application note

Lise-Meitner-Straße 6, D-89081 Ulm, Germany
Tel. +49 (0) 731 140 700, Fax. +49 (0) 731 140 70200
www.witec.de, info@witec.de

WITec
focus innovations

Confocal Raman Imaging: Solutions in Archaeology

Comprehensive investigations of archaeological samples can be challenging due to variations in the size, shape, structure, and composition of different samples. Therefore flexible investigation techniques are required which can be easily adapted to the particular sample characteristics.

A method useful for evaluating the properties of an archaeological sample in detail is confocal Raman microscopy, with which the distribution of the chemical components can be comprehensively analyzed. Raman microscopy is a non-destructive technique which needs minimal, if any, sample preparation. The spatial resolution is down to 200 nm. Due to the confocal setup of the WITec alpha300 and alpha500 microscope series depth scans and 3D chemical imaging are also possible, as well as the analysis of large samples up to 15 x 10 cm. In combination with the award-winning, patent-pending TrueSurface microscopy it is possible to confocally investigate rough or heavily inclined samples.

Revealing hidden details with Raman microscopy

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. The following examples shall serve to highlight some key analytical features of this technique for archaeological applications.

Example measurement:

Large area scan of a rock sample

A rock sample was studied using the large area scan mode of an alpha500 R, (sample courtesy of C. Heim and V. Thiel, University of Göttingen, Germany). A large area scan of 8 x 2 mm² was performed on the polished rock section (Fig. 1, orange rectangle). The color-coded Raman image and corresponding spectra are shown in Figure 2. The Raman image was generated by measuring a full Raman spectrum at every image pixel with an integration time of 36 ms per spectrum. The investiongation allow for the general assignment of mineral phases and their gross distribution over the scanned area. In addition to the mineralogical context information, organic components were identified, spectrally characterized and located.

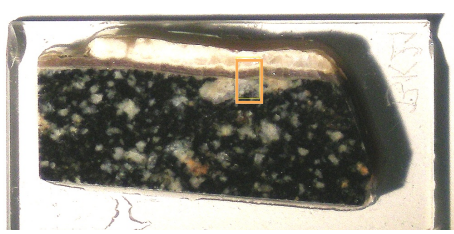


Fig. 1: Rock sample used for Raman analysis. Orange rectangle indicates scan position on polished rock section.

