**SUPPLEMENTARY MATERIAL**

**THE EFFECT OF LOW TEMPERATURE ON THE RAMAN SPECTRA OF CALCIUM-RICH SULFATES ON MARS**

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Table S1. Center and width parameters calculated for the three gypsum Raman bands.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temperature (K) | Center 1008 cm-1 | Center 3407 cm-1 | Width 3407 cm-1 | Center 3488 cm-1 | Width 3488 cm-1 |
| 273 | 1008.7 | 3406.0 | 33.7 | 3493.1 | 29.7 |
| 273 | 1008.8 | 3406.4 | 38.7 | 3493.1 | 30.7 |
| 273 | 1008.6 | 3406.2 | 34.6 | 3493.0 | 27.5 |
| 263 | 1008.7 | 3406.3 | 33.9 | 3492.4 | 30.7 |
| 263 | 1008.9 | 3406.7 | 35.9 | 3492.0 | 30.0 |
| 263 | 1008.8 | 3406.7 | 35.8 | 3492.2 | 25.2 |
| 253 | 1008.9 | 3406.5 | 32.7 | 3491.9 | 26.3 |
| 253 | 1008.8 | 3406.2 | 32.2 | 3491.7 | 23.9 |
| 253 | 1008.8 | 3406.3 | 27.8 | 3491.6 | 24.7 |
| 243 | 1008.9 | 3406.4 | 25.3 | 3491.4 | 25.5 |
| 243 | 1008.9 | 3406.7 | 30.4 | 3491.5 | 25.3 |
| 243 | 1008.9 | 3406.5 | 26.6 | 3491.7 | 20.9 |
| 233 | 1009.2 | 3406.7 | 24.5 | 3491.0 | 21.4 |
| 233 | 1009.0 | 3406.5 | 24.2 | 3490.9 | 19.8 |
| 223 | 1009.0 | 3406.9 | 22.9 | 3490.3 | 20.7 |
| 223 | 1009.1 | 3406.9 | 24.4 | 3490.3 | 20.2 |
| 223 | 1008.9 | 3406.8 | 23.6 | 3490.4 | 19.2 |
| 213 | 1009.1 | 3407.0 | 20.9 | 3489.7 | 19.1 |
| 213 | 1009.2 | 3407.0 | 22.0 | 3489.8 | 19.9 |
| 213 | 1009.2 | 3407.0 | 21.6 | 3490.0 | 18.1 |
| 203 | 1009.1 | 3407.0 | 20.9 | 3489.2 | 18.1 |
| 203 | 1009.2 | 3407.0 | 19.5 | 3489.1 | 18.0 |
| 203 | 1009.3 | 3407.2 | 20.3 | 3489.2 | 17.1 |
| 193 | 1009.2 | 3407.2 | 19.1 | 3488.7 | 17.4 |
| 193 | 1009.4 | 3407.3 | 18.8 | 3488.9 | 17.6 |
| 193 | 1009.1 | 3407.2 | 18.4 | 3488.7 | 16.6 |
| 183 | 1009.1 | 3407.3 | 18.6 | 3488.2 | 15.7 |
| 183 | 1009.2 | 3407.3 | 17.5 | 3488.2 | 16.2 |
| 183 | 1009.3 | 3407.3 | 17.6 | 3488.3 | 15.4 |
| 173 | 1009.2 | 3407.3 | 17.8 | 3487.7 | 15.7 |
| 173 | 1009.2 | 3407.5 | 17.2 | 3488.0 | 15.5 |
| 173 | 1009.4 | 3407.5 | 16.6 | 3488.0 | 16.1 |
| 163 | 1009.4 | 3407.7 | 16.1 | 3488.3 | 17.4 |
| 163 | 1009.4 | 3407.9 | 16.3 | 3488.6 | - |
| 163 | 1009.5 | 3407.7 | - | 3487.8 | - |
| 163 | 1009.5 | 3407.7 | - | 3488.6 | 14.9 |
| 153 | 1009.5 | 3407.8 | 16.2 | 3488.1 | - |
| 153 | 1009.5 | 3407.8 | 15.3 | 3488.3 | 16.4 |
| 153 | 1009.6 | 3407.8 | 16.5 | 3488.4 | 14.7 |
| 153 | 1009.2 | 3407.9 | - | 3488.0 | 13.5 |
| 143 | 1009.7 | 3408.0 | - | 3487.1 | 13.5 |
| 143 | 1009.7 | 3408.0 | 17.4 | 3487.2 | - |
| 143 | 1009.8 | 3408.1 | 15.0 | 3487.7 | 12.8 |
| 143 | 1009.8 | 3408.0 | 16.9 | - | 15.6 |
| 133 | 1010.1 | 3408.1 | 16.23 | 3487.6 | 16.1 |
| 133 | 1010.1 | 3408.1 | 16.1 | 3487.5 | 12.7 |
| 133 | 1010.1 | 3408.1 | 16.2 | 3487.0 | 11.9 |
| 133 | 1010.1 | 3408.2 | - | - | 11.6 |
| 123 | 1010.6 | 3408.4 | 17.1 | 3487.2 | 11.7 |
| 123 | 1010.6 | 3408.5 | 14.1 | 3487.1 | 9.6 |
| 123 | 1010.6 | 3408.5 | - | 3486.9 | 8.8 |
| 123 | 1010.6 | 3408.6 | - | 3487.2 | - |
| 113 | 1010.8 | 3408.7 | 16.2 | 3486.6 | 9.0 |
| 113 | 1010.8 | 3408.8 | 14.9 | 3486.0 | - |
| 113 | 1010.8 | 3408.8 | 18.4 | 3486.5 | 8.9 |
| 113 | 1010.7 | 3408.7 | 19.2 | 3486.9 | - |
| 103 | 1010.8 | 3408.9 | 14.4 | 3486.5 | 9.0 |
| 103 | 1010.8 | 3408.9 | 13.4 | 3486.6 | 9.0 |
| 103 | 1010.8 | 3408.9 | 17.9 | 3486.6 | 10.8 |
| 103 | 1010.8 | 3408.9 | - | 3486.6 | 11.8 |
| 93 | 1010.8 | 3409.1 | 17.4 | 3486.2 | 10.4 |
| 93 | 1010.8 | 3409.1 | 15.2 | 3486.3 | - |
| 93 | 1010.8 | 3409.2 | 13.0 | 3487.4 | - |
| 93 | 1010.8 | 3409.1 | 14.3 | 3486.1 | 11.7 |
| 83 | 1011.1 | 3409.2 | 15.2 | - | - |
| 83 | 1011.02 | 3409.2 | 13.4 | 3485.8 | - |
| 83 | 1011.08 | 3409.3 | 16.1 | 3486.5 | - |
| 83 | 1011.08 | 3409.2 | - | 3485.5 | - |

