

**Cathodoluminescence imaging and spectral analyses of phosphates in the Martian meteorites: A review.** A. Gucsik<sup>1\*</sup> ([gucsik@mpch-mainz.mpg.de](mailto:gucsik@mpch-mainz.mpg.de)), W.J. Protheroe Jr.<sup>2</sup>, J.A.R. Stirling<sup>3</sup>, K. Ninagawa<sup>4</sup>, H. Nishido<sup>5</sup>, T. Okumura<sup>5</sup>, N. Matsuda<sup>5</sup>, Sz. Bérczi<sup>6</sup>, Sz. Nagy<sup>6</sup>, A. Kereszturi<sup>6</sup> and H. Hargitai<sup>6</sup>; <sup>1</sup>Max Planck Institute for Chemistry, Department of Geochemistry, Becherweg 27, D-55128, Mainz, Germany; <sup>2</sup>AOL Inc., 8711 Beau Monde, Houston, TX 77099-1107, USA; <sup>3</sup>Geological Survey of Canada, 601 Booth St., Ottawa, ONT, K1A 0E8, Canada; <sup>4</sup>Department of Applied Physics, Okayama University of Science, 1-1 Ridai-cho, Okayama, 700-0005, Japan; <sup>5</sup>Research Institute of Natural Sciences, Okayama University of Science, 1-1 Ridai-cho, Okayama, 700-0005, Japan; <sup>6</sup>Eötvös Lóránd University of Budapest, H-1117 Budapest, Pázmány Péter sétány 1/c, Hungary.

**Introduction:** Cathodoluminescence (CL) is emission of visible light stimulated by energetic electrons. In the previous studies of CL properties of meteorites, it was demonstrated (compared to the standard optical microscopy) that its detection provides for a more complete investigation of specific minerals [1; and references therein]. The main purpose of the CL studies reported here is to provide an overview of the detailed mineralogical information the method provides on phosphates in Martian meteorites.

#### **Samples and Experimental Procedure:**

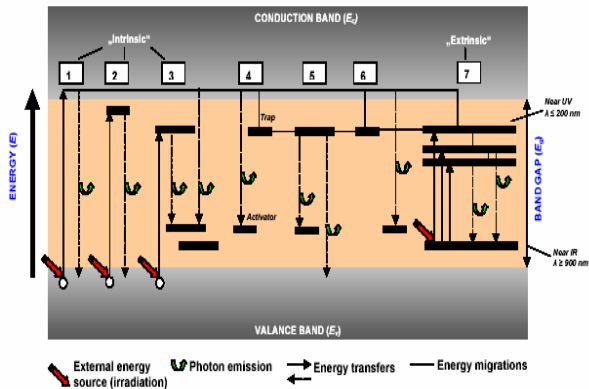
*Y000593 nakhlite:* We studied two polished thin sections of the Y000593 nakhlite Martian meteorite supplied from the National Institute of Polar Research (NIPR, Tokyo, Japan). SEM-CL imaging and CL spectral analyses were performed on the selected thin sections coated with a 20-nm thin film of carbon in order to avoid charge build-up. SEM-CL images were collected 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 parabolic mirror. The operating conditions for all SEM-CL investigation as well as SEM and backscattered electron (BSE) microscopy were accelerating voltage: 15 kV, and 3.0-5.0 nA at room 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 [2].

*ALH84001 sample N fragments (#3734, #3738, and #3739):* CL spectra were collected with a micro-computer-based solid state multichannel analyzer, integrated with a linear CCD-array silicon detector from 200-1100 nm, interfaced to the optical chain of a MBX Cameca microprobe. The separated grains were also analyzed with a SX50 microprobe at 20kV, 10 nA and 10 second peak counting time. The small size and limited stability of the minerals do not allow for longer counting times and higher beam currents. The sample had already been damaged by previous use of high beam currents and exposure times [3].

**The basics of cathodoluminescence emission:** To understand the CL signal, it is useful to consider energy diagrams of the electromagnetic spectrum. According to Boggs et al. [4] the energy difference between the top of the valence band (VB) and the bottom of the conduction band (CB) in minerals corresponds 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 region 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). 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) plot in 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.

