CATHODOLUMINESCENT FEATURES AND RAMAN SPECTROSCOPY OF MIOCENE HYDROTHERMAL BIOMINERALIZATION EMBEDDED IN CRYPTOCRYSTALLINE SILICA VARIETIES, CENTRAL EUROPE, HUNGARY A. Müller[1], M. Polgári[2], A. Gucsik[3], Sz. Nagy[4], M. Veres[5], E. Pál-Molnár[1], J. Götze[6], C. Cserháti[7], T. Németh[2], M. Hámor-Vidó[8], [1]Szeged University, Dept. of Mineralogy, Geochemistry and Petrology, 6702 Szeged, Egyetem str. 2-6, Hungary, basmacskin@gmail.com, [2]Institute for Geochemical Research, 1112 Budapest Budaörsi str. 45, Hungary, rodokrozit@gmail.com, [3]Max Planck Institute for Chemistry, Dept. of Geochemistry, Joh.- J. Becherweg 27, D-55128, Mainz, Germany, gucsik@mpch-mainz.mpg.de, [4]Eötvös University, Faculty of Science, Institute of Physics, Dept. Material Physics, H-1117 Budapest, Pázmány Péter sétány 1/a, Hungary, ringwoodit@yahoo.com, [5]Research Institute for Technical Physics and Material Sciences, H-1121 Budapest, Konkoly-Thege M. str. 29-33, Hungary, vm@szfki.hu, [6]TU Bergakademie, Freiberg, Department of Mineralogy, Germany, goetze@mineral.tu-freiberg.de, [7]University of Debrecen, Faculty of Science and Technology, Dept. of Solid State Physics, Debrecen, Bem tér 18, Hungary, cserhati@delfin.klte.hu, [8] Eötvös Lorand Geophysical Institue, 1145 Budapest, Kolumbusz str. 17-23, Hungary, vido@elgi.hu.

Introduction: At the southern part of the Mátra Mts. (Hungary), in the neighborhood of Gyöngyöstarján and Gyöngyösoroszi area, variable cryptocrystalline silica varieties occur en masse in the fractures and cavities of the andesite host rock near the surface [1]. The great variety of colour and morphology is caused by the different genetic and morphological features of variable microbial (bacterial and microcolonial fungi type) activity and interaction with inorganic hydrothermal vent system, which have embedded in cryptocrystalline silica matrix. The aim of this research is the characterisation of cathodoluminescent features of biomineralization products occurring in the samples, and the determination of the form of 1-3 wt. % carbon content, giving further evidences of microbial contribution.

Samples and methods: 150 polished surfaces and 83 thin sections were investigated by rock and optical microscopy (reflected and transmitted, Nikon Eclipse 600 microscope), and selected samples by cathodoluminescence (Reliotron cold cathod), fluorescence (Leica DM-RX research microscope), methods. X-ray powder diffraction measurements were carried out on 10 selected samples for determination of mineralogical composition (Philips PW 1710). Electron-microprobe analyses were made to determine element distribution and textural features on 8 thin sections (Nikon Eclipse 600 Hitachi S4300-CFE SEM with Bruker Quantax, XFlash 4010 detector). Additionally, the structural properties of the selected minerals were determined by a Renishaw-1000 Raman spectrometer, the laser wavelenght was 785 nm, with focused energy of 8 mW. The maximal focus was driven to 1 μm spot in diameter. The thin sections were mounted in epoxy material, and the sample thickness is 30 μm.

Results: Detailed determination and description of *textural features* of the samples showed signs of complex microbial and inorganic interactions. The microbially mediated way of explanation for the studied Miocene hydrothermal vent formation was raised and proved for the first time. The signs of microbial activity are supported by the weathering formation of the host andesite, the variable and numerous rock varnishes on their surface, microbial forms (filamentous, coccoid and microcolonial fungi type), and the textural features of the silica matrix, which genetic processes were modelling. The small and uniform grain size (phase dimension), the chemically poor occurrence also support the biogenic origin as well as the often occurring curved morphology and variable „large formats" built up from the same small units.

The *fluorescence study* showed the remnants of organic matter in the samples occurring by greenish yellow colour (Fig. 1).

The *electron-microprobe analyses* determined 1-3 wt. % C content in the silica matrix and in mineralized forms (Fig. 2). In a selected sample the inner mineralized filamentous microbial part is composed of 47.8 wt. % Si, 2.1 wt. % Fe, 0.6 wt. % Al, 0.2 wt. % Mg, 0.5 wt. % K, 0.2 wt. % Ca and 1.6 wt.% C on average (selected elements). The content of the supposed mineralized extracellular polymeric substance around the filamentous forms is 37.9 wt. % Si, 8.1 wt. % Fe, 0.8 wt. % Al, 2.6 wt. % K, 0.4 wt. % Ca, 0.7 wt. % Mg, 0.1 wt. % Na and 1.5 wt. % C. The silica matrix is composed of 45.7 wt. % Si, 0.3 wt. % Al and 2.4 wt. % C.

Deep purple, red dull *cathodoluminescence* of the microbial textures were often observed in the thin sections (Fig. 3). According to electron microprobe measurements these phases are Fe and Si rich.

Spectroscopic characterisation of the cathodoluminescence of biomineralization products is in progress. Cathodoluminescence results also showed the formation of silica phases on different temperature conditions, which was probably caused by the oscillating temperature geyser and vent activity in the surrounding environment.

