



Application Note AN R528

Minerals and Stones - Characterization by FT-Raman Spectroscopy

Introduction

Minerals are mostly inorganic crystalline compounds with a defined chemical structure formed by processes on earth, moon or other luminaries. In contrast to minerals, stones are heterogeneous compounds consisting of mineral aggregates.

The spectral information in a single Raman spectrum is complementary to the information that can be derived from Mid and Far Infrared (MIR and FIR) FT-IR spectra whereby lattice vibrations of inorganics are mainly present in the FIR part. Typically, Raman spectra reveal sharp spectroscopic signatures allowing for unambiguous determination of chemical substances and straight-forward data evaluation.

The fact that Raman spectroscopy requires almost no sample preparation and is non-destructive makes it easy to use and in combination with visualization a powerful technique for investigation and identification of minerals and stones.

Experimental

The stone researched in this work using a Bruker FT-Raman spectrometer MultiRAM (Figure 1) was obtained from Ural region, Russia in approximately 3300 m depth.

FT-Raman measurements were performed using 1064 nm excitation wavelength and a highly sensitive liquid nitrogen-cooled Germanium detector with 5 days hold time. The sample was placed on a Software controlled x,y-mapping stage R315/R and illuminated via a parabolic mirror objective R348-VAR including a video camera to additionally collect

Keywords	Instrumentation and Software
Raman	MultiRAM
Mapping	VERTEX and RAMII
Identification	Mapping stage R315/R
Chemical Image	OPUS Video Guided Measurement
Minerals and stones	

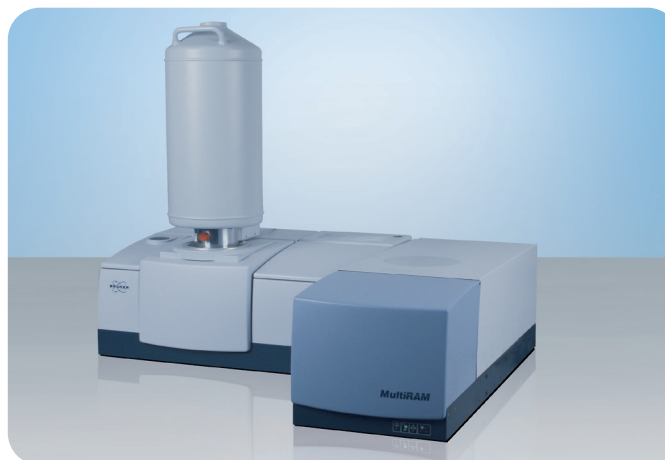


Figure 1: Stand-alone FT-Raman spectrometer MultiRAM with highly sensitive liquid nitrogen-cooled Germanium detector.

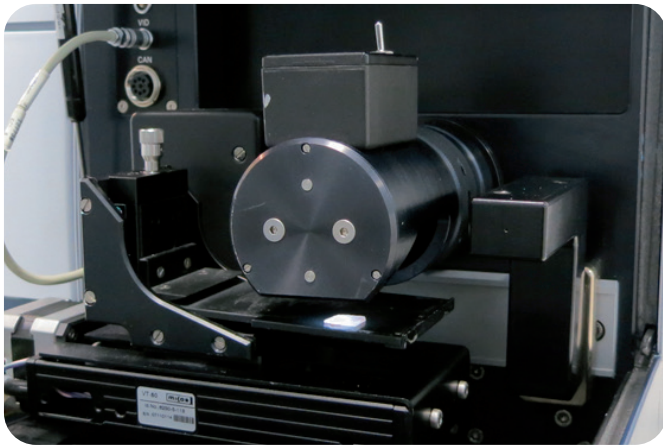


Figure 2: Stone sample placed on Software-controlled x,y-mapping stage R315/R and illuminated via parabolic mirror objective R348-VAR with video camera.

visual images of the sampling positions (Figure 2). For data acquisition a Laser excitation power of 500 mW, spectral resolution of 8 cm^{-1} , and 80 scans per spectrum were used. The whole number of sampling positions was 196 (14x14).

Results

A visual image of the stone sample is shown in Figure 3 wherein the green grid represents the sampling area. The colored marks in red, blue, and green highlight three characteristic sampling positions.

The spectrum recorded at the blue sampling position (in

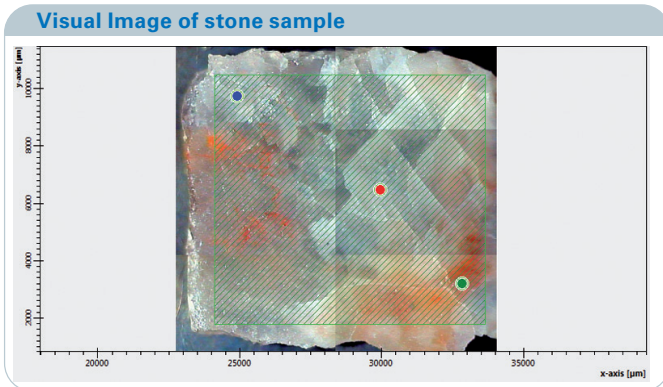


Figure 3: Visual image of stone sample. The green grid shows the sampling area (14x14 measurement positions) and colored marks in red, blue, and green highlight characteristic sampling positions.

