Raman spectroscopy of the joaquinite minerals

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Selected joaquinite minerals have been studied by Raman spectroscopy. The minerals are categorised into two groups depending upon whether bands occur in the 3250 to 3450 cm^{-1} region and in the 3450 to 3600 cm^{-1} region, or in the latter region only. The first set of bands is attributed to water stretching vibrations and the second set to OH stretching bands. In the literature, X-ray diffraction could not identify the presence of OH units in the structure of joaquinite. Raman spectroscopy proves that the joaquinite mineral group contains OH units in their structure, and in some cases both water and OH units. A series of bands at 1123, 1062, 1031, 971, 912 and 892 cm^{-1} are assigned to SiO stretching vibrations. Bands above 1000 cm^{-1} are attributable to the ν_{as} modes of the $(SiO_4)^{4-}$ and $(Si_2O_7)^{6-}$ units. Bands that are observed at 738, around 700, 682 and around 668, 621 and 602 cm^{-1} are attributed to $O-Si-O$ bending modes. The patterns do not appear to match the published infrared spectral patterns of either $(SiO_4)^{4-}$ or $(Si_2O_7)^{6-}$ units. The reason is attributed to the actual formulation of the joaquinite mineral, in which significant amounts of Ti or Nb and Fe are found. Copyright © 2007 John Wiley & Sons, Ltd.

INTRODUCTION

The joaquinite mineral group consists of unusual cyclosilicate minerals that are renowned for their association with other exotic minerals such as the sapphire blue benitoite, the red-black neptunite and the snow white natrolite. The minerals are hydrated silicates and form typically small, sparkling and brown to yellow, well-formed crystals. The joaquinite mineral group consists of the minerals bario-orthojoaquinite, byelorussite-(Ce), joaquinite-(Ce), orthojoaquinite-(Ce), orthojoaquinite-(La), strontiojoaquinite and strontio-orthojoaquinite.[1] The minerals are orthorhombic and monoclinic titanosilicates of the general formula $A_6(Ti,Nb)_2Si_8(O,OH)_{26}\cdot H_2O$ where A may be Ba,Ce, Fe^{2+}, Mn^{2+}, Na or Sr.[2] The minerals are found in the San Bonito County, California, USA.

Laird and Albee[3] first published the infrared spectrum of joaquinite. They observed infrared bands at around 3560 and 3500 cm^{-1} and concluded that the joaquinite mineral structure contained significant quantities of crystallographically ordered hydroxyl groups. Bands were also observed at 1610 and 3400 cm^{-1}, which were ascribed to physically adsorbed water. Laird and Albee concluded[3] that there are 3.3 OH units per Ba. A comprehensive study of cyclosilicates was undertaken by Povarennykh,[4] who concluded that there was a strict dependence of the antisymmetric stretching ν_3 and bending ν_3 vibrations of cyclosilicates and the ring sizes.[4] Rossman[5] using polarized infrared spectra of oriented joaquinite crystals observed absorption bands at 3561, 3500 and 1607 cm^{-1} and concluded that the bands are due to crystallographically ordered molecular water in joaquinite. Cannillo *et al.*[6] suggested that OH units or water occurred in cavities in the joaquinite structure and played no structural role. Rossman[5,7] used the polarised NIR spectrum of joaquinite to show the presence of water in the crystals and implied that the water was structurally ordered. Rossman[5] proposed a model in which water in joaquinite consists of water molecules well isolated from each other oriented parallel to [100] with the symmetry axis parallel to [010]. The model was consistent with the proposals of Cannillo *et al.*[6] in which water resided in the cavities of joaquinite similar to that of beryl. Semenov *et al.*[1] determined the differential thermal analysis (DTA) curves of joaquinite and showed an endotherm at 770 °C, which was attributed to water release. Other ring silicate minerals are known to lose water at temperatures above 700 °C. The thermal emission of water at such a high temperature is normally associated with dehydroxylation of OH units rather than the release of pre-existing molecular water.

In this work we report the Raman spectra of joaquinite and relate the spectra to the chemical composition and structure of the minerals.

