TEMPERATURE INFLUENCE ON RAMAN SPECTRA ON CALCIUM AND POTASIUM SULFATES ON THE MARTIAN SURFACE. J. Huidobro*[1], L. Coloma[1], I. Población[1], G. Arana[1], J. Aramendia[1], C. García-Florentino[1], E.H. Hausrath[2], K. Castro[1] and J. M. Madariaga[1], [1]Dep. Anal. Chem., University of the Basque Country (UPV/EHU), 48940 Leioa, Spain (jennifer.huidobro@ehu.eus); [2]UNLV, Las Vegas, NV, US

Introduction: Even if a significant portion of the current water on Mars is in the form of ice, there is a tiny amount of it that is found as water vapor, as liquid brine in solid areas and by forming part of the crystalline structure of other minerals that act as hosts. In fact, this last form is well known due to the detections of hydrated minerals made by OMEGA and CRISM visible/near infrared spectrometers on Mars. The main hydrated minerals detected by both instruments were from the sulfate and clay minerals family, such as kieserite, gypsum, a magnesium and calcium rich sulfate, kaolinite and montmorillonite [1,2], among others.

The state of crystalline water changes with decreasing temperature below zero Celsius degrees, and these changes can be observed by Raman spectroscopy [3]. Also, Raman spectroscopy can differentiate among the different polymorphs of hydrated salts, i.e. $CaCl_2.nH_2O$ ($0 \leq n \leq 6$) [3] $CaSO_4.nH_2O$ ($0 \leq n \leq 2$) [4]. Moreover, Raman spectroscopy can differentiate among single and mixed metallic salts, either anhydrous or hydrated, i.e. salts in the Na_2SO_4-K_2SO_4-H_2O system [5] or in the $CaSO_4$-K_2SO_4-H_2O one [6].

Raman spectroscopy is currently on Mars on board the Perseverance rover, as part of the SuperCam and SHERLOC instruments. Considering the extreme changes in temperature on Mars [7], the changes in crystallization water must be taken into account for a proper interpretation of the Raman spectra collected in the current mission and in future missions that will incorporate Raman spectrometers. With this in mind, it is of great importance for the science of the current and future Martian missions to have a quality temperature-Raman signal influence database that will streamline the data interpretation coming from the rovers and landers that are analyzing in situ the Martian surface.

In this sense, this work focuses on studying the influence of temperature on the Raman spectra of some hydrated sulfates that were found or are expected to be found on Mars. This work is a continuation of previously Raman studies on sulfate salts developed in our laboratory [4-6].

Samples: The studied samples were powdered gypsum [$CaSO_4.2H_2O$], syngenite [$K_2Ca(SO_4)_2.H_2O$] and görgeyite [$K_2Ca_5(SO_4)_6.H_2O$] that were previously synthesized and characterized in the laboratory [6]. The signals of the anhydrous forms were absent from these samples, ensuring that such Raman signals will appear only on the effects of temperature changes.

Instrumentation:

Micro Raman spectroscopy. This work was performed using the Renishaw inVia confocal micro-Raman spectrometer (Renishaw, UK). All the analyses were carried out with the 532 nm excitation diode laser (Renishaw UK RL532C50 with a nominal 300-mW output power). The instrument is equipped with a CCD detector cooled by Peltier effect, with a Leica DMLM microscope (Bradford, UK), implementing an XYZ stage control toolbar and with a micro camera. Although the instrument is equipped with several lenses, the 5x N PLAN (0.12 NA) was usually used for this experiment. Moreover, a 100% of nominal power was used for all samples.

Temperature-controlled stage. For the variable-temperature analysis, the inVia Renishaw Raman spectrometer was coupled with the THMS600/HFS600 temperature-controlled stage (Linkam Scientific Instrument, UK). This is a system that provides a stable temperature control from -196 to 600 ºC). The temperature stability is <0.1 ºC and the powder sample must be inside the stage between two cover slips (0.2 mm thick) to keep the sample in the correct place.

Methodology: For this work, all spectra were collected with the Raman and the temperature-controlled stage, which was placed inside the spectrometer. Moreover, all the spectra were acquired under the same measurement conditions: using the 532 nm excitation diode laser, adjustable laser power 1-100% , 1800 l/mm (vis) grating, 10 s of exposure time, 5x objective and a wavenumber range from 100 to 4000 cm^{-1}.

The analyses were carried out programming temperature and hold ramps, and collecting each spectrum at every -10ºC shift from +30 to -100 ºC. The 30 ºC was selected to avoid the partial dehydration of gypsum to bassanite [4] while -100 ºC was selected as the most extreme temperature on Mars. When de desired temperature was reached, a 6-minutes hold was programmed. During the hold time, four Raman measurements were performed for checking reproducibility.

After data acquisition, the Raman spectra were treated with the Wire software to subtract the baseline and to remove the cosmic rays. Finally, the center of each band was extracted for each spectrum by using a curve fitting (50% Lorentzian-Gaussian) option of the Wire software. In order to detect outliers, Dixon's Q test was carried out; and then, the mean and the standard derivation were calculated.