Table S2. Center position calculated for the three syngenite Raman bands and for the Görgeyite main band.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| SYNGENITE | | | |  | GÖRGEYITE | |
| Temperature (K) | Center 1006 cm-1 | Center 3153 cm-1 | Center 3307 cm-1 |  | Temperature (K) | Center 1006 cm-1 |
| 273 | - | 0.00 | 3305.3 |  | 273 | - |
| 273 | 1006.7 | 0.00 | 3306.0 |  | 273 | 1006.7 |
| 273 | 1006.8 | 0.00 | - |  | 273 | 1006.6 |
| 273 | 1006.6 | 0.00 | - |  | 273 | 1006.0 |
| 263 | 1006.9 | 0.00 | 3305.7 |  | 273 | - |
| 263 | 1006.9 | 0.00 | 3306.7 |  | 263 | 1006.7 |
| 263 | 1006.8 | 0.00 | 3306.8 |  | 263 | 1006.7 |
| 263 | - | 0.00 | - |  | 263 | 1006.1 |
| 253 | 1007.1 | 0.00 | 3306.6 |  | 253 | - |
| 253 | 1007.1 | 0.00 | 3306.3 |  | 253 | 1006.6 |
| 253 | 1007.0 | 0.00 | 3305.5 |  | 253 | 1006.9 |
| 253 | - | 0.00 | - |  | 253 | 1006.4 |
| 243 | 1007.0 | 3139.9 | 3305.8 |  | 243 | - |
| 243 | 1007.2 | 3140.1 | 3305.9 |  | 243 | 1006.7 |
| 243 | 1007.2 | 3145.4 | 3307.3 |  | 243 | 1006.9 |
| 243 | - | 3142.9 | 3306.9 |  | 243 | 1006.9 |
| 233 | 1007.4 | 3138.9 | 3305.8 |  | 233 | - |
| 233 | 1007.4 | 3134.8 | 3306.3 |  | 233 | 1006.7 |
| 233 | 1007.4 | 3133.6 | 3306.3 |  | 233 | 1007.0 |
| 233 | - | 3135.5 | 3306.2 |  | 233 | 1007.0 |
| 223 | 1007.5 | 3132.0 | 3304.6 |  | 223 | - |
| 223 | 1007.5 | 3130.2 | 3305.8 |  | 223 | 1006.8 |
| 223 | 1007.5 | 3131.2 | 3305.2 |  | 223 | 1007.0 |
| 223 | - | 3130.5 | 3305.7 |  | 223 | 1007.1 |
| 213 | 1007.7 | 3131.5 | 3305.8 |  | 213 | - |
| 213 | 1007.6 | 3125.4 | 3305.1 |  | 213 | 1007.1 |
| 213 | 1007.6 | 3127.9 | 3305.2 |  | 213 | 1007.2 |
| 213 | - | 3126.9 | - |  | 213 | 1007.6 |
| 203 | 1007.7 | 3126.3 | 3304.3 |  | 203 | - |
| 203 | 1007.8 | 3119.9 | 3304.4 |  | 203 | 1007.0 |
| 203 | 1007.8 | 3123.5 | 3304.2 |  | 203 | 1007.2 |
| 203 | - | 3123.9 | 3304.2 |  | 203 | 1006.8 |
| 193 | 1007.9 | 3123.0 | 3303.8 |  | 193 | - |
| 193 | 1008.0 | 3121.6 | 3303.7 |  | 193 | 1007.5 |
| 193 | 1008.1 | 3116.5 | 3304.0 |  | 193 | 1007.1 |
| 193 | - | 3122.9 | 3305.1 |  | 193 | - |
| 183 | 1008.3 | 3119.3 | 3302.8 |  | 183 | 1007.7 |