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EXPERIMENTAL

Minerals

The minerals used in this study, their formulae and origin are listed in Table 1. The minerals are labelled by number rather than by the cation, as most of the minerals contain a complex mixture of cations. Selected minerals were obtained from the Mineralogical Research Company and other sources including Museum Victoria. The samples were phase-analysed by X-ray diffraction, and for chemical composition by EDX measurements. For X-ray microanalysis (EDX), four samples were embedded in Araldite resin and polished with diamond paste on Lamplan 450 polishing cloth, using water as a lubricant. The samples were coated with a thin layer of evaporated carbon for conduction, and examined in a JEOL 840A analytical SEM at 12 kV accelerating voltage with full standard analysis and calculated on the basis of 16 oxygens. The results of some EDX analyses are reported in Table 2.

Raman microprobe spectroscopy

The crystals of the joaquinite minerals were placed and orientated on the stage of an Olympus BHSM microscope, equipped with $10 \times$ and $50 \times$ 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 He–Ne laser (633 nm) and at a resolution of 3.5 cm^{-1} in the range between 100 and 4000 cm^{-1}. Measurements were made at ambient temperature, which is set at 25 °C. Repeated acquisition using the highest magnification was accumulated to improve the signal-to-noise ratio. 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. Details of the technique have been published by the authors.[8–11]

Table 2. Chemical analysis of selected joaquinites

Mineral	Atom	Atom analysis	Oxide	Oxide analysis
joaquinite	Na	1.6	Na_2O	2.2
	Ce	19.8	Ce_2O_3	23.1
	Ti	3.4	TiO_2	5.6
	Nb	6.6	Nb_2O_5	9.4
	Fe	3.9	FeO	5.1
	Si	15.8	SiO_2	33.9
	F	0.67	–	–
	O	28.8	–	–
bariojoaquinite	Ba	20.9	BaO	23.3
	Sr	13.329	SrO	15.8
	Ti	7.28	TiO_2	12.1
	Fe	8.5	FeO	10.9
	Si	17.1	SiO_2	36.5
	O	28.8	–	–
strontiojoaquinite	Na	1.79	Na_2O	2.4
	Ba	21.4	BaO	23.9
	Sr	13.7	SrO	16.1
	Ti	7.5	TiO_2	12.4
	Fe	4.4	FeO	5.6
	Si	17.5	SiO_2	37.4
	O	33.6	–	–

Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enables 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 Lorentz–Gauss ratio was maintained at values greater than 0.7, and fitting was undertaken until reproducible results

Table 1. List of minerals, their origin and possible formulation

Name	Sample number	Origin	Formula
Strontio Joaquinite	1	Junilla Claim, Southern San Benito Co., California	$Sr_2Ba_2(Na,Fe^{2+})_2Ti_2Si_8O_{26}(O,OH)_2 \cdot H_2O$
Joaquinite-(cerium)	2	Benitoite Gem Mine, Southern San Benito Co., California	$NaBa_2FeCe_2(Ti,Nb)_2(SiO_3)_8O_2(OH,F)H_2O$
Strontio Joaquinite	3	Mina Numero UNO, San Benito Co., California	$Sr_2Ba_2(Na,Fe^{2+})_2Ti_2Si_8O_{26}(O,OH)_2 \cdot H_2O$
OrthoJoaquiinte-(cerium), Neptune, Crossite	5	Benitoite Gem Mine, Southern San Benito Co., California	$NaBa_2FeCe_2(Ti,Nb)_2(SiO_3)_8O_2(OH,F)H_2O$
Joaquinite-(cerium), Benitoite, Neptunite	7	Mina Numero UNO, San Benito Co., California	$NaBa_2FeCe_2(Ti,Nb)_2(SiO_3)_8O_2(OH,F)H_2O$
Bario-Ortho Joaquinite	8	Victo Claim, Southern San Benito Co., California	$(Ba,Sr)_4(Fe^{2+})_2Ti_2Si_8O_{26} \cdot H_2O$
Bario-Ortho Joaquinite	9	Benitoite Gem Mine, Southern San Benito Co., California	$(Ba,Sr)_4(Fe^{2+})_2Ti_2Si_8O_{26} \cdot H_2O$

were obtained with squared correlations of r^2 greater than 0.995.

## Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart-endurance, single-bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectral manipulations such as baseline adjustment, smoothing and normalisation were performed using the GRAMS software package (Galactic Industries Corporation, Salem, NH, USA).

