Time-resolved remote Raman study of minerals under supercritical CO₂ and high temperatures relevant to Venus exploration

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We report time-resolved (TR) remote Raman spectra of minerals under supercritical CO₂ (approx. 95 atm pressure and 423K) and under atmospheric pressure and high temperature up to 1003K at distances of 1.5 and 9 m, respectively. The TR Raman spectra of hydrous and anhydrous sulphates, carbonate and silicate minerals (e.g. talc, olivine, pyroxenes and feldspars) under supercritical CO₂ (approx. 95 atm pressure and 423K) clearly show the well-defined Raman fingerprints of each mineral along with the Fermi resonance doublet of CO₂. Besides the CO₂ doublet and the effect of the viewing window, the main differences in the Raman spectra under Venus conditions are the phase transitions, the dehydration and decarbonation of various minerals, along with a slight shift in the peak positions and an increase in line-widths. The dehydration of melanterite (FeSO₄ · 7H₂O) at 423 K under approximately 95 atm CO₂ is detected by the presence of the Raman fingerprints of rozenite (FeSO₄ · 4H₂O) in the spectrum. Similarly, the high-temperature Raman spectra under ambient pressure of gypsum (CaSO₄ · 2H₂O) and talc (Mg₃Si₄O₁₀(OH)₂) indicate that gypsum dehydrates at 518K, but talc remains stable up to 1003K. Partial dissociation of dolomite (CaMg(CO₃)₂) is observed at 973K. The TR remote Raman spectra of olivine, α-spodumene (LiAlSi₂O₆) and clino-enstatite (MgSiO₃) pyroxenes and of albite (NaAlSi₃O₈) and microcline (KAlSi₃O₈) feldspars at high temperatures also show that the Raman lines remain sharp and well defined in the high-temperature spectra. The results of this study show that TR remote Raman spectroscopy could be a potential tool for exploring the surface mineralogy of Venus during both daytime and nighttime at short and long distances.

Keywords: Venus mineralogy; time-resolved remote Raman spectroscopy; remote Raman spectra of minerals; high-temperature Raman spectra; high-pressure Raman spectra; supercritical carbon dioxide

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One contribution of 12 to a Theme Issue ‘Raman spectroscopic approach to analytical astrobiology: the detection of key geological and biomolecular markers in the search for life’.
Raman spectroscopy (RS) has been proposed as a candidate analysis system for missions to Mars and, more recently, as a potential mineralogical analysis system for Venus (e.g. Clegg et al. 2009; Wang 2009). This technique has several distinct advantages over other spectroscopic techniques that have been used on past missions. For planetary applications, the sharpness of the Raman spectral features of minerals allows for much less ambiguous detection, especially in the presence of mixtures. Visible, near-infrared, thermal, and reflectance and emission spectroscopy of minerals and compounds all suffer from broad overlapping spectral features (Wang et al. 1995) that complicate the interpretation of their spectra, from which more than one mineralogical solution can be typically derived. 

Small portable remote Raman systems, which are suitable for planetary rovers and landers, have been shown to be effective in identifying hydrous and anhydrous minerals, glasses of mineral compositions and ices. Most of the remote Raman systems have been tested up to a distance of 120 m (e.g. Sharma et al. 2002, 2003; Misra et al. 2005; Sharma 2007). Two of the most important advantages of time-resolved (TR) RS over other techniques for a mission to Venus are the rapid mineralogical analysis of both hydrous and anhydrous minerals and stand-off analysis at distances up to many metres. Rapid mineralogical analysis and stand-off analysis are very important for missions to Venus owing to the harsh environment at the planet’s surface. From the Soviet Venera missions it is known that on the Venusian surface the pressure is approximately 9.1 MPa (90 atm) and the temperature is near 735 K (Moroz 2002). For these reasons, the Venera surface probes had operational lifetimes of less than 2 h. The major gas in the Venusian atmosphere is CO₂, and under Venusean atmospheric conditions CO₂ exists in a supercritical phase near the surface. In 2003, the National Research Council recommended in its Solar System Exploration Decadal Survey (NRC 2003) that ‘NASA commit to significant new investments in advanced technology so that future high-priority flight missions can succeed’. These proposed high-priority flight missions were further discussed in NASA’s 2006 Solar System Exploration Roadmap (NASA 2006). Currently Venus is under consideration for NASA’s New Frontier Program. The Venus Exploration and Analysis Group (VEXAG) recommended that NASA should include a Venus In situ Explorer (VISE) in the Announcement of Opportunities of New Frontiers Class mission. The Explorer would investigate the composition and surface properties of Venus. It would also acquire and characterize a core sample from the surface of Venus, and measure the elemental composition and mineralogy of surface materials. VEXAG has also recommended that NASA should initiate a study of a Venus Flagship Mission at the earliest opportunity (VEXAG 2007). In light of these future NASA missions, it is beneficial to evaluate different analysis methods such as remote TR RS, which offers to greatly increase the scientific return from such a mission.

There have been prior reports indicating that under certain conditions a 248 nm laser beam failed to emerge from an optical cell containing supercritical carbon dioxide (sc-CO₂) because of the superior mirage effect in sc-CO₂ (Tang et al. 2000; Jain & Rothe 2005). These reports raised questions about whether the TR remote Raman spectra of surface minerals could be obtained under Venusean conditions or on the surface of Venus from a lander that uses a sapphire window as a viewing
port. To address some of these concerns, we have begun to evaluate TR remote Raman spectroscopic detection of minerals with 532 nm laser excitation under 95 atm of sc-CO₂ at 423 K, a temperature that is lower than the Venusian surface temperature of 735 K but encloses the sample under more dense sc-CO₂ than on the surface of Venus, to evaluate the possibility of focusing a laser beam in sc-CO₂ and to check for interference of fluorescence from the sapphire window in the pressure chamber. We have also evaluated TR remote RS in an environment with temperatures that are similar to those found on Venus, as blackbody radiation from the minerals on the Venusian surface could also interfere with Raman spectroscopic measurements. It should be noted that TR RS with a pulsed 532 nm laser has been shown to be an effective technique for high-temperature RS (Sharma 1989). Previous work has also shown that high temperatures can have a strong effect on the Raman spectra of minerals (Sharma 1989; Gillet 1996). These temperature effects include broadening of Raman lines, decrease in intensity of Stokes–Raman lines, phase transitions in minerals, and the dehydration and decarbonation of minerals. The RS technique has been successfully used in high-pressure studies on a number of materials at very high pressures (up to a few hundred gigapascals) in diamond anvil cells (e.g. Mao et al. 1985; Hemley et al. 1987; Sharma 1989; Gillet 1999; Knittle et al. 2001; Lin 2001; Auzende et al. 2004; Farrell-Turner et al. 2005; Kleppe et al. 2006; Pommier et al. 2008). The results of these high-pressure Raman investigations on minerals show that the Raman spectra of minerals at the Venusian surface pressure of 90 atm will show only a very small change in the positions of Raman lines. However, dehydration and decarbonation of minerals could be affected significantly by the high atmospheric pressure of CO₂ on Venus. Here we show results from a TR remote Raman study of minerals under approximately 95 atm of sc-CO₂ to 423 K from a distance of 1.5 m, and under 1 atm up to 1003 K from a distance of 9 m, which demonstrate the feasibility of using this technique for mineralogical analysis on the surface of Venus.

