application note

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Confocal Raman Imaging: Solutions in Geoscience

Raman spectroscopy has long been applied in geoscience, for example for the identification and characterization of minerals, or in the observation of mineral phase transitions in high and ultra-high pressure/temperature experiments. In most cases, measurements have been carried out in a micro-Raman set up, i.e. information was obtained from single or multiple points of interest on a sample. This way, little detail on the spatial distribution and association of components or mineral phases, or chemical variation could be observed, even though this information may contribute significantly to the understanding of a sample's complexity.

By means of Confocal Raman Imaging (CRI), such characteristics can be evaluated from large scale scans in the centimeter range to the finest detail with sub-micron resolution. WITec confocal Raman microscopes of the alpha300 or alpha500 series allow for such measurements with very high sensitivity and resolution. CRI is a tool that not only provides complementary information to data obtained by e.g. electron microprobe (EMP), energy dispersive X-ray analysis (EDX), or secondary ion mass spectrometry (SIMS). In addition to the quantitative and semi-quantitative elemental and/or isotopic data acquired by these techniques, confocal Raman imaging contributes the visualization of the distribution for molecular information over a defined sample area. Furthermore, considering that most geo-materials are transparent from the NUV to VIS and NIR to some degree, this information can be obtained three-dimensionally due to the confocal set-up of the microscopes. The following examples shall serve to highlight some key analytical features of this technique for geoscience applications.

I. Large Area Scan: overview and variation
A sample from the deep biosphere of Äspö, Sweden, was studied using the large area scan mode of an alpha500 R, aiming to characterize secondary cleavage fillings in a 1.8 to 1.4 Billion years old diorite (sample courtesy of C. Heim and V. Thiel, EMP data courtesy of A. Kronz, Geobiology Group, University of Göttingen, Germany). A section (Fig. 1 I) was obtained from a drill core from borehole KJ 0052 F01, run by SKB (Swedish nuclear fuel and waste management) and drilled from a tunnel at ~450 m below the surface, the sampling depth in the core was 12m.

A large area scan of 8 x 2 mm was performed on this polished section with 800 x 200 pixels and an integration time of 36 ms per spectrum using a 532 nm excitation wavelength. Intensities integrated from 140 to 300 rel. 1/cm are compared to EMP maps of Al, Si and Ca (Fig. 1 II-IV), and indicate an similar overall chemical contrast (Fig. 1 V). The color-coded Raman image (Fig.2 I) and corresponding spectra (Fig. 2 II) allow for the general assignment of mineral phases and their gross

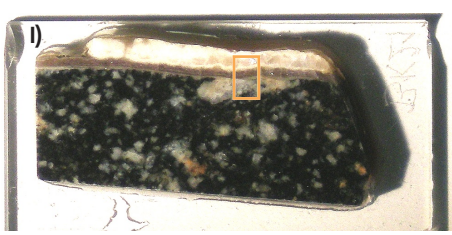

Fig. 1: I) Orange rectangle indicates scan position on polished rock section.

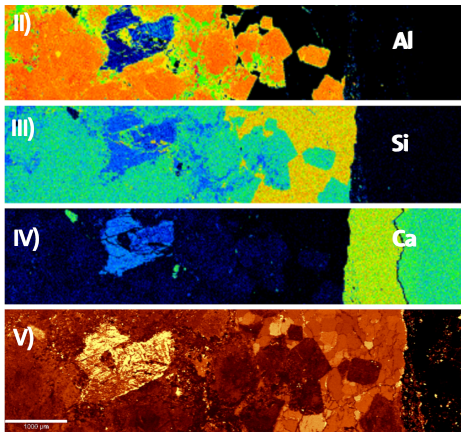

Fig. 1: II-IV) EMP maps showing elemental distribution; V) corresponding Raman image, integrated intensity 140-300 rel.1/cm.

