Nano-FTIR Chemical Mapping of Minerals in Biological Materials

S. Amarie\textsuperscript{1}, P. Zaslansky\textsuperscript{2}, Y. Kajihara\textsuperscript{1,4}, E. Griesshaber\textsuperscript{3}, W.W. Schmahl\textsuperscript{3} F. Keilmann\textsuperscript{1}

\textsuperscript{1}Max Planck Institute of Quantum Optics and Center for NanoScience, 85714 Garching, Germany
\textsuperscript{2}Max Planck Institute of Colloids and Interfaces, Golm, 14424 Potsdam, Germany
\textsuperscript{3}GeoBio-Center\textsuperscript{LMU} and Department of Earth and Environmental Sciences, Ludwig-Maximilians-Universität, 80333 München, Germany
\textsuperscript{4}Department of Basic Science, The University of Tokyo, Tokyo 153-8902, Japan

Imaging methods of nano-composites based on X-ray, electron, tunneling or force microscopies provide information about the shapes of nanoparticles, however, they all fail on chemical recognition. We demonstrate that infrared near-field microscopy solves this requirement at 20 nm spatial resolution, highlighting in its first application to natural nanostructures the mineral particles in shell and bone. "Nano-FTIR" spectral images result from Fourier-transform infrared (FTIR) spectroscopy combined with scattering scanning near-field optical microscopy (s-SNOM) [1].

We have extended the scattering near-field microscope (s-SNOM) that returns an optical image together with topography, both at <20 nm resolution, by operating with broadband infrared illumination [2,3]. Thus a continuous infrared spectrum from 4 to 15 micrometer wavelength can be recorded at each scanned pixel. As this covers the “molecular fingerprint” region one can determine the local chemical composition.

The probing depth is about equal to the spatial resolution, of the order of the tip radius of typically 20 nm [4]. Our new method should find many applications requiring a quantitative material analysis at the nanoscale, be it in general analytical chemistry, nanofabrication, mineralogy or condensed matter physics.

Our observations of phosphates and carbonates in the well-studied examples of M. edulis (Fig 1) and human dentin (Fig 2) reveal exquisite detail that matches what is observed by electron microscopy and nanoindentation. The achievement of chemical and structural mapping of biominerals opens new horizons for our understanding of mineral arrangements and variability in biological systems.

Results of imaging hard biological matter will be presented, where phosphate and carbonate nanocrystals evoke especially bright contrasts due to infrared phonon resonance, and where new insights into biomineral growth and decay mechanisms of biological and even medical interest can be expected.
Fig. 1. Polished section of Mytilus edulis viewed in monochromatic s-SNOM; (A) Topography, (B) infrared amplitude measured at 980 cm\(^{-1}\). The contrast in B originates from organic matrix at a relatively low level (black) calcite and aragonite biocrystals (red) and phosphate at enhanced amplitude (yellow). Right panel: (C) topography corresponding to the white box of left panel, (D) infrared amplitude and (E) infrared phase spectra along the dashed line in (C) identify calcite, phosphate and aragonite by their resonances at 872, 1018, and 857 cm\(^{-1}\), respectively.

Fig. 2. Tubule in human dentin and its surrounding imaged by AFM topography (a), spectrally averaged nano-FTIR (b), and backscattered electron image (c).