2. Instrumentation and experimental method

(a) TR remote Raman system

In a conventional Raman system utilizing a continuous-wave (CW) laser, a sample is excited with a continuous beam of photons but only a very small fraction (approx. 10⁻⁷) of these incident photons are scattered as Raman photons. In such systems, the Raman spectra of samples are collected by integrating the signal over several seconds under dark conditions, which helps to maintain a low background signal. When exposed to daylight, these systems become unusable, because the detector becomes oversaturated from the high background light level. The high surface temperature (approx. 735 K) on Venus produces considerable blackbody radiation from the sample, which will also interfere with the Raman spectra of minerals. In addition, fluorescence from the viewing window of a lander or rover could interfere with the Raman spectra of the surface minerals. One solution to this problem is to generate large numbers of Raman photons in a relatively short time and then detect them more efficiently. A remote Raman system for daytime operation has two critical components: (i) a pulsed laser and (ii) a gated detector. A TR Raman system significantly improves the Raman

Phil. Trans. R. Soc. A (2010)
Figure 1. Schematic of a directly coupled time-resolved remote Raman spectrograph system shown in coaxial geometry.

signal-to-background ratio and successfully measures Raman spectra in daylight as well as from samples that are at high temperature. Using a laser with pulse widths of a few nanoseconds, the target is excited by large numbers of photons within the nanosecond time frame. The Raman scattering has a very short lifetime (approx. $10^{-13}$ s), producing a signal that lasts only a few nanoseconds after the laser pulse exposure. If the detector is only activated within this small time window, the number of Raman photons is large compared with the background photons, resulting in high signal-to-background ratio. In general, for a given target the number of Raman photons generated is directly proportional to the pulse energy of the laser. Similarly, the amount of background light detected by the system is directly proportional to the gate width of the detector. Therefore, precise time-gating of the detection system is critical in capturing the maximum number of Raman photons and minimum background light. The directly coupled and portable remote pulsed Raman system used in the current investigations is described in detail elsewhere (Sharma et al. 2003; Misra et al. 2005; Sharma 2007), but a schematic diagram of the system is shown in figure 1.

To simulate a remote Raman system for a Venus mission, a Questar 3.5 inch (∼90 mm) telescope (Questar, New Hope, PA, USA) was used to collect the light scattered from samples located at a distance of 1.5 m from the telescope inside a pressure chamber (hereafter referred to as the Venus chamber) filled with approximately 95 atm of sc-CO$_2$ at 423 K, a temperature much lower than the 740 K Venusian surface temperature. Mineral samples were excited with less than 17 mJ per pulse of 532 nm wavelength from a frequency-doubled Nd:YAG laser operating at 15 Hz. The scattered light was analysed with a custom-built compact Raman spectrograph (Sharma et al. 2009) based on a holographic HoloPlex grating from Kaiser Optical Systems, Inc. (Ann Arbor, MI, USA) and a gated, thermo-electrically cooled intensified charge-coupled device (ICCD) detector, with $1024 \times 256$ pixels (IMAX, Princeton Instruments, Trenton, NJ, USA). The
TR remote Raman study of minerals

spectral resolution of the spectrograph was 20 cm\(^{-1}\) in the low-frequency (100–1500 cm\(^{-1}\)) region and 13 cm\(^{-1}\) in the high-frequency (2500–3600 cm\(^{-1}\)) region with a 100 \(\mu\)m slit.

For high-temperature and ambient-pressure Raman measurements at approximately 9 m, the remote TR Raman system consists of a 5 inch (125 mm) diameter telescope (Meade, ETX-125, f/10), a frequency-doubled mini Nd:YAG pulsed laser source (model Ultra CFR, Big Sky Laser, 532 nm, maximum energy of 35 mJ per pulse, 20 Hz, pulse width 8 ns, central laser spot divergence approx. 0.5 mrad), and a Kaiser Optical Systems f/2.2 HoloSpec spectrometer equipped with a gated, thermo-electrically cooled ICCD detector. The telescope is directly coupled to the spectrometer through a camera lens (50 mm, f/1.8). A 532 nm holographic SuperNotch filter (SNF) is placed in front of the camera lens to minimize the reflected and Rayleigh scattered photons from the target. The signal is then directed through a fixed mechanical slit of 100 \(\mu\)m width into the spectrograph. The entire system is mounted atop a pan-and-tilt scanner, which is electronically controlled, on a portable trolley. Since the entire system moves together, optical alignment between the laser, telescope and spectrograph is always maintained when the system is configured in the coaxial mode. A 10× beam expander is mounted in front of the laser to allow focusing of the laser spot at targeted distances. For Raman measurements, the laser beam diameter at the sample is kept to 8 mm. The laser is operated at 30 mJ per pulse with a frequency of 20 Hz. The HoloSpec spectrograph is equipped with a volume phase holographic grating capable of measuring Stokes-shifted Raman spectra in the range of 50–2500 cm\(^{-1}\). For some analyses, this grating was replaced by a HoloPlex grating (Kaiser Optical Systems), which extends the spectral range to 4500 cm\(^{-1}\) while maintaining a resolution of approximately 13 cm\(^{-1}\).

All spectra presented here were measured with the ICCD detector operating in the gated mode. A gate width of 30 ns was used to measure the Raman spectra of minerals inside the Venus chamber, and a gate width of 2 \(\mu\)s was used to capture the Raman signals excited by the laser pulses from samples inside the high-temperature furnace at 1 atm pressure. Samples were also measured with an integration time of 1–30 s, which is equivalent to an exposure of 20–600 laser pulses for our system operating at 20 Hz, and 15–450 laser pulses for the laser operating at 15 Hz. In other words, the sample analysis time was 1–30 s per sample.