Figure 3) showing major bands at 207 cm^{-1} and 467 cm^{-1} is identified as quartz (silicon dioxide) which is supported by comparison with Raman spectral libraries.

For the spectrum recorded at the red sampling position a good correlation to an aluminosilicate called laumontite with major bands at 285 cm^{-1} , 481 cm^{-1} , and 510 cm^{-1} was found.

The respective FT-Raman spectra of the blue and red sampling position as well as matching spectra from comparison with Raman spectral libraries are depicted in (Figure 4)

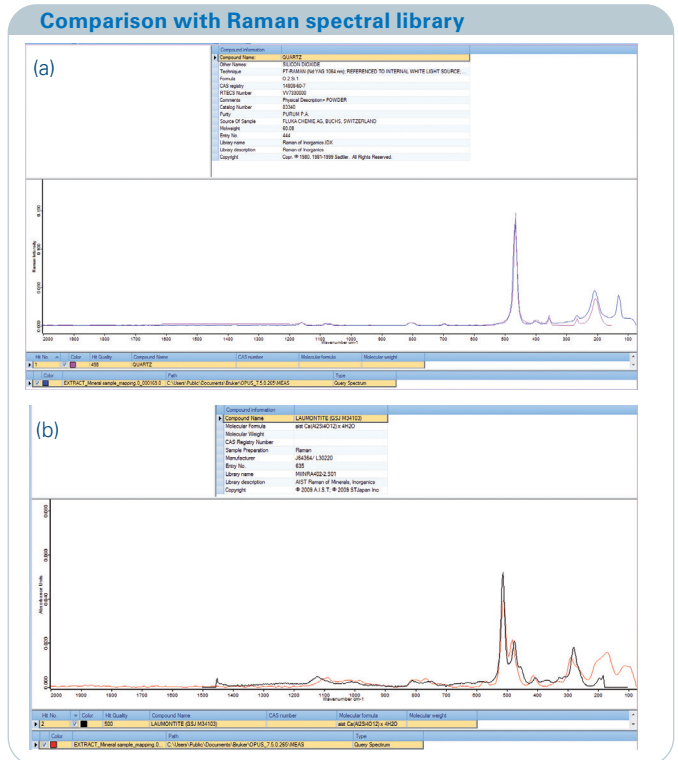


Figure 4: The Raman spectra measured at blue and red sampling position (shown in Figure 3) are displayed in blue (a) and red (b). A spectral check against library shows for the blue spectrum a match for quartz (a) and for the red spectrum a match for laumontite (b).

The Raman spectrum at the green sampling position (in Figure 3) is measured on some of the red colored part of the stone. It can be observed that major bands at 285 cm^{-1} , 481 cm^{-1} , and 510 cm^{-1} within the spectrum are in agreement with the findings for laumontite (red sampling position). The most dominant band at 1085 cm^{-1} as well as the band at 285 cm^{-1} can be assigned to Calcium carbonate. The spectrum measured at the green sampling position and matching spectra found from comparison with Raman spectral libraries of laumontite and Calcium carbonate are shown in Figure 5.

In order to determine the chemical distribution of quartz, laumontite, and Calcium carbonate across the stone surface their spectra were integrated.

For quartz the peak intensity relative to the local baseline at the band between $255-164 \text{ cm}^{-1}$ is used as integration value (OPUS software integration method K). The distribution of quartz across the stone surface (chemical image of quartz) is displayed in Figure 6. It can be seen that the quartz is present on the left side of the sampling area only.

For laumontite an area integral of the band between $538-492 \text{ cm}^{-1}$ is formed using a horizontal baseline determined by a defined baseline point at 626 cm^{-1} (OPUS software integration method B). It is evident that the Calcium carbonate can be found inclusion-like in the laumontite domain across the stone surface.

integration method D). The chemical image of laumontite (Figure 7) reveals that it is located on the right side of the sampling area.

