COMBINED MICRO-RAMAN AND CATHODOLUMIESCENCE APPROACH TO IDENTIFY BIOSIGNATURE IN CARBONATES. T. Kuyama[1], K. Ninagawa[1] (ninagawa@dap.ous.ac.jp), A. Gucsik[2], Sz. Bérczi[3], Á. Kereszturi[3], H. Hargitai[3], and Sz. Nagy[3], [1]Okayama University of Science, 1-1 Ridai-cho, Okayama, 700-0005, Japan; [2]Max Planck Institute for Chemistry, Department of Geochemistry, Becherweg 27, D-55128, Mainz, Germany; [3]Eötvös Lóránd University of Budapest, H-1117 Budapest, Pázmány Péter sétány 1/c., Hungary,

Introduction: The putative fossil microbes occur in carbonate globules in the Martian meteorite, ALH84001 [1]. We intend to introduce a new method to describe/distinguish whether or not minerals are from biogenic or geologic origin. Cathodoluminescence (CL) is a very informative method for detecting trace elements and lattice defects in minerals. In some cases, CL reveals outlines and internal structures of fossils that are invisible in the standard optical microscopy [2]. CL spectra of carbonate shells have two peaks near 630 nm and near 480 nm. The peak near 630 nm is related to Mn^{2+}. This signal was applied to themoluminescence dating of fossil calcite shell [3]. Recently, difference of temperature dependence of CL spectra between shocked and unshocked quartz was reported [4].

Experimental Procedure: In this study, calcium carbonates of Skarn Deposit (Dalnegorsk, Russia) and hydrothermal vein in Alkaline rock (Sand Fly Bay, Otago, New Zealand) are used as geologic samples. Modern Pectinidae Pecten (Notovola) ablicans (SCHÖTER), Foraminifera Nuttallides (Paleocene/Eocene), and Brachiopoda (Jurassic, Hungary) are used as biologic reference samples. The calcium carbonates have usually two types of crystal structure, calcite and aragonite. Raman spectroscopy is used to distinguish the crystal structures. The Laser Raman spectroscopy are carried out using a NRS-2100 (JASCO CO.) with an Ar laser of 514.5 nm wave length. The sample excitation and Raman scatter collection was performed using a 100 X optical lens on the Raman microscope. Energy of about 40 mW is transferred to the sample surface. The Raman spectra were recorded from 120 to 1400cm^{-1} after accumulation of 4 single spectra of a collecting time of 30 s.

SEM-CL spectral analyses were performed using a Scanning Electron Microscope (SEM), JEOL 5410LV, equipped with a CL detector, Oxford Mono CL2, which comprises an integral 1200 grooves/mm grating monochromator attached to reflecting light guide with a retractable paraboloidal mirror. The operating conditions for measuring BSE (backscattered electron) images, CL images, and CL spectra were accelerating voltage: 15 kV, and 2.0 nA at room and liquid nitrogen temperature. CL spectra were recorded in the wavelength range of 300-800 nm, with 1 nm resolution by the photon counting method using a photomultiplier detector, Hamamatsu Photonics R2228.

Results and Discussions: By means of Raman spectra, calcium carbonates of the Skarn Deposit (Dalnegorsk, Russia) and the hydrothermal vein in an alkaline rock (Sand Fly Bay, Otago, New Zealand) are ascertained to be calcite and aragonite, respectively. Margin part of the Modern Pectinidae Pecten (Notovola) ablicans (SCHÖTER) is also identified being calcite and its muscle scar part is aragonite. Foraminifera Nuttallides (Paleocene/Eocene), and Brachiopoda (Jurassic, Hungary) are both made of calcite (Figs. 1a-c).