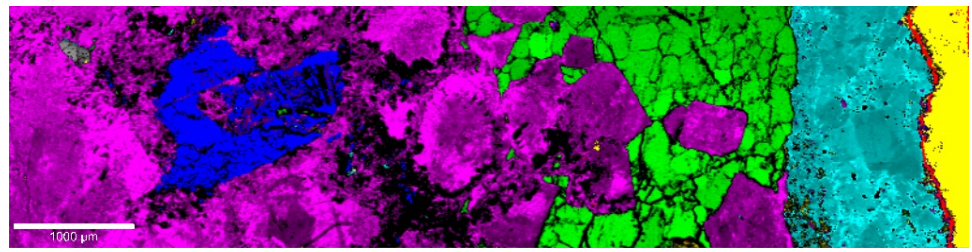

Fig. 2: I) Combined false color image and the corresponding color-coded spectra.

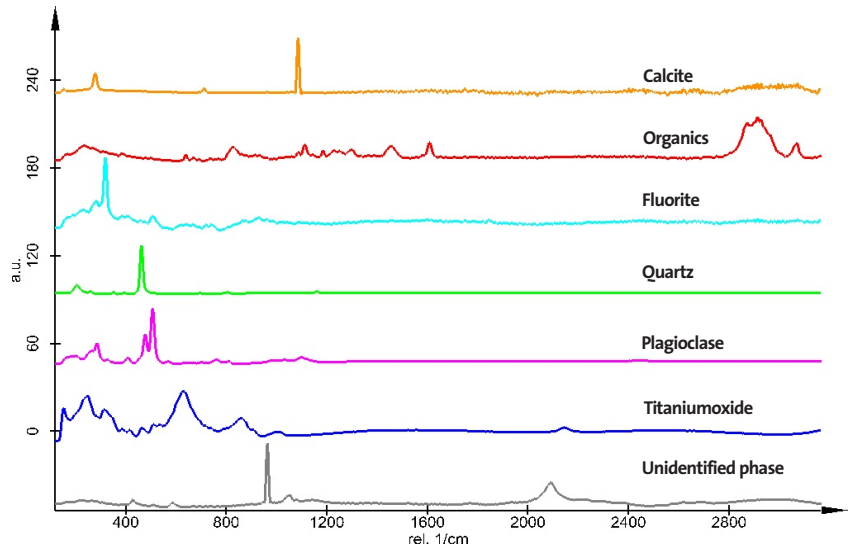

Fig. 2: II) Corresponding Raman spectra.

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distribution over the scanned area. In addition to the mineralogical context information, organic components were identified, spectrally characterized and located, trapped between two generations of hydrothermal precipitates (Fluorite and Calcite), indicating at which point in time a "deep biosphere" was active within these rocks.

Cluster analysis of the data set using the WITec Project software package revealed discrete areas of variation in the mineral phases (Fig. 3). This is exemplified by the Plagioclase phase, in which two distinct spectra show differential distribution within the sample regions identified as Plagioclase (Fig. 3 I). The Rutile phase is represented by the blue and yellow spectra and corresponding regions, an unidentified Ti-bearing phase and its variation is represented by the red and green spectra and corresponding regions (Fig. 3 II). Four distinct regions were identified for the Quartz phase based on variations in relative peak intensity (Fig. 3 III), note the discrete edges around Plagioclases.

II. High resolution: spectral and spatial information

High spectral and spatial resolution is necessary to observe chemical variations when they occur on micron-sized features. The spectral resolution is required to distinguish minor compositional changes, and the spatial resolution allows the depiction of such, changes at the required (sub-)micron level.

This is exemplified by small pancake-shaped carbonate structures, so-called globules, from the Martian meteorite ALH84001 and a terrestrial analogue from Svalbard (mantle peridotite xenolith from the Bockfjorden volcanic complex, BVC) (see Steele et al., 2007 for further description). Figure 4 shows the results of confocal Raman imaging studies combined with a high spectral resolution set-up for the carbonate composition in the ALH84001 and the BVC xenoliths. Images in row I of Fig. 4) show the overall carbonate distribution with relative intensity integrated over the peaks around 1090 cm-1 (spectra showing the peak center in Fig. 4 row I). Various carbonate reference samples were measured to demonstrate chemical variation, including Calcite (Ca), Siderite (Si) and Magnesite (Ma) (Fig. 4, spectra row II). The images in row II) of this figure represent peak center shifts of the carbonate ~330 cm-1 peak and clearly delineate discrete zones of chemical variation separated from one