No cosmic ray or baseline corrections were applied to the spectra presented in this study. This is an additional advantage of using the gated mode: the ICCD acquires the spectrum only during the interval for which the gate is open, and a gate width of 30 ns to 2 \(\mu\)s significantly reduces the probability of capturing a cosmic ray. Thus, most spectra are free from cosmic ray peaks.

We commonly use the atomic emission lines of a neon lamp to calibrate our remote Raman spectrometer. In addition, liquid cyclohexane and atmospheric nitrogen (band at 2331 cm\(^{-1}\)) were used as Raman standards to spectrally calibrate the system. The positions of the strong and sharp Raman lines of various minerals reported here are within ±2 cm\(^{-1}\) of their standard literature values. Two commercial computer programs were used for data collection and spectral processing: WinSpec, a 32-bit WINDOWS software package (Roper Scientific) for spectral data acquisition, and the GRAMS/32 software package (Galactic Industries) for data processing.
Figure 2. Photograph of the high-pressure and high-temperature Venus chamber with a sapphire window used for investigating the Raman spectra of minerals under gaseous and supercritical carbon dioxide environments.

(b) High-pressure and high-temperature cell

The high-pressure and high-temperature (HP–HT) cell from Thar Tech, Inc., Pittsburgh, PA, USA, used in these studies and referred to as the Venus chamber, is shown in figure 2. The HP–HT cell is made of a 30.5 cm long and 4.4 cm diameter cylindrical block of stainless steel that has a 12.5 mm diameter horizontal bore along its main axis and 12.5 mm ports on both ends. Sapphire windows (25.4 mm outer diameter and 12.5 mm thick) are sealed on the ends with O-ring gaskets. The Venus chamber was heated externally with a clamshell heater and the temperature was monitored with an iron–constantan (J-type) thermocouple. The O-ring seals restricted the maximum operating temperature of the Venus chamber to 423 K. For TR remote Raman measurements, the cell was mounted horizontally and the sample was located at the far end of the cell. A frequency-doubled Nd:YAG pulsed laser (532 nm, 15 mJ per pulse, 15 Hz and 8 ns pulse width) with 5x beam expander was used to focus the laser beam on the sample inside the HP–HT cell.

Mineral samples were heated to high temperature in a windowless furnace (figure 3) 9 m away from the telescope. The furnace is heated with a platinum–10 per cent rhodium wire, and temperatures up to 1400 K can be achieved.
The mineral is placed inside the furnace, close to the centre on a ceramic tube, and the laser beam is focused with the 10× beam expander mounted on the top of the telescope. The backscattered light from the sample is collected by the telescope and focused on the slit of the gated Raman spectrometer. Some of the Raman measurements of minerals at high temperature and under 1 atm CO₂ pressure were made with the sample in an atmosphere of CO₂, achieved by locating the furnace inside a 120 cm long fish tank filled with carbon dioxide gas at 9 m from the telescope of the TR remote Raman system.

(c) Mineral samples

The rock-forming minerals (dolomite, gypsum, dunite rock, spodumene, albite, microcline and talc) were purchased from Ward’s Natural Science Establishment, Inc. (Rochester, NY, USA). The polycrystalline dolomite sample was from Bamble, Norway. Gypsum of the selenite variety was from Washington County, Utah, USA. The dunite rock containing 90 per cent fine-grain olivine crystal was from Balsam, North Carolina, USA. Spodumene, albite, microcline and talc mineral samples were, respectively, from Cluster, South Dakota, USA, Keystone, South Dakota, USA, Madawaska, Ontario, Canada, and Balmat, NY, USA. Melanterite (FeSO₄·7H₂O) crystals were synthesized from reagent-grade chemicals (Chio et al. 2007). Clino-enstatite (MgSiO₃) crystals were provided by Professor Subrata Ghose of the University of Washington, Seattle, USA. A small fragment of each of these samples was mounted inside the furnace and was excited with the 532 nm pulsed laser without further cleaning or polishing.
3. Results and discussion

(a) TR Raman spectra of hydrated sulphates, talc and dolomite

Figure 4 shows the CW Raman and fluorescence spectrum of the Venus chamber containing gaseous CO$_2$ under 61 atm and 295 K excited by the 532 nm laser beam with an energy of 15 mJ per pulse at 1.5 m distance from the telescope. The ICCD was operated in the CW mode with the intensifier gain set to 50. The Raman spectrum of the Venus chamber is dominated by the strong and broad band at approximately 3819 cm$^{-1}$ (approx. 667.7 nm), and two sharp and strong lines at 4360 and 4389 cm$^{-1}$ corresponding to the absolute positions at 692.8 nm (R$_1$) and 694.1 nm (R$_2$), respectively. In addition, a relatively weak Raman doublet (1284 and 1388 cm$^{-1}$) of CO$_2$ is also visible in the spectrum (figure 4). The broad band at approximately 667.7 nm and the sharp R$_1$ and R$_2$ lines are fluorescence emission from trace amounts of Cr$^{3+}$ impurity in the sapphire window (Pringsheim 1949). In RS, the $v_1$ totally symmetric stretching vibration of CO$_2$ (1305.4 cm$^{-1}$) is active for the isolated molecule (e.g. the monomer) and is in Fermi resonance with the 2$v_2$ overtone of the bending mode of the molecule ($v_2 \sim 667$ cm$^{-1}$). As a consequence, two lines are observed, giving rise to the so-called Fermi doublet, situated at 1284 and 1388 cm$^{-1}$ (Herzberg 1945, p. 215; Cabaço et al. 2008).

Figure 5 shows the TR Raman spectra of gypsum in the Venus chamber under ambient conditions with the ICCD operating with maximum intensifier gain of 81.6 at the setting of 255 in the gated mode and gate width varying from 500 to 30 ns. It is evident from figure 5 that, in the spectra recorded with a gate width of 500 to 200 ns, the broad fluorescence band at a Stokes–Raman shift of
TR remote Raman study of minerals

Figure 5. Time-resolved remote Raman spectra of gypsum (CaSO₄·2H₂O) at 1.5 m in the Venus chamber under 1 atm of CO₂ and 295 K as a function of gating (500–30 ns) of the intensifier marked on each spectrum. (Laser 532 nm, 15 Hz, 15 mJ per pulse, integration time 1 s.)

Figure 6. Time-resolved remote Raman spectra of gypsum at 1.5 m in the Venus chamber under gaseous CO₂ (1 and 57.84 atm at 295 K) and supercritical CO₂ (95 atm at 423 K). (Laser 532 nm, 15 Hz, 17 mJ per pulse, 30 ns gate, integration time 10 s.)

