bands associated with (a) OH units; (b) the sulphate and (c) phosphate anions.

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