RESULTS AND DISCUSSION

In the literature there have been significant discussions on whether minerals in the joaquinite group contain water units or hydroxyl units in the structure. Current understanding is that water, and not hydroxyls, is present in the structures.[3–6] The Raman spectra of joaquinite minerals are shown in

Figs 1(a) (samples 1–3 and 5) and 1(b) (samples 7–9). In Fig. 1(a) the joaquinite samples 2 and 5 have similar spectra, and the spectra of samples 1 and 3 are very similar. The difference between the two groups is the observation of bands in the 3250 to 3450 cm^{-1} region. In a similar manner, the Raman spectra of samples 8 and 9 are similar in the OH stretching region and the Raman spectrum of sample 7 contains additional bands in the 3300 to 3450 cm^{-1} region. We propose that the bands in the 3250 to 3450 cm^{-1} region can be attributed to the stretching modes of water. Both infrared and Raman spectra of joaquinites show a band at 1600 cm^{-1} assigned to the bending mode of water. The fact that the band is observed in the Raman spectrum suggests that the water molecules are in a position of symmetry. The bands in the 3450 to 3600 cm^{-1} are assigned to OH stretching modes. The implication is that samples 2 and 5, namely, joaquinite-(Ce) and orthojoaquinite-(Ce), contain both water and OH units in the structure. The minerals 1 and 3, which are both strontiojoaquinites, have only OH units in their structure and no water molecules. Joaquinite
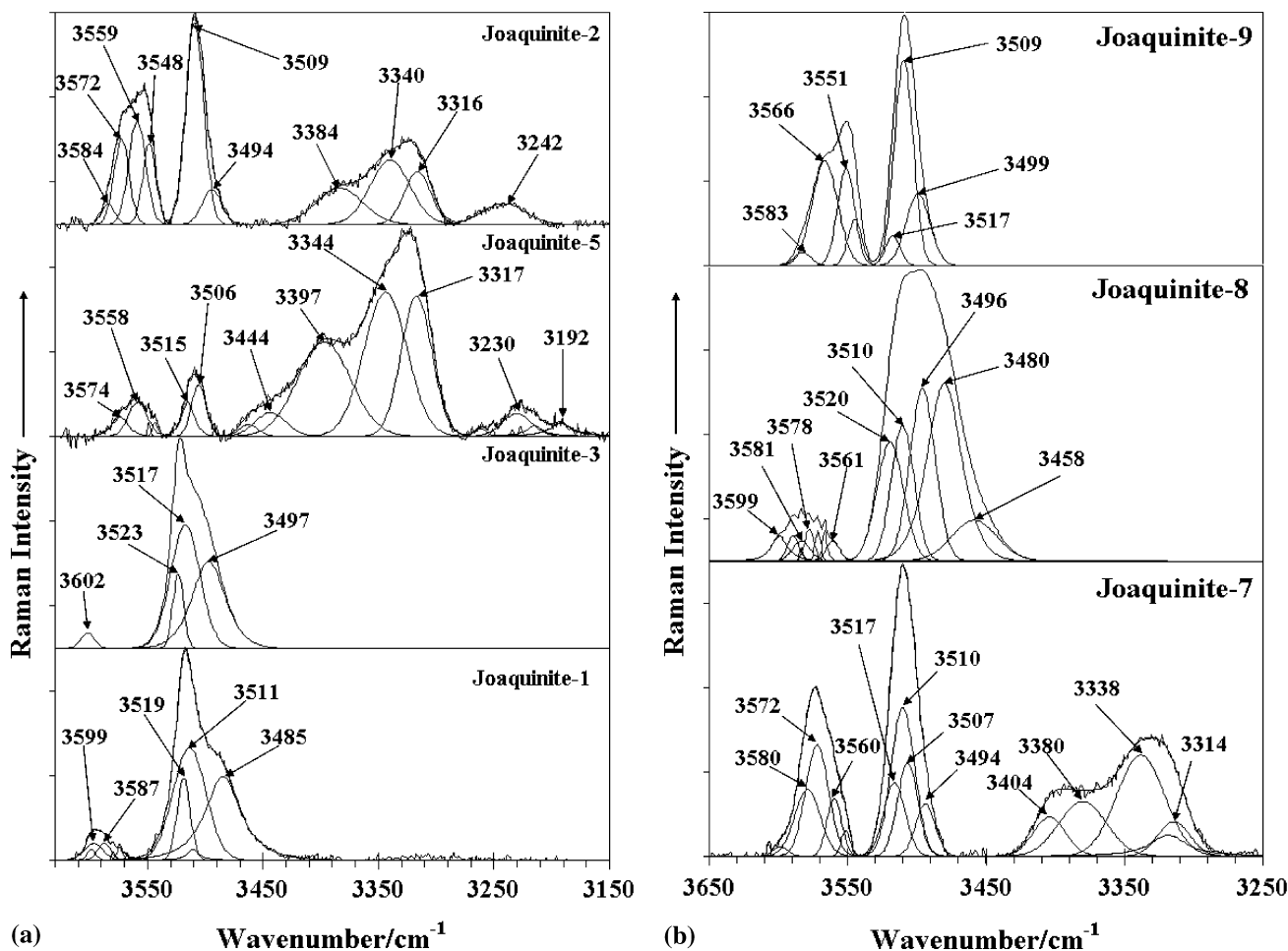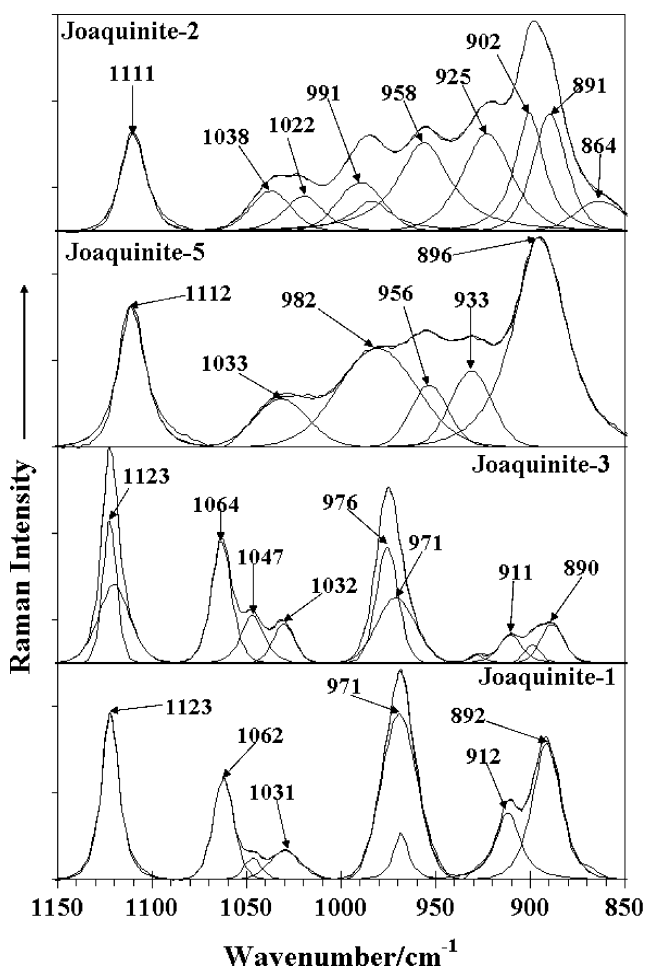