3819 cm⁻¹ strongly interferes with the O–H stretching modes of water molecules in the 3000–3600 cm⁻¹ region. The fluorescence interference is minimized in the Raman spectra measured with a gate width of less than 100 ns. Using a 30 ns gate width, figure 6 compares the TR Raman spectra of gypsum at a distance of 1.5 m from the telescope in the Venus chamber at different temperatures and pressures of CO₂ (1 and 57.84 atm at 295 K), and under sc-CO₂ (95.26 atm at 423 K).
423 K). At 423 K, the Raman spectrum of gypsum contains the strongest SO$_4^{2-}$ symmetrical stretching line at 1007 cm$^{-1}$, and the symmetric stretching modes of water molecules are observed at 3403 and 3498 cm$^{-1}$, shifted from their respective positions of 3404 and 3492 cm$^{-1}$ at 295 K. In addition, the Fermi resonance doublet of CO$_2$ (consisting of Raman bands at 1284 and 1388 cm$^{-1}$) is also observed under sc-CO$_2$ and gaseous CO$_2$ at 57.84 atm and 295 K.

Figure 7 shows the effect of increasing temperature on the Raman spectrum of gypsum. TR high-temperature Raman spectra of gypsum at 9 m under ambient atmosphere measured at 303, 373 and 518 K are shown. The line widths of the strongest Raman line at 1008 cm$^{-1}$ of $v_1$(SO$_4^{2-}$), the Raman fingerprint of sulphate ions in gypsum, at various temperatures are listed in table 1. On increasing the temperature from 303 to 373 K, the Raman lines of gypsum in the 100–1300 cm$^{-1}$ region show a shift to lower wavenumber and their line widths increase. The peak position of the H$_2$O(I) stretching mode at 3404 cm$^{-1}$ observed at 303 K decreases to 3403 cm$^{-1}$ at 373 K whereas the H$_2$O(II) stretching mode of water molecules shows an increase in the peak position to 3498 cm$^{-1}$ at 373 K (table 1). These results are consistent with previous high-temperature micro-Raman laboratory studies of gypsum (Prasad et al. 2001; Chio et al. 2004). On heating the gypsum sample to 518 K, the $v_1$(SO$_4^{2-}$) peak appears at 1021 cm$^{-1}$ with a line width of 25 cm$^{-1}$, and in the O–H stretching region a band appears at 3558 cm$^{-1}$. These changes suggest that there is a phase transition in gypsum. Previous studies have shown that heating gypsum above 373 K causes it to lose a water molecule during the heating process, forming $\gamma$-CaSO$_4$ (soluble form of anhydrite) and hemihydrate (CaSO$_4$·0.5H$_2$O, also known as bassanite) (Abriel et al. 1990; Chang et al. 1999). The Raman $v_1$(SO$_4^{2-}$) lines of hemihydrate and $\gamma$-CaSO$_4$ appear at 1014 and 1026 cm$^{-1}$, respectively. The large (25 cm$^{-1}$) line width of the Raman line at 1021 cm$^{-1}$ and the presence of the band at 3558 cm$^{-1}$ indicate that both
Table 1. Raman peak positions and line widths\(^a\) (cm\(^{-1}\)) of the major lines of gypsum, talc and dolomite at various temperatures.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>(T = 303) K</th>
<th>(T = 373) K</th>
<th>(T = 518) K</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>gypsum</td>
<td>1008 ((\omega = 13.3))</td>
<td>1007 ((\omega = 13.6))</td>
<td>1021 ((\omega = 25))</td>
<td>(\nu_6(\text{SO}_4))</td>
</tr>
<tr>
<td></td>
<td>3404 ((\omega = 40.5))</td>
<td>3403 ((\omega = 53))</td>
<td>(\nu_6(\text{H}_2\text{O} \text{ I}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3492 ((\omega = 41))</td>
<td>3498 ((\omega = 56))</td>
<td>(\nu_6(\text{H}_2\text{O} \text{ II}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3558 ((\omega = 36))</td>
<td>3558 ((\omega = 36))</td>
<td>(\nu_6(\text{H}_2\text{O}))</td>
<td></td>
</tr>
<tr>
<td>talc</td>
<td>678 ((\omega = 21.5))</td>
<td>672.3 ((\omega = 29.4))</td>
<td>670.2 ((\omega = 32.3))</td>
<td>(\nu_6(\text{Si}-\text{O}-\text{Si}))</td>
</tr>
<tr>
<td></td>
<td>3677 ((\omega = 12.4))</td>
<td>3667.5 ((\omega = 17.8))</td>
<td>3662.3 ((\omega = 23.1))</td>
<td>(\nu(\text{O}–\text{H}))</td>
</tr>
<tr>
<td>dolomite</td>
<td>1094 ((\omega = 14.7))</td>
<td>1087.5 ((\omega = 22.2))</td>
<td>1081 ((\omega = 23.8))</td>
<td>(\nu_6(\text{CO}_3))</td>
</tr>
</tbody>
</table>

\(^a\)\(\omega\) = full line width at half-maximum height (cm\(^{-1}\)).

Hemihydrate and \(\gamma\)-CaSO\(_4\) phases are present in the heated sample at 518 K. Heating of gypsum to 633 K results in the formation of \(\alpha\)-CaSO\(_4\) (anhydrite) (Prasad et al. 2001).