| 183 | 1008.1 | 3120.3 | 3303.3 |  | 183 | 1007.6 |
| 183 | 1008.2 | 3114.8 | 3304.8 |  | 183 | 1007.4 |
| 183 | - | 3116.6 | 3304.2 |  | 183 | - |
| 173 | - | - | - |  | 173 | - |
| 173 | 1008.4 | 3118.3 | 3303.5 |  | 173 | 1007.8 |
| 173 | 1008.4 | 3104.7 | 3303.5 |  | 173 | 1007.5 |
| 173 | 1008.3 | 3119.2 | - |  | 173 | 1007.5 |
| 173 | - | 3096.3 | - |  | 163 | 1008.0 |
| 163 | 1008.7 | 3095.8 | 3303.3 |  | 163 | 1008.2 |
| 163 | 1008.6 | 3081.6 | 3303.3 |  | 163 | 1008.1 |
| 163 | 1008.7 | - | 3303.3 |  | 163 | 1008.7 |
| 163 | 1008.7 | - | 3303.2 |  | 153 | 1009.1 |
| 153 | 1010.0 | 3072.7 | 3302.9 |  | 153 | 1009.1 |
| 153 | 1009.8 | - | 3303.1 |  | 153 | 1009.1 |
| 153 | 1010.0 | - | 3302.9 |  | 153 | - |
| 153 | 1009.9 | - | 3303.0 |  | 143 | 1009.3 |
| 143 | 1010.1 | 3074.8 | 3302.9 |  | 143 | 1009.3 |
| 143 | 1010.2 | - | 3303.0 |  | 143 | 1009.4 |
| 143 | 1009.9 | - | 3303.1 |  | 143 | 1009.4 |
| 143 | 1010.2 | - | 3303.0 |  | 133 | 1009.4 |
| 133 | 1010.3 | 3034.7 | 3302.6 |  | 133 | 1009.5 |
| 133 | 1010.3 | - | 3302.7 |  | 133 | 1009.4 |
| 133 | 1010.3 | - | 3302.6 |  | 133 | 1009.5 |
| 133 | 1010.3 | - | 3302.6 |  | 123 | 1009.5 |
| 123 | 1010.4 | 3024.1 | 3301.7 |  | 123 | 1009.6 |
| 123 | 1010.5 | - | 3301.7 |  | 123 | 1009.6 |
| 123 | 1010.4 | - | 3301.8 |  | 123 | 1009.5 |
| 123 | 1010.4 | - | - |  | 113 | 1009.6 |
| 113 | 1010.7 | 3065.4 | 3301.2 |  | 113 | 1009.6 |
| 113 | 1010.7 | 3038.5 | 3301.1 |  | 113 | 1009.5 |
| 113 | 1010.8 | 2996.2 | 3301.1 |  | 113 | 1009.5 |
| 113 | 1010.7 | - | - |  | 103 | 1009.7 |
| 103 | 1010.7 | 3024.8 | 3300.9 |  | 103 | 1009.7 |
| 103 | 1010.8 | 3026.9 | 3300.9 |  | 103 | 1009.7 |
| 103 | 1010.8 | - | 3300.8 |  | 103 | 1009.7 |
| 103 | 1010.8 | - | 3301.0 |  | 93 | 1009.8 |
| 93 | 1010.8 | 2926.5 | 3300.6 |  | 93 | 1009.8 |
| 93 | 1010.9 | - | 3300.5 |  | 93 | 1010.0 |
| 93 | 1010.9 | - | 3300.6 |  | 93 | 1009.8 |
| 93 | 1010.9 | - | 3300.6 |  | 83 | 1009.9 |
| 83 | 1011.0 | 2981.4 | 3300.3 |  | 83 | 1010.3 |
| 83 | 1011.0 | 2924.8 | 3300.3 |  | 83 | 1010.0 |
| 83 | 1011.0 | - | 3300.4 |  | 83 | 1010.4 |
| 83 | 1011.1 | - | - |  | 83 | - |