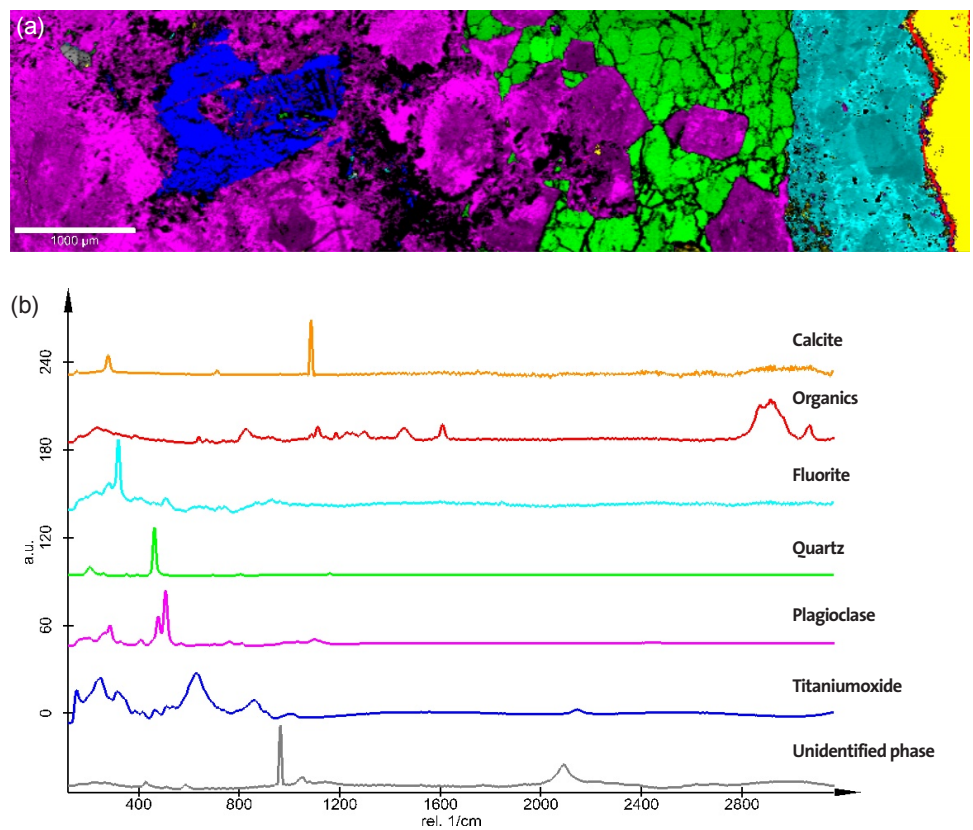


Fig. 2: Color coded Raman image and corresponding color-coded spectra. (a) Color coded Raman image generated through Raman mapping using a 532 nm excitation wavelength. The image shown consists of 800 x 200 pixels. (b) Corresponding Raman spectra of the different chemical components found in the rock sample.

application note

Lise-Meitner-Straße. 6, D-89081 Ulm, Germany
Tel. +49 (0) 731 140 700, Fax. +49 (0) 731 140 70200
www.witec.de, info@witec.de

Example measurement:
Optical Profilometry with TrueSurface Microscopy for confocal Raman imaging of rough samples

TrueSurface Microscopy allows confocal Raman imaging along heavily inclined or very rough samples with the surface held in constant focus while maintaining the highest confocality. Thus is is possible to perform confocal imaging measurements parallel with and guided by a large area topographic scan.

The profilometric capabilities of the True Surface Imaging mode allows scan ranges of up to 50x100 mm with a spatial resolution on the order of 40-120 nm vertically and 10-25 µm laterally. The large area topographic coordinates from the profilometer measurement can be precisely correlated with the large area confocal Raman imaging data.

An inclined rock sample (Fig. 3 a) was analyzed by TrueSurface optical profilometry following confocal Raman imaging. Therefore the topogaphy of the sample was first analyzed using the TrueSurface imaging option. Figure 3 (b) shows the resulting height profile. This profile was then used to guide the measurement of the identical sample area in confocal Raman imaging mode. In figure 3 (a) the topography profile is overlaid with the obtained Raman imaging data. The scan range was 2x2 mm², the topography range was over 1.7 mm.

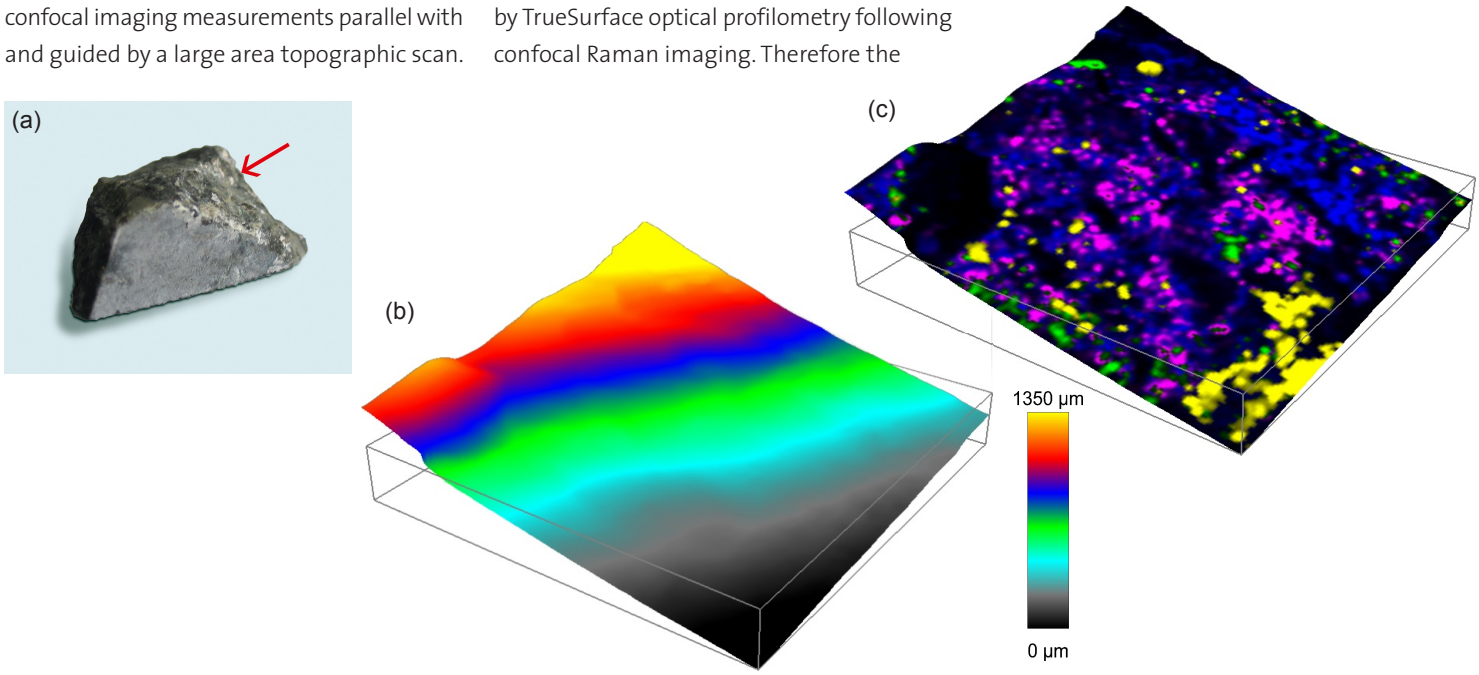
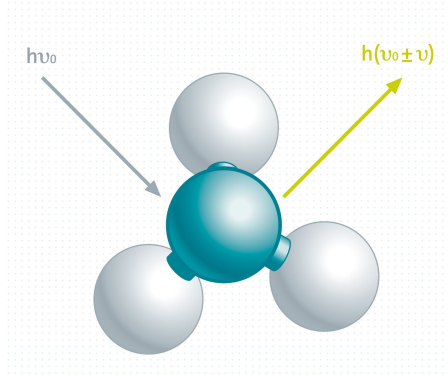