Figure 1. (a) Raman spectra of selected joaquinites (group 1) in the 3150 to 3600 cm^{-1} region. (b) Raman spectra of selected joaquinites (group 2) in the 3150 to 3600 cm^{-1} region.

sample 7 is of a different origin and contains both water and OH units. Minerals 8 and 9, which are both bario-orthojoaquinites, show OH stretching vibrations only in their Raman spectra.

The joaquinite minerals 2, 5 and 7 show bands at around 3328 and 3397 cm^{-1} (Fig. 1(b)). The bands are ascribed to symmetric and antisymmetric stretching vibrations of water. For joaquinite samples 1, 2 and 3, bands are observed at around 3600, 3519 and 3485 cm^{-1}. These bands are attributed to the OH stretching vibrations. The observation of more than one distinct OH stretching mode implies that there are more than one non-equivalent OH unit in the joaquinite structure. It appears that joaquinite samples 2, 5 and 7 are all joaquinite-(Ce) or orthojoaquinite-(Ce) samples that contain significant amounts of Na, Ce and Nb in the formulation. These joaquinites all contain water in the structure. Minerals 1, 3, 8 and 9 are either strontio- or bariojoaquinites. These minerals have only OH units in their structure. Chemical analyses of selected joaquinites are reported in Table 2.