Figure 8 shows TR Raman spectra of hydrated FeSO\(_4\) inside the Venus chamber at 1.5 m distance, excited with 15 mJ per pulse of 532 nm laser light under 1 atm air without the sapphire window, under 58 atm of gaseous CO\(_2\) at 295 K with the window, and under sc-CO\(_2\) (85 atm, 423 K). These spectra were collected with 450 laser pulses (30 s integration time) and the ICCD gated for 30 ns. The room-temperature remote Raman spectrum of FeSO\(_4\) \(\cdot\) 7H\(_2\)O (melanterite) is similar to that reported by Chio et al. (2007) from their micro-Raman studies of FeSO\(_4\) \(\cdot\) 7H\(_2\)O and FeSO\(_4\) \(\cdot\) 7D\(_2\)O, and shows the strong symmetric stretching mode \(\nu_1\) of sulphate ions at 978 cm\(^{-1}\) and broad overlapping \(\nu_1\) and \(\nu_3\) stretching modes of the hydrated water at approximately 3246 and 3419 cm\(^{-1}\). Weak Raman lines at 1101 and 1148 cm\(^{-1}\) of \(\nu_3\), the antisymmetric stretching mode of SO\(_4\) ions, and weak lines at 240, 450 and 615 cm\(^{-1}\), respectively corresponding to the translational modes of \(\nu(\text{Fe}^{2+},\text{H}_2\text{O})\), \(\nu_2(\text{SO}_4)\) and \(\nu_4(\text{SO}_4)\), are also observed (figure 8). The Raman spectrum of FeSO\(_4\) \(\cdot\) 7H\(_2\)O under 58 atm of gaseous CO\(_2\) at 295 K does not show any shift in the positions of the major Raman lines of FeSO\(_4\) \(\cdot\) 7H\(_2\)O as is expected, but the Raman lines of sapphire in the window at 380, 418 and 645 cm\(^{-1}\) overlap with the \(\nu_2(\text{SO}_4)\) and \(\nu_4(\text{SO}_4)\) modes. The Fermi resonance doublet of CO\(_2\) (consisting of Raman lines at 1284 and 1388 cm\(^{-1}\)) is also observed in the spectrum recorded under 58 atm CO\(_2\). In the 2600–4000 cm\(^{-1}\) region, the residue of the broad fluorescence band of the Cr\(^{3+}\) ion from the sapphire window overlaps with the broad \(\nu_3(\text{H}_2\text{O} \text{ I})\) and \(\nu_5(\text{H}_2\text{O} \text{ II})\) modes even in the TR Raman spectrum with 30 ns gating (figure 8). The TR Raman spectrum under sc-CO\(_2\) at 423 K exhibits a sudden shift in the position of \(\nu_1(\text{SO}_4)\) to 991 cm\(^{-1}\) and there is also a change in the band shape and position of the O–H stretching band. These changes in the spectrum suggest dehydration of FeSO\(_4\) \(\cdot\) 7H\(_2\)O to FeSO\(_4\) \(\cdot\) 4H\(_2\)O (rozenite). In the room-temperature micro-Raman

Phil. Trans. R. Soc. A (2010)
Figure 8. Time-resolved remote Raman spectra of melanterite (FeSO$_4$·7H$_2$O) at 1.5 m in the Venus chamber in air without sapphire window, and under gaseous CO$_2$ (59.8 atm at 295 K) and supercritical CO$_2$ (85 atm at 423 K). The observed changes in the Raman spectrum under supercritical CO$_2$ indicate dehydration of melanterite into rozenite (FeSO$_4$·4H$_2$O). (Laser 532 nm, 15 Hz, 15 mJ per pulse, gating 30 ns, integration time 30 s.)
TR remote Raman study of minerals

Figure 9. Time-resolved remote Raman spectra of talc \((\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2)\) at 1.5 m in the Venus chamber under 1 atm air with and without the sapphire window, and under gaseous CO\(_2\) (61.2 atm at 295 K). (Laser 532 nm, 15 Hz, 17 mJ per pulse, gating 30 ns, integration time 10 s.)

The TR Raman spectra of \(\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2\) (talc) at 1.5 m inside the Venus chamber excited by the 532 nm laser beam of 17 mJ per pulse are shown in figure 9. These spectra were recorded with the ICCD in gated mode using 30 ns gate and at 295 K with the Venus chamber under ambient air (with no sapphire window), and under 1 and 61.2 atm of gaseous CO\(_2\). Figure 10 illustrates the TR Raman spectra of talc at 8 m under 1 atm CO\(_2\) inside the high-temperature furnace at various temperatures up to 1003 K. The 1 atm and high-temperature Raman spectra were measured in the gated mode with a 1 μs gate, which was sufficient to suppress the signal from the bright laboratory lights, and the spectra were integrated for 10 s (over 200 laser shots). The positions and the line widths of the major Raman lines of talc at 678 and 3677 cm\(^{-1}\) at various temperatures are summarized in table 1. In the Raman spectra of talc under 1 atm of air and 1 atm of CO\(_2\) at 295 K inside the Venus chamber (figure 9), the strong Raman line at 678 cm\(^{-1}\) is attributed to the \(v_s(\text{Si–O–Si})\) symmetric stretching mode of talc and the Raman line at 3677 cm\(^{-1}\) to O–H stretching modes (Rosasco & Blaha 1980). The spectrum of talc measured inside the windowless Venus chamber in air (figure 9) also shows the Raman lines of talc at 127 (w), 196 (m) 466 (w), 1001(w) and 1051 cm\(^{-1}\) (w), where m and w refer to Raman lines of medium and weak intensities, respectively. In the Raman spectrum of talc under 61.2 atm of CO\(_2\) at 295 K, the sharp 678 and 3677 cm\(^{-1}\) Raman lines of talc are observed above the fluorescence background, along with strong Fermi resonance Raman lines of CO\(_2\) at 1284 and

spectrum of FeSO\(_4\)·4H\(_2\)O, \(v_1(\text{SO}_4)\) is observed at 990 cm\(^{-1}\) (Chio et al. 2007). In addition, the Raman lines at 1284 and 1388 cm\(^{-1}\) of the Fermi doublet of CO\(_2\) and weak shoulders at 1265 and 1409 cm\(^{-1}\) are also visible in the spectrum measured under sc-CO\(_2\). These weak shoulders show an increase in intensity with increasing temperature up to 423 K and are attributed to hot bands (HB) of the CO\(_2\) molecules (Kawakami et al. 2003).
1388 cm$^{-1}$. The intensities of these strong Raman lines of talc are comparable to the intensities of the lines of the Fermi doublet of CO$_2$, indicating that talc has a relatively lower Raman cross section. In the spectra of talc recorded inside the Venus chamber with its sapphire window under air and gaseous CO$_2$, the weak Raman lines of the sapphire at 378 and 418 cm$^{-1}$ are clearly visible and the weak sapphire line at 645 cm$^{-1}$ appears as a shoulder on the strong 678 cm$^{-1}$ line of talc. There is no significant shift in the frequencies of the Raman lines of talc in the spectrum with 61.2 atm CO$_2$ pressure as anticipated from the observed frequency shift of the $v_s$(Si–O–Si) and $v$(OH) modes with pressure at a rate of approximately 1 cm$^{-1}$ GPa$^{-1}$ (Holtz et al. 1993; Comodi et al. 2007).

On heating talc in 1 atm CO$_2$ inside the high-temperature furnace, both the Raman lines of $v_s$(Si–O–Si) and $v$(OH) modes of talc shift towards lower frequency and their line widths increase with increasing temperature (figure 10 and table 1). The $v$(OH) talc Raman line is, however, present in the 1003 K spectrum of talc, indicating that talc is stable up to 1003 K. The results of TR RS are in agreement with previous studies on thermal decomposition of talc, which have shown that at 1 atm pressure dehydroxylation of talc takes place at 1073 K and above (e.g. Daw et al. 1972; Koshi & Gillies 1979; Bose & Ganguly 1994).