Fig. 3: (a) Inclined rock sample analyzed by TrueSurface Topography. The red arrow marks the area of interest. The identical sample area was measured using TrueSurface imaging option (b) and confocal Raman imaging mode (c). Scan range: 2x2 mm²; topography range: >1.7 mm).

The Raman Principle

A Raman spectrum shows the energy shift of the excitation light (laser) as a result of inelastic scattering by the molecules in a sample. Different molecular species consist of different atomic bonds, so each molecule can be easily identified by its unique Raman spectrum. In Raman imaging the Raman spectra are collected with a high-throughput confocal microscope & Raman spectrometer combination.



Raman Principle

Raman microscope alpha500 R

application note

Lise-Meitner-Straße. 6, D-89081 Ulm, Germany
Tel. +49 (0) 731 140 700, Fax. +49 (0) 731 140 70200
www.witec.de, info@witec.de

WITec
focus innovations

Examples of archaelogical publications by WITec customers

Analyst

RSC Publishing

Cite this: DOI: 10.1039/c3an00609c

Quantifying degradation of collagen in ancient manuscripts: the case of the Dead Sea Temple Scroll†

R. Schütz,[ab] L. Bertinetti,[a] I. Rabin,[b] P. Fratzl[a] and A. Masic*[a]

Since their discovery in the late 1940s, the Dead Sea Scrolls, some 900 ancient Jewish texts, have never stopped attracting the attention of scholars and the broad public alike, because they were created towards the end of the Second Temple period and the "time of Christ". Most of the work on them has been dedicated to the information contained in the scrolls' text, leaving physical aspects of the writing materials unexamined. They are, however, crucial for both historical insight and preservation of the scrolls. Although scientific analysis requires handling, it is essential to establish the state of degradation of these valued documents. Polarized Raman Spectroscopy (PRS) is a powerful tool for obtaining information on both the composition and the level of disorder of molecular units. In this study, we developed a non-invasive and non-destructive methodology that allows a quantification of the disorder (that can be related to the degradation) of protein molecular units in collagen fibers. Not restricted to collagen, this method can be applied also to other protein-based fibrous materials such as ancient silk, wool or hair. We used PRS to quantify the degradation of the collagen fibers in a number of fragments of the Temple Scroll (11Q19a). We found that collagen fibers degrade heterogeneously, with the ones on the surface more degraded than those in the core.