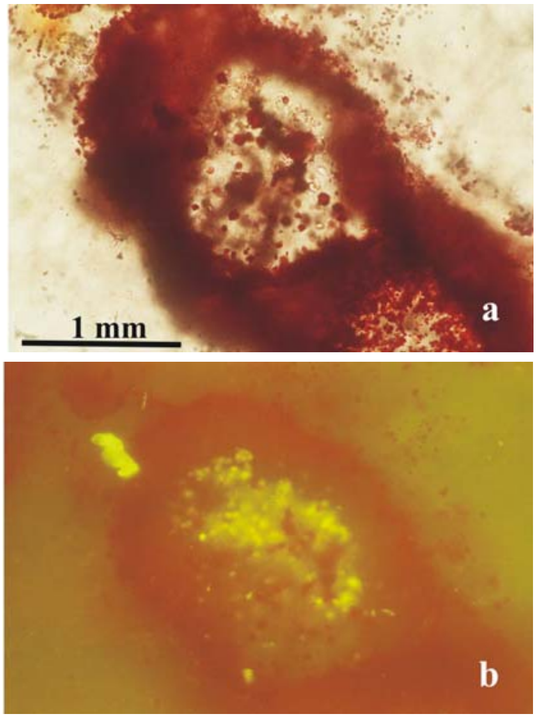

Fig. 1. Thin section (a, 1N) and fluorescence photo (b) of biomineralization products

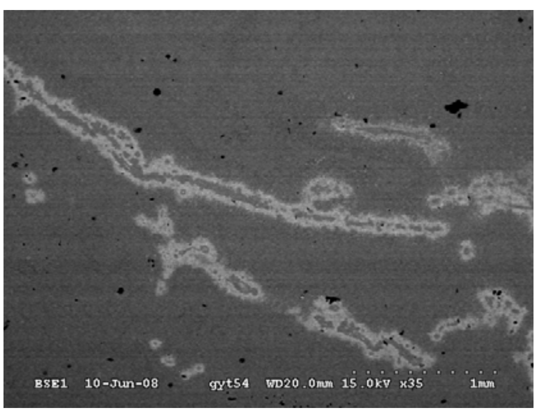

Fig. 2. BEI of mineralized filamentous bacterial forms (light phase) in cryptocrystalline silica matrix.

XRD mineralogy of the samples consists of opal CT, quartz, goethite, hematite, nontronite, and celadonite.

Raman spectroscopy was also used to study the products of biomineralization. Characteristic peaks of calcite (at 1085 cm^{-1}), hematite (at 226 and 608 cm^{-1}), goethite (at 298, 385, 438 and 548 cm^{-1}), α-quartz (at 261, 353, 393, 462, 463 and 801 cm^{-1}), moganite (at 501 cm^{-1}) and different carbonaceous materials (at 1340, 1380, 1548 and 1572 cm^{-1}) were found in the spectra (Fig. 4) [2]. The broad bands of the latter phase indicate amorphous carbon phases.

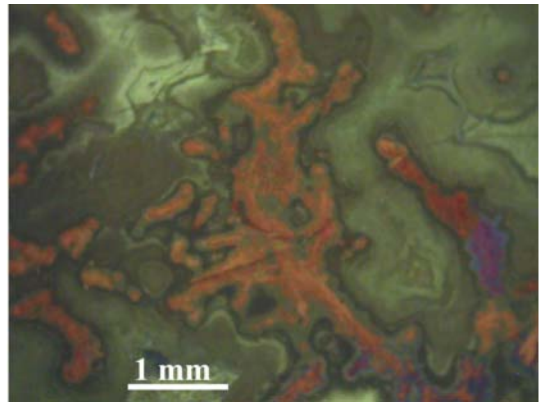

Fig. 3. Cathodoluminescence of mineralized filamentous microbial forms

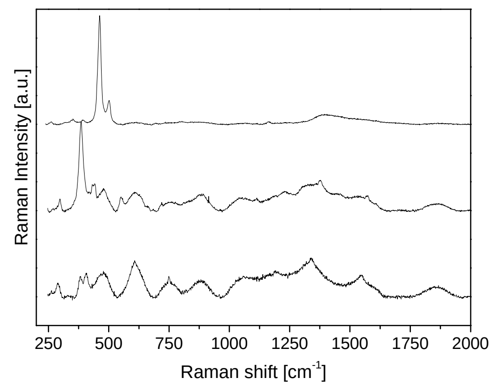

Fig. 4. Typical Raman spectra measured in the area of mineralized filamentous microbial forms.

Conclusion: Dull purple red cathodoluminescence and greenish yellow fluorescence of variable biomineralization products embedded in cryptocrystalline silica matrix were observed. Electron microprobe element measurements showed Fe-rich silica phases, with 1-3 wt. % C, and in most cases less that 1 wt.% trace element contents (Al, Ca, Mg, K) for the samples. The occurrence of amorphous carbon phases in the samples can be further evidences of microbial origin, and/or might be connected with hydrothermal contamination processes, which could serve as organic nutrients for heterotroph microbes in the system. This is also supported by the presence of moganite, which was found to form in the surrounding of organic carbonaceous phases [3]. Spectral characterisation of cathodoluminscence is proceeded.

References: [1] Czakó T. and Zelenka T. (1981) *Advances in Space Research*, 1, 289-298. [2] Kuebler et al., (2006) LPSC XXXVII, #1907 [3] Kovács Kiss V. (2000) PhD thesis.