

CATHODOLUMINESCENCE AND ITS APPLICATION FOR BIOSIGNATURE ANALYSIS OF Mn-CONTAINING BIOGENIC MINERALS: A REVIEW J. Denson,¹ D.M. Ivey², D.W.G. Sears¹, A. Gucsik¹ and R. Vidéki³. ¹W.M. Keck Laboratory for Space Simulations, Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, ²Department of Biological Sciences, University of Arkansas, Fayetteville, AR 72701, USA; University of West Hungary, H-9400, Sopron, Bajcsy Zs. u. 4., Hungary (jdenson@uark.edu)

Introduction: Cathodoluminescence (CL) is a useful technique and has many applications in the geosciences. However the CL properties of biogenic minerals have not been extensively investigated, to date. This technique could provide a novel analytical methodology for differentiating biogenic vs abiogenic minerals, providing a new tool for both astrobiologists and biogeochemists alike. CL could also potentially be used for remote applications including the analysis of Martian minerals.

The basics of cathodoluminescence emission: To understand CL signal, it is useful to consider energy diagrams of the electromagnetic spectrum. According to Boggs et al. [1] noted that the energy difference between the top of the valence band (VB) and the bottom of the conduction band (CB) in minerals, which is equivalent to approximately 400 nm. Thus, even a small amount of energy from the electron beam causes electrons to enter the CB, from where they then fall back and move randomly through the crystal structure until they encounter a trap or recombination center. As electrons return to lower energy states via traps, they can produce photons with energies in the visible portion of the spectrum, or even in the near-infrared region. If they return directly from the CB to the VB, they emit photons in the UV region of the spectrum. It is important to note that minerals are insulators or wide-band gap materials, in which the band gap between conduction and valence bands is too large for simple thermal excitation to promote electrons from lower-energy states to the higher-energy states [1].

Figure 1 shows the hypothetical energy level diagrams of the energetical transitions in an ideal mineral structure. The relationship between energy and wavelength (nm) can be expressed as follows: energy (eV) = 1239.8 wavelength (nm) (Remond et al., 2000). The broad bands and narrow emission lines were converted from wavelength (nm) into energy (eV) using this simple equation. The y-axis in Fig. 1 indicates the energy differences of the recombination centers or traps. The near-ultraviolet (near UV) range is located in the upper part of the band gap between the conduction and valence bands in (Fig. 1). This indicates that higher energy (in eV) charge traps or recombination centers (broad bands between 200-400 nm) are plotted to the upper part of the band gap. The lower energy trap positions (bands between 400-800 nm) can be found in the center of the band gap or close to the valence band.

In general, CL is used in the Earth Sciences for the characterization of crystallization effects, identification of the microdeformations and 3-D mapping of trace element microdistribution in minerals. If biologically produced minerals differ in these features from those produced geochemically CL should provide a novel analytical tool.

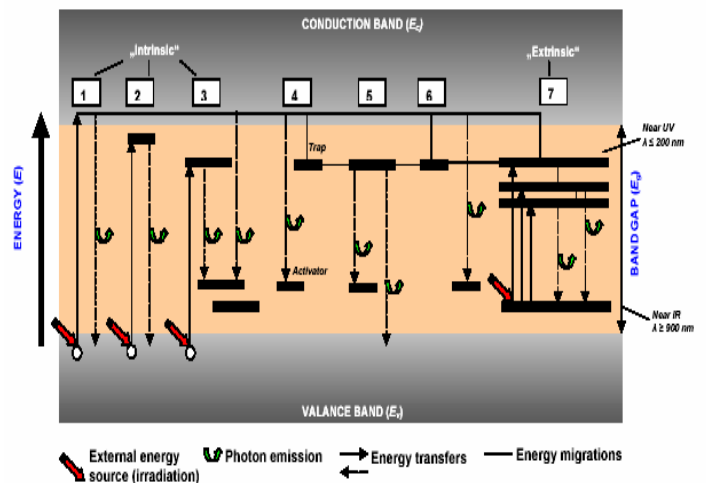


Figure 1. Hypothetical Energy Levels of CL Emission Centers [2].

Biogenic Minerals: It is well known and understood that a wide variety of geological processes are largely biologically driven, including the formation of minerals of biogenic origin. Biogenic minerals can be produced a number of distinct ways including intracellularly, within the cellular envelope, within a biofilm, or in bulk extracellularly. These syntheses can be both directly related to a biological process or as a secondary effect of that process, including simply nucleation involving the microbe itself. [3,4]. Many of the metabolic processes that result in mineral formation date to the earliest history of life and hence it has been proposed that by directly modifying their extracellular environment microorganisms could potentially gain an advantage in energy acquisition [3]. The formation of many of these minerals is directly related to the metabolic activities of the organisms, particularly oxidation and reduction reactions and can involve a wide variety of elements and their compounds including Fe, P, S, Ca, Mg and Mn. Biologically produced minerals have the potential to provide a wealth of knowledge about

the history of life on Earth and a valuable tool for searching for its presence elsewhere.