Received 28th March 2013
Accepted 17th June 2013

DOI: 10.1039/c3an00609c

www.rsc.org/analyst

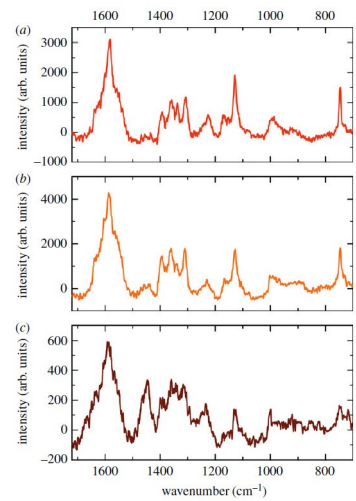
JOURNAL OF THE ROYAL SOCIETY Interface

J. R. Soc. Interface
doi:10.1098/rsif.2012.0174
Published online

Preservation of 5300 year old red blood cells in the Iceman

Marek Janko[1–4], Robert W. Stark[2–4] and Albert Zink[2,5,*]

The figure on the right shows a comparison of blood samples from air-dried whole blood (a), a single red blood cell (b), and the corpuscle found in 5300-year-old Iceman tissue (c). The data reveal the presence of blood in the mummy tissue and provide an indication of possible injuries and cause of death.



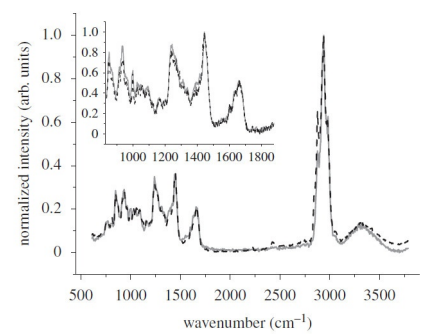
PROCEEDINGS OF THE ROYAL SOCIETY B

Proc. R. Soc. B
doi:10.1098/rspb.2010.0377
Published online

Nanostructure and mechanics of mummified type I collagen from the 5300-year-old Tyrolean Iceman

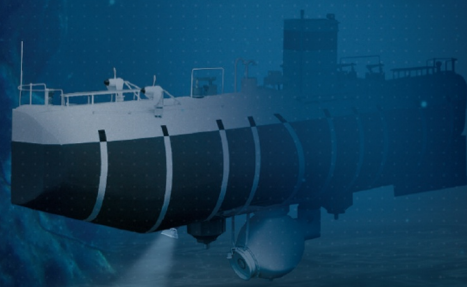
Marek Janko[1,2], Albert Zink[2,3], Alexander M. Gigler[1,2], Wolfgang M. Heckl[1,2,4] and Robert W. Stark[1,2,*]

The figure on the right shows the comparison of recent human skin collagen with 5300-year-old Iceman collagen. The obtained results provide hints toward the process of mummification and the degradation process involved.

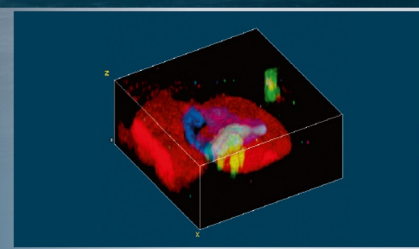


WITec
focus innovations

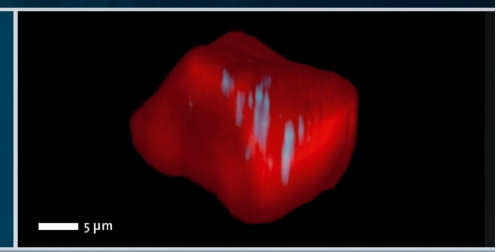
PIONEERS BY PROFESSION



The Bathyscaph Trieste arrived at the Earth's most extreme depth on 23. January 1960.



3D Raman image of a fluid inclusion in garnet



3D Raman image of a diamond inclusion (red) in quartz (black) with impurities (blue)

WITec's 3D Raman Imaging provides unprecedented depth and lateral resolution for chemical imaging down to the 200 nm diffraction limit. Our alpha300 and alpha500 series with optimized throughput and sensitivity establishes the benchmark in ultrafast spectra acquisition and low light-level microscopy.

Achieve a deeper understanding than ever before with WITec's pioneering technology.

PITTCON Editors' Gold Award · R&D 100 2007 · Microscopy Today Innovation Award · Prism Awards

alpha300 R
First 3D confocal Raman imaging system

alpha500 AR
First automated Raman/AFM system for large samples

alpha300 SR
First SNOM system using patented cantilever sensors

alpha300 AR+
First fully integrated Raman Imaging/AFM combination

WITec Headquarters
WITec GmbH, Lise-Meitner-Str. 6, 89081 Ulm, Germany, phone +49 (0)731 140700, info@witec.de

www.witec.de