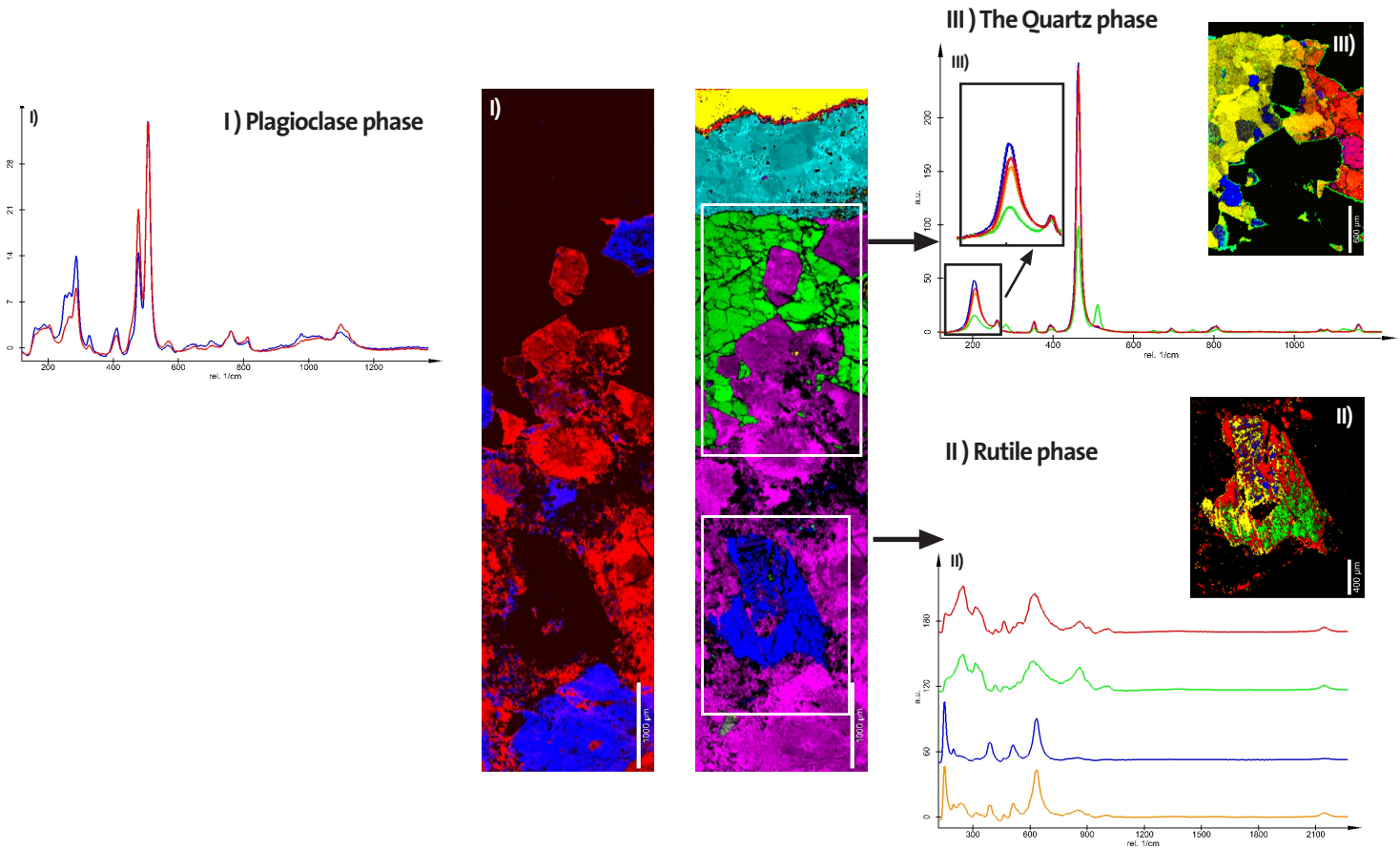

Fig. 3: Discrimination of varoations in the I) the Plagioclase phase: two distinct spectra show distinct distribution; II) the Rutile/Ti-phases: two different materials in two distinguishable configurations; III) the Quartz phase: distinct regions are reflected in variation of relative peak intensities in the spectra, note edges around Plagioclases.