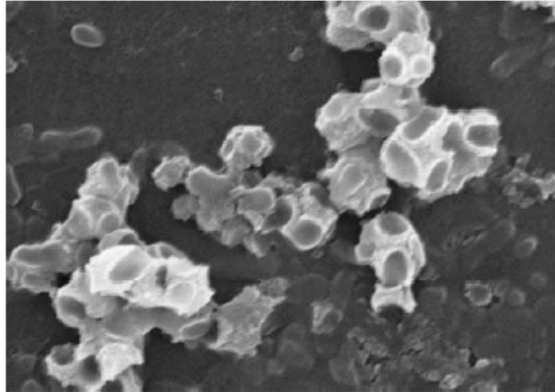


Figure 2. Scanning electron micrograph of Mn oxidizing Bacteria with Mn Containing exocellular secretions. [10]

Mn-containing Minerals: A large number of biogenic minerals have the potential to be analysed by CL. Manganese is an especially interesting target. It is an ideal mineral to test the efficacy of CL in distinguishing biogenic vs abiogenic, as a variety of manganese containing minerals of both forms are easily obtainable. Known biogenic Mn-containing minerals are produced by a wide variety of microorganisms ranging from Mn-oxides by various environmental isolates of *Pseudomonas sp.* (Fig. 2) to the hyperthermophilic archaea *Pyrobaculum* which has been reported to produce the Mn-carbonate rhodochrosite [11]. The utility of CL in acquiring good spectra from manganese is well documented. Some large scale terrestrial deposits of manganese ores have been attributed to a biological origin and the production of the manganese containing minerals birnessite and todorokite by sub-surface microbes has been recently documented [6,7,8]. CL could also be applied to a better understanding of the early history of life on Earth though the analysis of purported biogenic manganese features, such as ancient metallogenium-like fossils, stromatolite like structures, or other diverse mineral deposits of a possible biological origin. It is intriguing mineralogical target from a planetary science perspective in that manganese oxides are known to be abundant on Mars. Desert varnish which consists of Fe and Mn oxides thought to be produced terrestrially through a combination of microbial action and weathering have also been viewed extensively on Mars (Fig. 3). Minerals of unknown origin within meteoritic specimens could also provide an additional application [4,8].

Ongoing Research: CL analysis of a variety of biogenically produced manganese containing minerals is currently underway. These include both Mn-oxides as well as Mn-reduction linked minerals such as the previously mentioned carbonate containing Mn rhodochrosite. Experiments utilizing laboratory based cultures of a variety of microorganisms producing known Mn containing minerals will be utilized. Known abiogenic minerals of similar composition will be obtained and analysed when available, as well as a variety of naturally occurring Mn minerals. The comprehensive comparison of these diverse samples will serve as a pilot study and help to determine the utility of CL for differentiating biogenic mineral signatures from their geologically formed counterparts. If successful this could provide a basis for utilizing CL analysis for both terrestrial biogeochemical applications as well as in the planetary sciences.



Figure 3. Image taken by Spirit Sol (601) illustrating desert varnish like features on Mars. (<http://marsrovers.jpl.nasa.gov>)

Acknowledgements: This program is funded by the University of Arkansas Center for Space and Planetary Sciences.

References: [1] S. Boggs S. *et al* (2001) *Meteoritics Planet. Sci.* 36, 783-797. [2] Nasadala L. *et al* (2002) *Chem. Geol.*, 191, 121-140. [3] Fortin D. (2004) *Science*, 303, (1618-1619). [4] Ehrlich H. L. (1999) *Geomicro. J.*, 16, 135-153 [5] Stein L.Y. and Neelson K.H.. (1999) Manganese, Metallogenium, and Martian Microfossils. Paper presented at the Fifth International Conference on Mars.6133.pdf [6] Boston P.J. *et al.* (2001) *Astrobiology*, 1, 25-55. [7] Polgári M. (2005) *Clay Science*, 19, 36-42. [8] McKay D. S. *et al.* (1996) *Science*, 273, 924-930. [9] Northup D. E. *et al* (2001) *Geomicro J.*, 18, 199-222. [10] Fernand S.O. (2005) *Biometals* 18:483-492. [11] Kashefi K (2000) *Appl. Environ. Micro.* 66:1050-56.