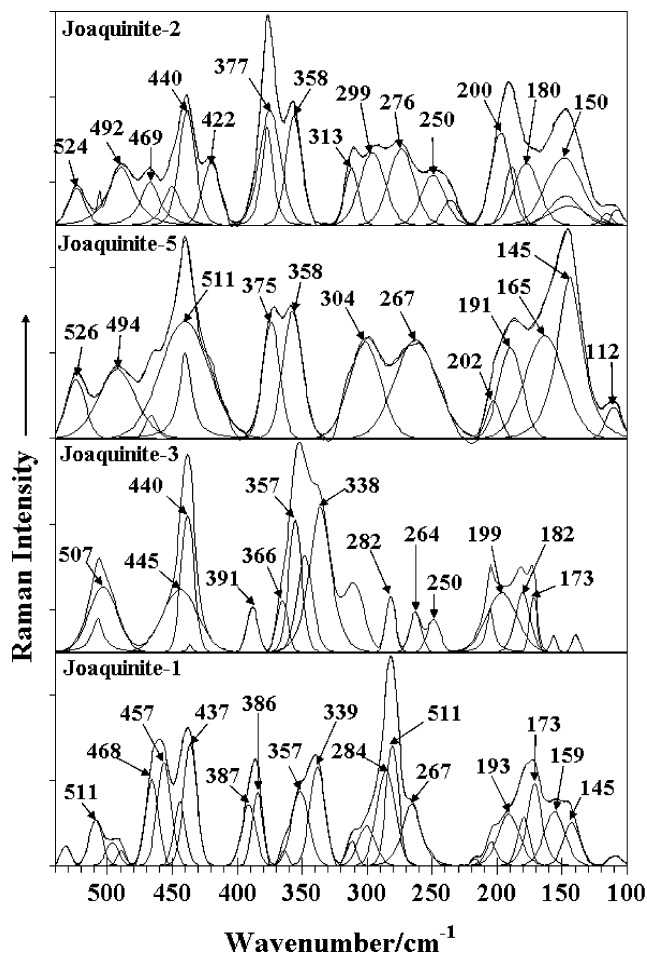The Raman spectra of selected joaquinites in the 850 to 1150 cm^{-1} region are shown in Fig. 2, in the 550 to

Figure 2. Raman spectra of selected joaquinites (group 1) in the 850 to 1100 cm^{-1} region.
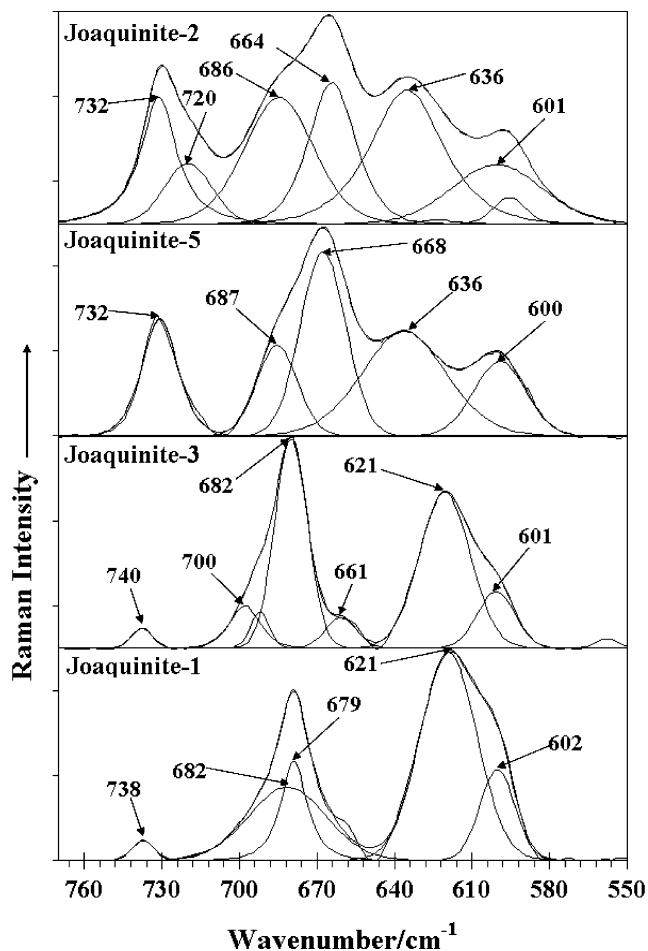
Figure 3. Raman spectra of selected joaquinites (group 1) in the 550 to 800 cm^{-1} region.