As the surface temperature of Venus is 735 K, hydrous phases of hydrated sulphates will not be stable and will convert to anhydrous phases. The current high-temperature remote Raman measurements on gypsum and melanterite exhibit the potential of the Raman technique to search for hydrous phases and their thermal decomposition products on the Venusian surface measured from a lander. On the other hand, the TR remote Raman spectra of talc show that the phase could be stable at the Venustian surface temperature of 735 K. On the basis of the high D/H ratio in the Venustian atmosphere, it has been suggested that the planet may once have had a greater abundance of water (Donahue et al. 1997; Svedhem et al. 2007). If so, the detection of hydrous minerals on Venus would prove that it had more water in the past. Laboratory investigations on hydrous amphibole minerals, such as tremolite, under Venus-like conditions have shown...
that these minerals, if formed on the surface of Venus during a wetter past, could still exist under current conditions on the planet’s surface today (Johnson & Fegley 2003).

Figure 11 shows the TR Raman spectra of dolomite (CaMg(CO$_3$)$_2$) at 1.5 m inside the Venus chamber at 295 K under 1 atm air with and without the sapphire window, under 1 and 59.8 atm of gaseous CO$_2$ and under sc-CO$_2$ (89.4 atm, 423 K). The Raman lines of dolomite at 174, 297, 723 and 1094 cm$^{-1}$ (Bischoff et al. 1985; McMillan & Hofmeister 1988) are clearly visible in all the spectra. The spectra measured inside the Venus chamber with the sapphire window show the sapphire lines at 378, 418 and 645 cm$^{-1}$. The strong Fermi resonance doublet (1284 and 1388 cm$^{-1}$) of CO$_2$ is present in the spectra of gaseous CO$_2$ under high pressure (59.8 atm) and sc-CO$_2$. The high-temperature TR Raman spectra of dolomite at 9 m distance at various temperatures up to 973 K are shown in figure 12. The line widths of the 1094 cm$^{-1}$ Raman line at various temperatures are listed in table 1. The strongest 1094 cm$^{-1}$ Raman band is the fingerprint of carbonate ions corresponding to the $v_1$(CO$_3$) symmetric stretching mode of carbonate oxygen atoms. The low-frequency Raman bands at 174 and 297 cm$^{-1}$ are the Raman fingerprints of the dolomite lattice. The 723 cm$^{-1}$ band corresponds to the $v_4$(CO$_3$) in-plane bending mode. A couple of additional lines are seen in figure 12 that were not obvious in figure 11. The very weak band at 1439 cm$^{-1}$ corresponds to the $v_3$(CO$_3$) antisymmetric stretching mode of carbonate ions. Another weak band at 1752 cm$^{-1}$ is an overtone mode of the infrared-active $2v_2$(A$_g$) mode (Bischoff et al. 1985).

In general, it is possible to distinguish various minerals within the same functional group from each other by the positions of the low-frequency lattice modes and the mid-frequency internal modes (Bischoff et al. 1985; McMillan &
Hofmeister 1988; Sharma et al. 2002, 2003). The lattice modes of dolomite (CaMg(CO$_3$)$_2$) (174 and 297 cm$^{-1}$), calcite (156 and 282 cm$^{-1}$) and magnesite (MgCO$_3$) (212 and 329 cm$^{-1}$) are widely separated and easily identifiable. Because of their unique Raman patterns and clear, distinguishable peaks, the identification of minerals and inorganic compounds from their Raman spectra becomes promising. In fact, RS can be used as an unambiguous analytical tool for the identification of a mineral of interest by comparing its spectrum with the library of Raman patterns.

With increasing temperature up to 723 K, the Raman lines of dolomite in the TR remote Raman spectrum (figure 12) shift to lower frequencies and their widths increase (table 1). At 973 K the Raman spectrum of dolomite shows a sudden decrease in the line intensities and there are marked changes in the low-frequency lattice mode region. These changes in the 973 K Raman spectrum of dolomite indicate a phase transition in the material. Differential thermal analysis and high-temperature X-ray diffraction studies have shown that, on heating, dolomite dissociates into CaCO$_3$ and MgO between 833 and 1038 K (Engler et al. 1989). MgO is a cubic crystal and therefore in the bulk has no first-order Raman spectrum, as it possesses inversion symmetry. It is, therefore, not possible to detect MgO from the Raman spectrum (Schlecht & Böckelmann 1973). The changes in the structure of dolomite on heating to 973 K are, however, observed in the spectrum of the carbonate phase. The dolomite Raman spectrum at 973 K represents an intermediate phase in the thermal decomposition process and partly resembles that of the calcite spectrum. These high-temperature Raman measurements suggest that the carbonates could be a stable phase at the Venustian surface temperature of 735 K, and, if present, it could be detected with the TR remote Raman system. However, the corrosive, sulphuric-acid-containing atmosphere of Venus could cause the transformation of carbonate minerals into anhydrous sulphates.
Figure 13. Time-resolved remote Raman spectra of olivine (Mg_{2-x}Fe_xSiO_4) at 1.5 m in the Venus chamber under gaseous CO_2 (1 atm and 61.2 atm at 295 K) and supercritical CO_2 (95.26 atm at 423 K). (Laser 532 nm, 15 Hz, 17 mJ per pulse, gating 30 ns, integration time 1 s.)

(b) Raman spectra of anhydrous silicate minerals

Figure 13 illustrates the Raman spectra of an olivine crystal inside the Venus chamber under gaseous CO_2 (1 and 61.2 atm, 295 K), and under sc-CO_2 (95.3 atm and 423 K). All the spectra show the Raman fingerprints of olivine at 824 and 855 cm\(^{-1}\) over the fluorescence background, with additional weak Raman lines of the sapphire window at 418 and 645 cm\(^{-1}\). Relatively weak Raman lines of the CO_2 Fermi resonance are also observed in the spectra measured under CO_2 pressures of 61.2 and 95.3 atm. The intensity of the molecular CO_2 Fermi resonance doublet in the spectrum under sc-CO_2 (figure 13) is decreased compared with the intensity of the corresponding doublet observed under gaseous CO_2 at 61.2 atm and 295 K due to the decrease in the density of the sc-CO_2 fluid. The intensity of the olivine doublet is stronger than that of the Fermi resonance doublet of CO_2, indicating that the olivine doublet has a relatively higher Raman cross section (Stopar et al. 2005).