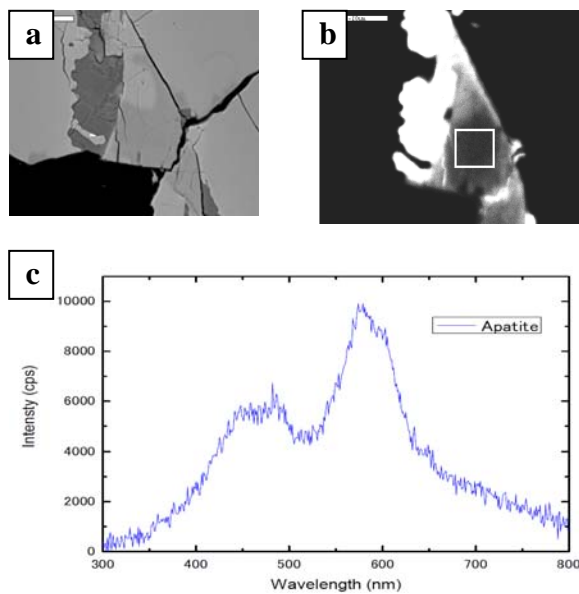
In general, CL is used in the Earth Sciences for the characterization of crystallization effects, identification of the microdeformations and 3-D mapping of trace elements in minerals.



**Figure 1.** Idealized energy levels of CL emission centers [1, and personal communication with Lutz Nasdala, 2003].

### Results and Discussion:

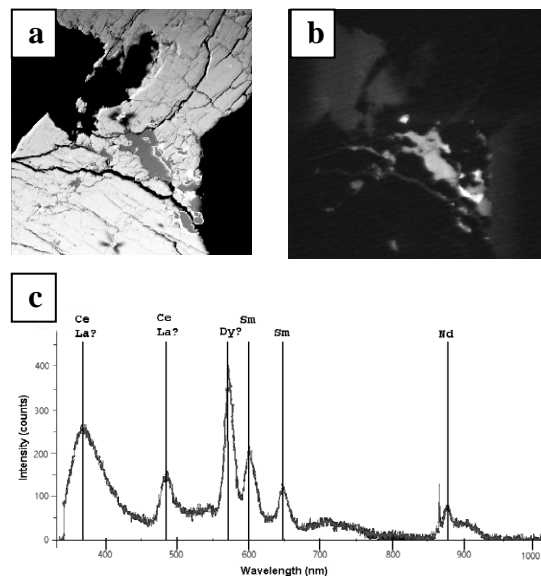
**Y000593 nakhlite:** Apatite (Ap) was found in the mesostasis of this nakhlite meteorite, which occurs in veins between mostly clinopyroxene (Cpx) and plagioclase (Pl) (Fig. 2a). A detailed mineralogical description of the Y-000593 nakhlite can be found in Imae et al [5]. In their petrological studies the apatite content (0.21 wt%) was determined by EPMA. This mineral appears as yellow CL color in the Luminoscope images and CL-bright areas in the SEM-CL images (Figs. 2b,c). CL spectral analysis and chemical composition data of apatite are shown in Figure 2c [2]. The results indicate that apatite is chloroapatite, which is an anhydrous phosphate containing unfamiliar anions F, Cl, O, OH, as well as cations of medium and large size: Mg, Cu, Zn, and Ca, Na, K, Ba, Pb [6].



**Figure 2.** BSE (a), CL (b) images and CL spectrum (c) of Y000593 nakhlite sample. The width of the

images is approximately 500  $\mu\text{m}$  [2].

**ALH84001 sample N fragments (#3734, #3738, and #3739):** The CL spectra results are very preliminary and the peaks have been labeled as indicated by the probe analysis and CL spectral analysis of standards at the Geological Survey of Canada. The results suggest the presence of the Ca-phosphates, which are often called whitlockite, which, however, are better described as  $\beta$ -Ca-phosphates as discussed by E. Dowty. It is important to note that the calculated formula closely matches that suggested by E. Dowty (Figs. 3a,b,c) [3,7].



**Figure 3.** BSE (a), CL (b) images and CL spectrum (c) of ALH84001 (N fragments) sample. The width of the images is approximately 500  $\mu\text{m}$  [3].

**Conclusions:** CL spectroscopy combined with SEM-CL imaging is a potentially powerful technique in the study of phosphates. As a consequence the CL technique can play a key role in in-situ investigations of records of atmospheric-fluid-rock interactions on Mars, such as formation of sulfates, carbonates, and phosphates.

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**References:** [1] Marshall D.J. (1988) *Cathodoluminescence of geological materials*. Unwin Hyman, Boston, 146 pp. [2] Matsuda N., Gucsik A., Nishido H., Ninagawa K., Okumura T. and Kayama M. (2007) *LPS XXXVIII* Abstract #1061. [3] Protheroe W. J., Jr. and Stirling J. A. R. (2000) *LPS XXXI*, Abstract #2021. [4] Boggs S. et al (2001) *Meteoritics Planet. Sci.* 36, 783-797. [5] Imae N. et al. (2005) *Meteoritics Planet. Sci.*, 40, 1581-1598. [6] Barbarand J. and Pagel M. (2001) *Amer. Min.* 86, 473-484. [7] Dowty et al. (1977) *EPSL* 35, 347-351.