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another on the (sub-)micron scale (the lighter colors show a peak shift toward higher wavenumbers). The letters A, B, C and D represent distinct chemical zones in the carbonate globule of the Martian meteorite, the numbers 1 and 2 show zoning in the BVC carbonates. The conclusions drawn from these observations contribute further to understanding the processing of volatile and biologically relevant compounds (CO_2 and H_2O) on Mars and illustrate the importance of high spectral and spatial resolution in confocal Raman microscopy studies (for detailed discussion see Steele et al., 2007).

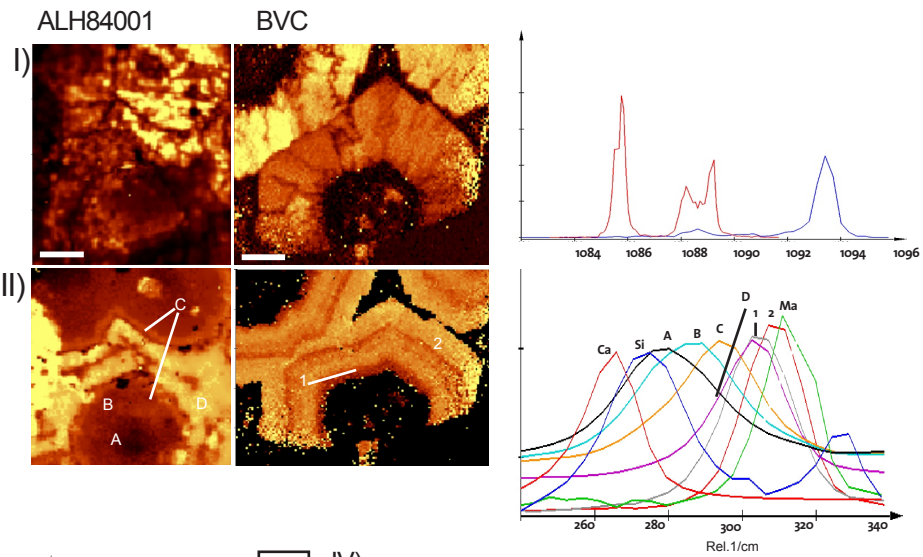
III. High sensitivity: revealing hidden details

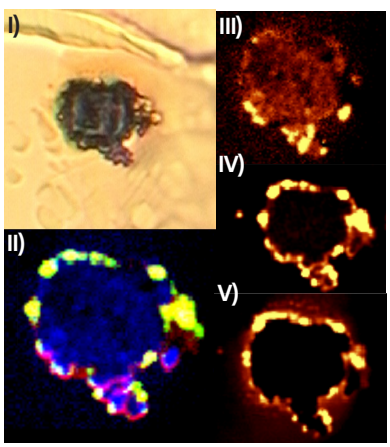
Valuable compositional and structural information may be contained even in the smallest sample volumes. In order to uncover such information it is not only a requirement to be able to spectrally and spatially resolve chemical features at the highest resolution, it is furthermore essential to work with the highest possible sensitivity. Confocal Raman microscopes of the WITec alpha series provide this level of sensitivity due to the highest possible throughput of Raman photons from the sample surface to the detector. This allows for the analysis of very small and delicate samples without the risk of irreversible sample alteration or destruction.

In geosciences such materials can, for example, be aerosols or interstellar dust particles (IDPs). Figure 5 shows a collage of confocal Raman images of an IDP (Fig. 5 I; for further detail see Toporski et al., 2004). The combined false color image in II) shows that distinct regions for the components illustrated in the images in III) to V) can be separated from one another. Not further identified mineral phases (Fig. 5 III) are separated from hematite/Carbon-bearing phases (Fig. 5 IV) and hematite phases (Fig. 5 V) and could be associated with to distinct regions in the sample. To allow for such differentiation and to enable the separation of labile components and at the same time avoid sample alteration due to excessive excitation laser energy, high sensitivity is a prerequisite. This has also been demonstrated on particles returned from comet 81P/Wild2 by the NASA Stardust spacecraft (Rotundi et al., 2008).

The study of small, precious and unstable samples further benefits from CRI being non-destructive, so that samples can subsequently be investigated using other, more invasive, micro-analytical techniques (e.g. SIMS, ToF-SIMS, TEM, etc.).