750 cm^{-1} region in Fig. 3 and in the 100 to 500 cm^{-1} region in Fig. 4. There have been two comprehensive treatises on the infrared spectroscopy of silicates.[12,13] All the bands in the 850 to 1150 cm^{-1} region are attributed to $(SiO_4)^{4-}$ vibrations. Lazarev in his treatise[13] (the figure on page 61) shows possible differences in the infrared spectra of the SiO_4, Si_2O_7, Si_3O_{10} type structures. On the basis of the crystal structure of joaquinite, both the first two units occur in the structure and consequently infrared spectra will result from each of the units independently. The triply degenerate ν_{as} $(SiO_4)^{4-}$ vibration belongs to F_2 species of the T_d group and will always be both Raman and infrared active. The reason for the mulitplet nature of the spectra is the removal of the degeneracy for a lower site symmetry of the $(SiO_4)^{4-}$ units. Lazarev[13] also states that additional bands can be obtained by resonance interactions between translationally non-equivalent $(SiO_4)^{4-}$ tetrahedra. Fermi resonance with overtones and combination bands of the bending and deformation modes may also complicate the spectrum. The Raman spectra of joaquinite samples 1 and 3 show clear, well-separated bands. One possible assignment,

Figure 4. Raman spectra of selected joaquinites (group 1) in the 100 to 550 cm^{-1} region.

mineral. The minerals contain significant amounts of Ti or Nb together with other elements, e.g. Fe. These elements may readily substitute for Si in the structure. Consequently, the bands may be due to bending vibrations of the type $O-Ti-O$ and $O-Si-O-Ti-O$ and similar structures. Another reason for the complexity is that symmetry of the units $(SiO_4)^{4-}$ and $(Si_2O_7)^{6-}$ is reduced and all degeneracies are removed. The Raman spectra of selected joaquinites in the 100 to 550 cm^{-1} region are shown in Fig. 4. This spectral region is complex and, no doubt, the number of bands present is due to the reasons listed above.

CONCLUSIONS

The mineral group joaquinite has not been largely studied by vibrational spectroscopy. X-ray diffraction studies of these minerals are unable to prove whether the minerals contain OH units and or water units. Thus the formula of the minerals is quite uncertain, as it is not known whether to ascribe oxygens to these molecular units. Raman spectroscopy of the minerals identifies bands that can be attributed to both OH units and water units. For Ba-joaquinite and Sr-joaquinite, both OH units and water units are determined. For joaquinite, in which Na is the major cation, only OH units seem to be observed.

Acknowledgements

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based upon the analyses of Lazarev, is to define the bands below 1000 cm^{-1} as due to the ν_s of the $(SiO_4)^{4-}$ and $(Si_2O_7)^{6-}$ units, and the bands above 1000 cm^{-1} as attributable to the ν_{as} modes of the $(SiO_4)^{4-}$ and $(Si_2O_7)^{6-}$ units. Therefore the bands at 1123, 1064, 1047 and 1031 cm^{-1} are ascribed to the ν_{as} modes of the $(SiO_4)^{4-}$ and $(Si_2O_7)^{6-}$ units and the bands at 971, 912 and 892 cm^{-1} to the ν_s modes of the $(SiO_4)^{4-}$ and $(Si_2O_7)^{6-}$ units. The Raman spectra of samples joaquinite 2 and 5 show more complexity, and only through band component analysis can the position of the bands be determined.

The Raman spectra in the 550 to 850 cm^{-1} region are shown in Fig. 3. The spectra are strikingly similar for all four minerals. Bands are observed at 738, around 700, 682 and around 668, 621 and 602 cm^{-1}. These bands are attributed to $O-Si-O$ bending modes. The patterns do not appear to fit the suggested patterns of either $(SiO_4)^{4-}$ or $(Si_2O_7)^{6-}$ units. The reason may be the actual formulation of the joaquinite