Figure S1. Linear Regressions for the band position of (A) main Gypsum band, (B) first –OH Gypsum band, (C) second –OH Gypsum band, (D) main Syngenite band, (E) first –OH Syngenite band, (F) second –OH Syngenite band, and (G) main Görgeyite band. The calibration data, needed to calculate the global uncertainty, is also provided, being m the slope, σm the uncertainty of the slope, b the intercept of the line, σb the uncertainty of the intercept, R2 the coefficient of determination (0-1), Sx/y is the standard error of the regression and n the points of the calibrate.



Figure S2. Raman spectra of (A) main Gypsum band, (B) –OH Gypsum bands, (C) main Syngenite band, (D) –OH Syngenite bands and (E) main Görgeyite band.



Figure S3. Linear Regressions for the first and second hydration band position of gypsum. Orange data correspond to the values obtained in this work, while the green ones correspond to those of Chio et al. (Chio et al., 2004).

Table S3. Raman-temperature estimations obtained in this work for the temperature-sensitive Raman bands of gypsum, syngenite and görgeyite. This table also shows the Raman shift of each band and the narrowing of the bands as temperature decreases.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **GYPSUM** |  | **SYNGENITE** |  | **GÖRGEYITE** |  |
| Band Position () = -0.01277 . T (K) + 1011.88 |  | Band position (1006 cm-1) = -0.02606 . T (K) + 1013.41 | **→** | Band position (1006 cm-1) = -0.02180 . T (K) + 1011.99 | **→** |
| Band Position (3407 cm-1) = -0.01621 . T (K) + 3410.451 |  | Band position (3153 cm-1) = 0.418 . T (K) + 3039.1 | **←** | **-** | **-** |
| Band Position (3488 cm-1) = 0.0349 . T (K) + 3482.67 |  | Band position (3307 cm-1) = 0.0344 . T (K) + 3297.60 | ← | **-** | **-** |