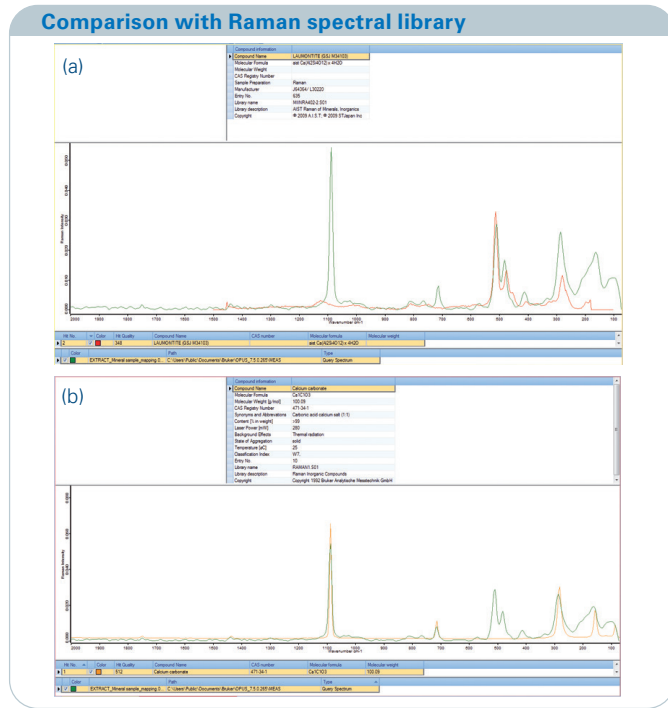


Figure 5: The Raman spectrum measured at green sampling position (shown in Figure 3) is an overlay of the two individual components laumontite (a) and Calcium carbonate (b) which can be derived from comparison with Raman spectral libraries.

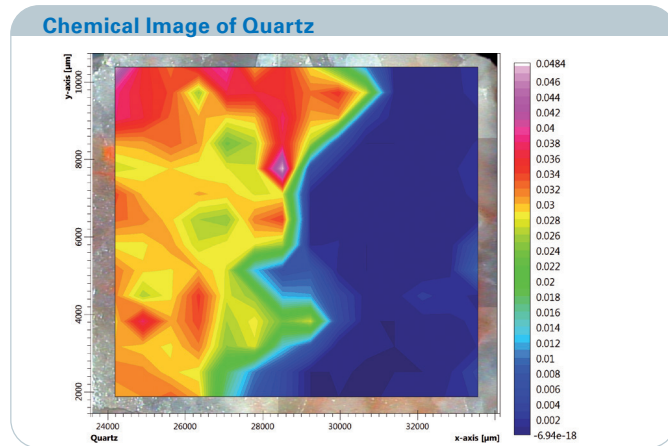


Figure 6: Distribution of quartz across stone surface derived from peak intensity for band between 255-164 cm^{-1} . The quartz is present on the left side only.

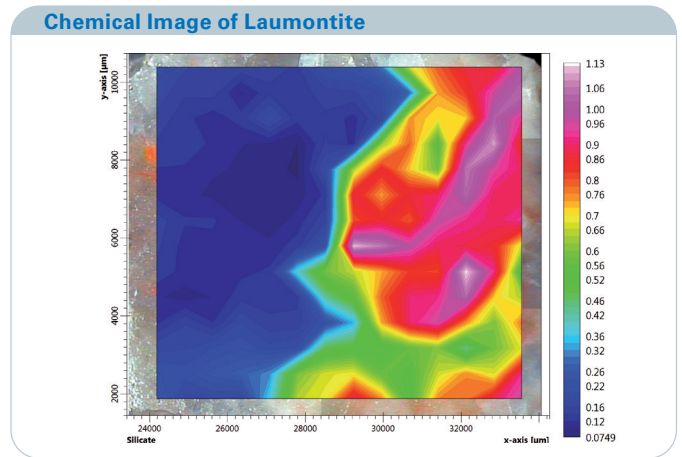


Figure 7: As a result of area integration for band between 538-492 cm^{-1} the laumontite is distributed on the right side of stone surface.

The Calcium carbonate chemical image displayed in Figure 8 originates from area integration performed above a straight baseline defined between 1114-1060 cm^{-1} (OPUS software integration method B). It is evident that the Calcium carbonate can be found inclusion-like in the laumontite domain across the stone surface.

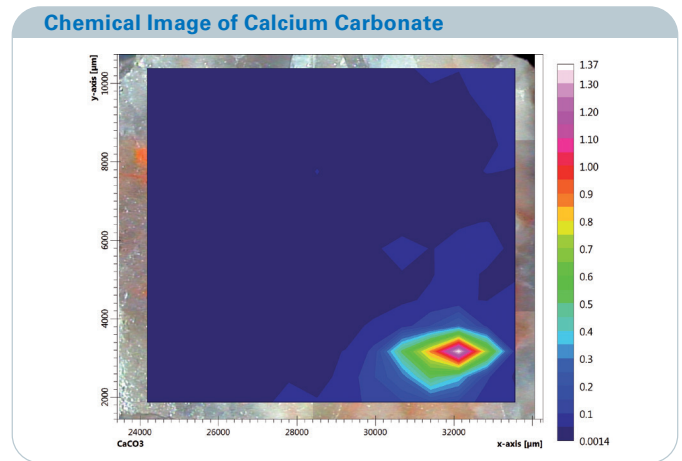


Figure 8: Based on areal integration above straight line between 1114-1060 cm^{-1} the Calcium carbonate is found inclusion-like in the laumontite domain.

Conclusion

It could be shown that FT-Raman spectroscopy using video capabilities nicely enables to identify several minerals and determine their distribution via integration of spectral information across a stone surface.

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