Fig. 4: Carbonate composition in ALH84001 and BVC xenoliths. Images in row I) show the carbonate distribution integrated over ~1090cm-1 peak, the spectra in row I) show the center distribution of the carbonate signal for these images. Images in row II) represent peak center shifts of the carbonate ~330 cm-1 peak and corresponding spectra (light color = higher wavenumber). Scale bar ca. 20 µm. Images courtesy of Meteoritics and Planetary Sciences; from Steele et al., 2007.





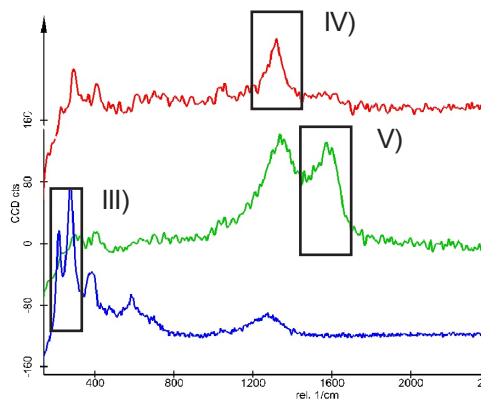


Fig. 5: Image collage of an IDP; I) video image; II) combined false color image of the images III) - V), colors as in the spectra; III) relative intensity distribution resulting from integration over the two peaks around 200 - 300cm-1 (blue spectrum); IV) relative intensity map of combined hematite / Carbon D band phases (1280 - 1400 cm-1; red spectrum); V) relative intensity map of hematite phases (green spectrum).

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IV. 3-D analysis: unveil the information trapped inside

Fluid inclusions were discovered in ultra-high pressure (diamond-grade) garnets from the Kokchetav Massif in northern Kazakhstan (samples and data courtesy of Andrey Korsakov, Siberian Branch of the Russian Academy of Science, Novosibirsk, Russia). Characterization of the inclusion contents regarding composition and petrographic context in this case may provide information on micro-thermometry. Due to confocality, CRI allows for the non-destructive and non-invasive analysis of such features.

The garnet was polished so that the inclusion remained intact some tens of microns below the surface (Fig. 6 I). As can be seen in Fig. 6 IIb), the garnet shows significant variation in relative peak intensities across the scanned area. The spectra in Fig 6 IIa) are normalized to the peak near 900 rel. 1/cm. Differences are apparent between the red and the magenta spectra (peaks near 850 and 360 rel.1/cm). The orange spectrum possibly represents a Carbonate phase in direct proximity to, or as part of, the inclusion. This variation is confirmed in the depth scan (Fig.6 IIIa and b). Here too, spectra are normalized to the peak near 900 rel.1/cm, differences are apparent between the red and the magenta spectra (peaks near 850 rel.1/cm and near 360 rel.1/cm; Fig. 6 IIIa). Interestingly, the aqueous phase showed significant variation, which can clearly be seen from the spectra shown in Figs. 6 IIc and IIIc, both for the X-Y- and the X-Z-scan. Variations may be attributed to the presence of H_2O in liquid and gaseous phase, or the presence of hydrous silicate phases. Changes in garnet peak intensities appear only around the inclusion. This may either indicate a differential stress regime attributable to the influence of the fluid inclusion, or may be due to slight variations in the garnet composition adjacent to the inclusion.

References:

Rotundi A. and 19 other authors (2008) Combined micro-Raman, micro-Infrared, and field emission scanning electron microscopy analysis of comet 81P/Wild2 particles collected by Stardust. Meteoritics and Planetary Science, **43**, 367-397.

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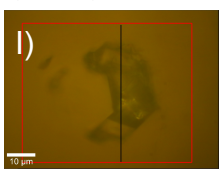

Fig. 6: Fluid inclusion in garnet: I) video image showing the sub-surface inclusion; the black line indicates position of the X-Z-scan; IIb) combined false color image X-Y-scan; IIa): extracted spectra of the garnet and carbonate (?) phase (color coding corresponding to colors in image), IIc): extracted spectra of the aqueous phase; IIIa-c) X-Z-scan: combined false color image and spectra, as above.