The high-temperature TR Raman spectra of olivine in the dunite rock, which contains 90 per cent fine-grain olivine crystals, at 9 m under 1 atm of air and at 303, 718 and 878 K are shown in figure 14. These spectra were recorded with the 125 mm diameter telescope remote Raman system equipped with a 20 Hz 35 mJ per pulse frequency-doubled (532 nm) Nd:YAG laser, by integrating the spectra over 200 laser shots and with the ICCD detector gate set to 2 \(\mu\)s. The remote Raman spectrum of olivine at 303 K shows lines at 125, 194, 227, 365, 430, 544, 589, 676, 824, 855, 918 and 962 cm\(^{-1}\). As discussed before, the 824 and 855 cm\(^{-1}\) doublet in the Raman spectrum of olivine at 303 K is the Raman fingerprint of olivine. In addition to the Raman lines of olivine, the spectra also contain a weak fluorescence background and Raman lines of atmospheric O\(_2\) (1556 cm\(^{-1}\)) and N\(_2\) (2331 cm\(^{-1}\)). The peak frequency and line widths of the most prominent Raman lines in the 800–850 cm\(^{-1}\) region at various temperatures are listed in table 2. These high-temperature Raman spectra are in agreement with the results.
Figure 14. Time-resolved high-temperature Raman spectra of olivine in a dunite rock at 9 m in air. (Laser 532 nm, 20 Hz, 35 mJ per pulse, gating 2 μs, integration time 10 s.)

Table 2. Peak positions and line widths\(^a\) (cm\(^{-1}\)) of strong Raman lines of olivine and clino-enstatite at selected temperatures.

<table>
<thead>
<tr>
<th>olivine</th>
<th>(T = 303) K</th>
<th>(T = 718) K</th>
<th>(T = 878) K</th>
<th>assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>824 ((\omega = 18.41))</td>
<td>816 ((\omega = 24.5))</td>
<td>813 ((\omega = 29.1))</td>
<td>(v_s(SiO_4))</td>
</tr>
<tr>
<td></td>
<td>855 ((\omega = 19.6))</td>
<td>850 ((\omega = 25.4))</td>
<td>847 ((\omega = 26.6))</td>
<td>(v_s + v_{as}(SiO_4))</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>clino-enstatite</th>
<th>(T = 293) K</th>
<th>(T = 473) K</th>
<th>(T = 873) K</th>
<th>assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>668.6 ((\omega = 10.7))</td>
<td>665.7 ((\omega = 17.9))</td>
<td>663 ((\omega = 20.7))</td>
<td>(v_s(Si-O-Si))</td>
</tr>
<tr>
<td></td>
<td>691.6 ((\omega = 10.7))</td>
<td>688.2 ((\omega = 17.9))</td>
<td>683.6 ((\omega = 17.8))</td>
<td>(v_s(Si-O-Si))</td>
</tr>
<tr>
<td></td>
<td>1015.2 ((\omega = 12))</td>
<td>1012.0 ((\omega = 16))</td>
<td>1007.3 ((\omega = 20.6))</td>
<td>(v_s(Si-O_{nbr}))</td>
</tr>
<tr>
<td></td>
<td>1037.4 ((\omega = 15))</td>
<td>1034.6 ((\omega = 15.6))</td>
<td>1027.3 ((\omega = 18.3))</td>
<td>(v_s(Si-O_{nbr}))</td>
</tr>
</tbody>
</table>

\(^a\)\(\omega\) = full line width at half-maximum height (cm\(^{-1}\)).

of high-temperature conventional Raman spectroscopic studies of olivine crystals (Gillet et al. 1991; Sharma et al. 1992). Figure 14 shows that it is possible to measure the Raman spectra of olivine to 878 K at 9 m with a good signal-to-noise ratio within 10 s.

Forsterite (Fo, Mg\(_2\)SiO\(_4\)) and fayalite (Fa, Fe\(_2\)SiO\(_4\)) are the end-member minerals of the olivine group. At room temperature, the signature double peaks of forsterite are observed at 825 and 857 cm\(^{-1}\). The corresponding Raman lines of fayalite at room temperature appear at 812 and 835 cm\(^{-1}\). These Raman lines are due to the \(v_1\)- and \(v_3\)-derived vibrational modes of orthosilicate (SiO\(_4\)) units. The \(v_1\) and \(v_3\), respectively, correspond to the Si–O\(_{nbr}\) symmetric and antisymmetric stretching modes of the SiO\(_4^{1-}\) tetrahedra, where O\(_{nbr}\) refers to non-bridging

Phil. Trans. R. Soc. A (2010)
oxygen. The frequencies of these $v_1$- and $v_3$-derived modes show small variations with substitution of Fe or Ca for Mg (Piriou & McMillan 1983; Lam et al. 1990; Chopelas 1991; Mohanan et al. 1993).

On increasing the temperature of olivine crystals in dunite rock to 718 K, the Raman lines shift to lower frequency and their band widths increase (table 2). This trend continues up to 878 K, a temperature that is higher than the Venusian surface temperature of approximately 735 K. In the olivine spectrum at 878 K, the line widths of the 813 and 847 cm$^{-1}$ Raman lines are, respectively, 29.1 and 26.6 cm$^{-1}$. Evidently, the TR remote Raman system could easily detect olivine on the surface of Venus.

Figure 15 illustrates the Raman spectra of $\alpha$-spodumene ($\alpha$-LiAlSi$_2$O$_6$) pyroxene polycrystals inside the Venus chamber at 295 K under 1 atm air without the sapphire window, under 57.8 atm gaseous CO$_2$ and under sc-CO$_2$ (95 atm, 423 K). The Raman lines at 707 and 1073 cm$^{-1}$ that originate from the $v_s$(Si–O–Si) and $v_s$(Si–O$^-$) symmetric stretching modes of $\alpha$-spodumene (Sharma & Simons 1981) are detected in all the spectra above the fluorescence background. In addition, the Fermi resonance doublet of CO$_2$ at 1284 and 1388 cm$^{-1}$ accompanied by weak hot band shoulders of CO$_2$ at 1265 and 1409 cm$^{-1}$ are also visible in the spectra measured under gaseous CO$_2$ and sc-CO$_2$ (figure 15).

Figure 16 depicts the TR Raman spectra of clino-enstatite (MgSiO$_3$) measured at a distance of 75 mm from the collecting lens inside the furnace at 293, 373, 473, 673 and 873 K (Sharma 1989). In the spectrum at 293 K, the $v_s$(Si–O–Si) modes
of silicate chains appear at 668.6 and 691.5 cm\(^{-1}\), and the \(\nu_s(\text{Si–O}_{\text{nbr}})\) modes of silicon–non-bridging oxygen stretching of the pyroxene chain appear at 1007.3 and 1027.3 cm\(^{-1}\).