Results and discussion: At room temperature, the Raman spectrum of gypsum is characterized (±1 cm^{-1}) by the bands that appear at 412 (υ_2), 494 (υ_2), 616 (υ_4), 669 (υ_4), 1008 (υ_1), 1131 (υ_3), 3406 (υ_{H2O}) and 3494 (υ_{H2O}) cm^{-1}, corresponding these last two to water bands. At the same conditions, the Raman spectrum of syngenite is characterized by the bands that appear at 132, 179, 200, 239, 428, 441, 473 (υ_2), 493, 608, 621, 633, 644, 661, 982 (υ_1), 1006 (υ_1), 1083, 1140, 1166 and 3308 (υ_{H2O}) cm^{-1}. Finally, the Raman bands that characterized the görgeyite are 429, 439, 475, 480, 604, 631, 661, 980, 1005 (υ_1), 1012 (υ_1), 1116, 1138, 1163, 1188, 1216, 3302 (υ_{H2O}), 3412 (υ_{H2O}), 3498 (υ_{H2O}) and 3522 (υ_{H2O}) cm^{-1}. For all cases, the Raman bands that were the most affected under the influence of temperature were υ_1 and υ_{H2O} Raman bands.

Table 1 shows the tendencies that gypsum υ_1 and the υ_{H2O} suffered. As seen, the υ_1 position shifted very little to higher wavenumbers when temperature decreased. The same happened with the first water band. For both Raman bands, the change is so small that is under the spectral resolution values of SuperCam-Raman and SHERLOC instruments. However, when temperature decreases, the position of the second water band shifted appreciably (more than 6 cm^{-1} units) to lower wavenumbers.

Table 1. Gypsum Raman bands vs. temperature.

T^a / ºC	υ_1 /cm^{-1}	υ_{H2O} /cm^{-1}	υ_{H2O} /cm^{-1}
30	1008.1	3405.4	3494.3
20	1008.3	3405.7	3493.6
10	1008.2	3405.8	3493.1
0	1008.3	3406.0	3492.7
-10	1008.4	3406.2	3492.0
-20	1008.5	3406.1	3491.4
-30	1008.5	3406.3	3491.3
-40	1008.5	3406.2	3490.6
-50	1008.6	3406.5	3490.1
-60	1008.7	3406.6	3489.6
-70	1008.7	3406.7	3488.9
-80	1008.7	3406.9	3488.6
-90	1008.7	3407.0	3488.1
-100	1008.7	3407.2	3487.9

Table 2 shows the tendencies that syngenite υ_1 doublet and the two υ_{H2O} suffered. The first water signal is not defined above -30 ºC. When temperature decreases, the first υ_1 band is nearly constant while the second υ_1 shifted slightly to higher wavenumbers, unlike υ_{H2O} bands that shifted towards lower wavenumbers.

Finally, Table 3 shows the tendencies that görgeyite doublets υ_1 and υ_{H2O} suffered. In this case, the two υ_1 bands of görgeyite and the second υ_{H2O} increase slightly when temperature decreases. However, the first υ_{H2O} band is maintained constant with temperature decrease.

Table 2. Syngenite Raman bands vs. temperature.

T^a / ºC	υ_1 /cm^{-1}	υ_1 /cm^{-1}	υ_{H2O} /cm^{-1}	υ_{H2O} /cm^{-1}
30	982.1	1005.8	-	3308.2
20	982.2	1006.0	-	3307.7
10	982.1	1006.2	-	3307.3
0	982.3	1006.5	-	3306.8
-10	982.1	1006.4	-	3306.4
-20	982.1	1006.6	-	3306.1
-30	982.2	1006.7	3142.1	3306.5
-40	982.2	1006.8	3135.7	3306.1
-50	982.2	1006.9	3131.0	3305.3
-60	982.2	1007.1	3127.9	3304.5
-70	982.1	1007.2	3123.4	3304.3
-80	982.3	1007.4	3121.0	3304.2
-90	982.3	1007.6	3117.7	3303.8
-100	982.3	1007.8	3109.6	3302.9

Table 3. Görgeyite Raman bands vs. temperature.

T^a / ºC	υ_1 /cm^{-1}	υ_1 /cm^{-1}	υ_{H2O} /cm^{-1}	υ_{H2O} /cm^{-1}
30	1005.1	1011.8	3300.2	3521.2
20	1005.3	1012.1	3301.8	3521.9
10	1005.5	1012.4	3302.1	3522.3
0	1005.9	1012.9	3302.6	3522.8
-10	1006.0	1012.8	3301.8	3525.9
-20	1006.1	1013.0	3302.5	3526.6
-30	1006.2	1014.1	3303.6	3527.2
-40	1006.4	1013.2	3304.1	3526.5
-50	1006.4	1013.4	3302.5	3526.6
-60	1006.7	1014.2	3302.3	3528.1
-70	1006.5	1013.2	3302.6	3527.4
-80	1006.5	1013.9	3305.4	3527.6
-90	1007.0	1014.3	3300.2	3529.6
-100	1007.0	1013.0	3300.7	3526.2

Conclusions: The υ_1 and υ_{H2O} bands of gypsum, syngenite and görgeyite change with temperature, being the second υ_{H2O} band the most sensitive one for a proper Raman assignation in unknown samples.

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