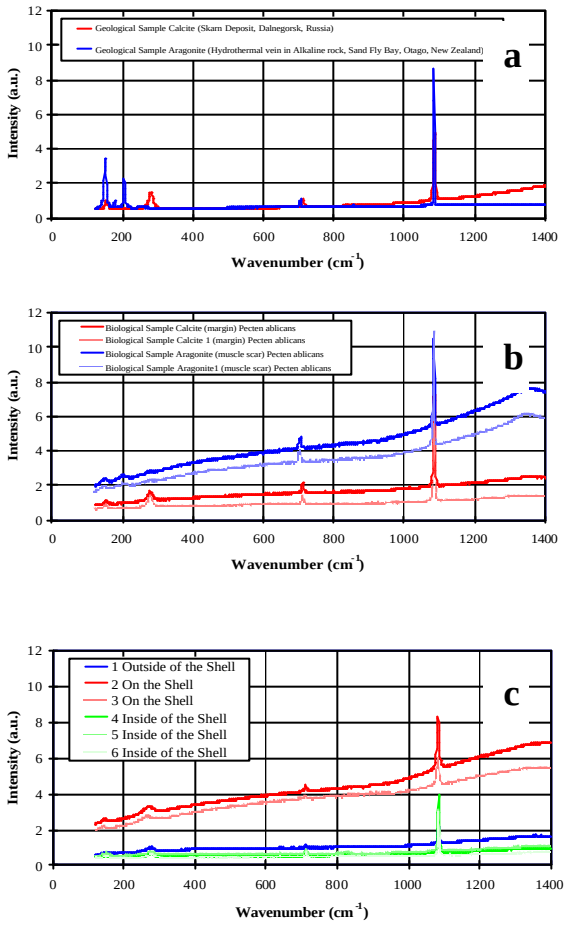

Figure 1. Raman spectra of calcium carbonates of the Skarn Deposit (Dalnegorsk, Russia) (a) and the hydrothermal vein (Sand Fly Bay, Otago, New Zealand) (a) Modern Pectinidae Pecten (Notovola) (b) ablicans (SCHÖTER) Brachiopoda (Jurassic, Hungary) (c).

Figure 2 shows CL spectra of geological samples at room temperature and liquid nitrogen temperature. Calcite of the Skarn Deposit (Dalnegorsk, Russia) shows large peak at 620nm, related to Mn^{2+}. Manganese is also detected by EDS compositional analysis. CL intensity is increased at liquid nitrogen temperature. This phenomenon is well known as temperature quenching effect. Aragonite of the hydrothermal vein in Alkaline rock (Sand Fly Bay, Otago, New Zealand) shows weak CL intensity, and its intensity is increased as a whole.

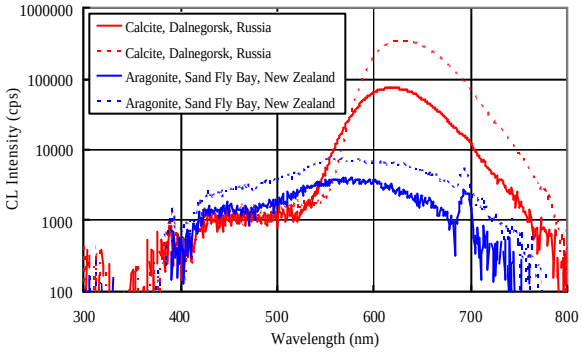

Figure 2. CL spectra of geological samples. Solid lines are room temperature. Dotted lines are liquid nitrogen temperature.

CL spectra of biological samples at room temperature and liquid nitrogen temperature. Calcite of the margin part of the Modern Pectinidae Pecten and the foraminifer Nuttallides (Paleocene/Eocene) shows relatively weak CL intensity. The peak at 620 nm is decreased at liquid nitrogen temperature in spite of increasing in 480 nm region. Aragonite of the muscle scar part shows weak CL intensity, and its intensity is increased as a whole. This tendency is the same as the geological aragonite (Fig. 3).

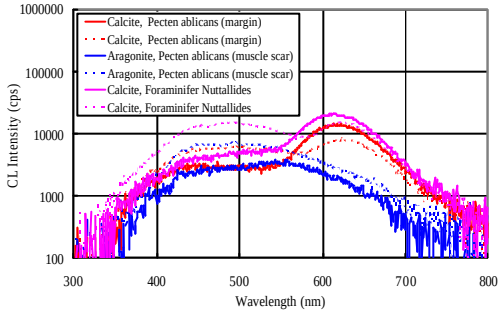

Figure 3. CL spectra of biological samples. Solid lines are room temperature. Dotted lines are liquid nitrogen temperature.

When we compare CL spectra between room temperature and liquid nitrogen temperature, CL intensities near 620nm and 480 nm of both biological and geological aragonites increased. CL intensity near 480nm of biological calcite increased, but CL intensity near 620 nm was decreasing. On the other hand, CL intensity near 480nm of geological calcite is constant, but CL intensity near 620 nm was increasing. There is possibility that this difference would make distinguish biological calcite from geological one.

CL spectra of the Brachiopoda (Jurassic, Hungary) show the same behavior under varied temperature as the biological calcite. As shown in Fig.1-c, backgrounds of raman spectra on the shell of the Brachiopoda are higher than those of outside and inside of the shell. There is a possibility that raman background is also an indicator of biosignature.

Consequently, we noted that these results on the water-related rocks can also aid to understand more about the astrobiological aspects of fluid-rock-atmosphere interaction in present and past of Mars. Moreover, these data might support an in-situ planetary cathodoluminescence spectroscopy of the robotic mission to Mars.

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