With increasing temperature, all the Raman lines of clino-enstatite shift towards lower wavenumber and their line widths increase. The frequencies and the line widths of the \(\nu_s(\text{Si–O–Si})\) and \(\nu_s(\text{Si–O}_{\text{nbr}})\) modes at selected temperatures are listed in Table 2. It is clear from Figure 16 that, even at 873 K, the Raman spectrum of clino-enstatite has good signal-to-noise ratio, and the fingerprint lines of pyroxene corresponding to the \(\nu_s(\text{Si–O–Si})\) and \(\nu_s(\text{Si–O}_{\text{nbr}})\) modes are clearly visible. These results show that TR RS is capable of detecting pyroxene minerals on the surface of Venus.

Figures 17 and 18 show the Raman spectra of albite and microcline feldspar minerals at 1.5 m measured with 30 ns gate of the ICCD detector and 10 s integration time inside the Venus chamber at 295 K under 1 atm of air and 58 atm of gaseous CO\(_2\), and under sc-CO\(_2\) at 423 K. These spectra were excited with an energy of 15 mJ per pulse of the 532 nm laser beam operating at 15 Hz. The characteristic Raman lines of feldspars are visible in the spectra in addition to the Raman lines of the sapphire window at 380 (sh), 417 (m) and 645 cm\(^{-1}\) (w), and the Fermi resonance doublet of CO\(_2\) at 1284 and 1388 cm\(^{-1}\) accompanied by weak hot band shoulders of CO\(_2\) at 1265 and 1409 cm\(^{-1}\) in the spectra measured under gaseous and sc-CO\(_2\) (figures 17 and 18). In the Raman spectra of albite, the fluorescence background has been subtracted to show the weak Raman bands of albite.
Figure 17. Baseline-corrected time-resolved remote Raman spectra of albite (NaAlSi$_3$O$_8$) at 1.5 m in the Venus chamber under 1 atm air without the sapphire window, under gaseous CO$_2$ (58 atm at 295 K) and supercritical CO$_2$ (89.4 atm at 423 K). (Laser 532 nm, 15 Hz, 15 mJ per pulse, gating 30 ns, integration time 10 s.)

Figure 18. Time-resolved remote Raman spectra of microcline (KAlSi$_3$O$_8$) at 1.5 m in the Venus chamber under 1 atm air without the sapphire window, gaseous CO$_2$ (58 atm at 295 K) and supercritical CO$_2$ (95.2 atm at 423 K). (Laser 532 nm, 15 Hz, 15 mJ per pulse, gating 30 ns, integration time 30 s.)
The doublet consisting of bands at 479 and 508 cm\(^{-1}\) is the fingerprint of the \(\nu_s(T-O-T)\) symmetric stretching modes of four-membered rings of TO\(_4\) tetrahedra, where \(T = Si\) or \(Al\) (Sharma et al. 1983; Matson et al. 1986). The weak and broad Raman lines at approximately 1015 and 1088 cm\(^{-1}\) correspond to the \(\nu_{as}(T-O-T)\) the antisymmetric stretching mode of the bridging oxygen. The broad nature of the \(\nu_{as}(T-O-T)\) of albite indicates that the albite used in the current study has a higher degree of Si–Al disorder. In the spectra of microcline, the corresponding Raman lines of \(\nu_s(T-O-T)\) of four-membered rings of TO\(_4\) tetrahedra appear at 476 and 513 cm\(^{-1}\) and the weak and broad \(\nu_{as}(T-O-T)\) lines appear at approximately 997 and 1126 cm\(^{-1}\) (figure 18). On the basis of the difference in the positions of the \(\nu_s(T-O-T)\) lines in the TR remote Raman spectra, it should be possible to distinguish between the Na- and K-feldspar mineral phases. Mernagh (1991) and Freeman et al. (2008) have investigated the Raman spectra of a wide range of Na-, K- and Ca-containing feldspar minerals and found that, from the positions of the prominent Raman peaks in the spectrum, four types of feldspars can readily be identified: orthoclase (microcline), albite, high-temperature plagioclase and anorthite. McKeown (2005) has reported the Raman spectra of low albite under 1 atm air pressure from 298 K to above the 1391 K melting temperature. All the Raman lines of albite show broadening with temperature, from 9 cm\(^{-1}\) at 298 K to approximately 25 cm\(^{-1}\) at 1373 K, and the frequency of the Raman lines between 600 and 1200 cm\(^{-1}\) decreases by 15–27 cm\(^{-1}\) as the temperature is raised from 298 to 1373 K. The 477 cm\(^{-1}\) Raman line of albite observed at 298 K appears at 468 cm\(^{-1}\) in the spectra at 1313 K and the position of the 505 cm\(^{-1}\) Raman line does not change on heating (McKeown 2005). The difference between the room-temperature values of the lines (468 and 505 cm\(^{-1}\)) in the albite doublet study by McKeown (2005) and the corresponding lines observed at 476 and 509 cm\(^{-1}\) in the current study most likely reflects the difference in the composition and degree of Si–Al order–disorder in the two samples. The results of the referenced studies and the current TR Raman study show that it should be possible to detect feldspar minerals on the surface of Venus and to differentiate between Na-, K- and Ca-bearing feldspars.

4. Conclusions

We have demonstrated that it is possible to measure the Raman spectra of minerals inside a Venus chamber charged with a supercritical CO\(_2\) atmosphere, and viewing through a sapphire window. The window is necessary to enclose the high-pressure atmosphere in the chamber for these experiments, but it is also necessary for a Venus lander feasibility study because the lander instruments would need protection from the hot, high-pressure atmosphere on Venus. The interference of the fluorescence from Cr\(^{3+}\) impurities in the sapphire window with the Raman spectra of the H\(_2\)O and OH groups of minerals can be minimized by gating the CCD detector to 100 ns or less. We have also shown that there was no difficulty in focusing the 532 nm laser beam on the sample inside the 30.5 cm long Venus chamber containing sc-CO\(_2\). We have shown that it is feasible to measure the high-temperature Raman spectra of minerals with a TR remote Raman system during daytime and nighttime. The results of the present investigation show that RS could provide information about the dehydration and decarbonation reaction products of minerals, and for measuring molecular species
in the atmosphere. The time-resolved Raman system could be very useful in future lander and rover missions to Venus for investigating surface mineralogy and profiling molecular species in the Venusian atmosphere.

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Phil. Trans. R. Soc. A (2010)


TR remote Raman study of minerals


Phil. Trans. R. Soc. A (2010)