CATHODOLUMINESCENCE AND ITS APPLICATION IN THE PLANETARY SCIENCES: A REVIEW.

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Basics of the cathodoluminescence: When an energetic electron beam impinges on the solid surface its energy generates a number of physical processes including emission of secondary electrons (SE), backscattering of electrons (BSE), electron absorption (”sample current”), characteristic X-ray, and cathodoluminescence (CL) emission. Much of the total incident beam energy is transformed into heat resulting nonradiative emissions such as phonons. In general, the penetration depth of electrons according to the energy of the electrons (10-20 keV) is approximately in the range of 2-8 µm. Cathodoluminescence is a visible radiation in the range of wavelengths between 400 and 700 nm, corresponding to energies between 1.77 and 3.10 electron volts. The relationship between energy and wavelength can be expressed as follows: energy in electron volts (eV) = 1239.8/(wavelength in nm) [1,2]. It was demonstrated by Boggs et al. [3] and Gucsik et al. [4] that the SEM-CL imaging of the shock-deformed minerals (e.g., quartz) provides better resolution (down to 1 µm or less) than does the petrographic microscope and is faster and easier to use than the Transmission Electron Microscope (TEM).

Lunar samples: Sippel and Spencer [5] observed that the shock metamorphism caused peak shifts from green peak toward the red peak, peak broadening and decrease of luminescence intensity than in the undamaged counterpart in the CL spectra of shock-metamorphosed lunar feldspars. They noted that the distortions or disorder in the crystal field results in crystal field perturbations and these local variations occur broadened distribution of excited state energies. Recently, CL spectral measurements were performed on natural and experimentally shocked oligoclases (An19.7 single crystal shocked between 10.5 GPa and 45 GPa) and plagioclases from the equilibrated ordinary chondrites (Dar al Gani, Tenham) [6]. They observed disappearance of the crystal field sensitive Mn^{2+} and Fe^{3+}-related peaks resulting from breakdown of the crystal structure (i.e., occurrence of diaplectic glass) at around 35 GPa. Mn^{2+} and Fe^{3+}-related peaks in the green luminescing lunar plagioclases were also identified by Götze et al. [7]. More recently, changes in CL spectra of the shocked plagioclase (including peak broadening, peak disappearances or shifts, decreases in peak intensities are related to not only a local variations in the crystal field strength such as distance changes between coordinated $–O^-$ and Mn^{2+} activator ion, but also changes (lacking or absence of recombination centers) of distance between electron traps in band gap between the conduction and valance bands resulting non-radiative emission at the amorphous-filled planar microdeformations [8].

Martian samples-an astrobiological aspect: The concentration of MnO in typical Martian soil is estimated at approximately 0.5% (wt). Thus it may be reasonable to suspect that carbonates formed in a sedimentary basin similar to those on Earth may also incorporate Mn^{2+} into their crystal stucture. In studying rocks from terrestrial sedimentary basins, CL often illuminates the internal structures and outlines of fossils that may be invisible in reflected light. Also, studies of CL in modern (recently living) coralline red algae, foraminifera, and mollusks indicate the carbonate minerals in their bodies can also cathodoluminescence due to incorporation of Mn^{2+}. Therefore, a CL image may be detecting fossil structures or remnants of biomineralization (shells or shell fragments) that would be missed missed in reflected light. On the other hand, Martian carbonates exhibiting CL behavior would be unexpected because of the high concentration of Fe in the surface chemistry of Mars (trace amounts of Fe in the carbonate crystal structure acts as a CL quencher). If it could be shown that bio-mineralization processes can be effective fractionation method for Fe, any observed carbonate CL would imply a formation process that selectively partioned out Fe from the sorrounding matrix, and hence, the observation of CL in Martian carbonates could be possible indicators of biological activity. Often, structural defects can also induce luminescence. CL can also determine crystal lattice site and charge of the state of the detected elements. It allows the detection of chemical zonations that are not often detected by electron probe microanalysis or using back-scattered electron imaging or conventional optical microscopy. It may be possible to identify different generations of mineral growth as well as embedded fossils. Moreover, in case of the in situ instruments, the Martian conditions provide an adequate background to obtain high-resolution CL images and spectral features from minerals, because of the natural-induced electron excitation (i.e., relatively strong sunlight energy because of the thin atmosphere) and permanently cold environment.

Shock-metamorphosed quartz: Owen and Anders [9], in a pioneering study, have showed that- whereas quartz from extrusive igneous sources shows pale blue CL -quartz from intrusive igneous and high-grade metamorphic rocks show darker purple-blue CL, quartz from low-grade metamorphic rocks luminesces reddish-brown, but shocked quartz from the Cretaceous-Tertiary (K/T) boundary shows CL colors similar to low-grade metamorphic quartz. These authors were able to demonstrate that shocked quartz from the K-T boundary is not derived from volcanic sources. At the time, this was an important contribution to the study of the then controversial, volcanic or impact events marking the K-T boundary. Seyedolali et al. [10] reported on CL studies of a shocked quartz grain from impact structures and stratigraphic units (e.g., the Jurassic-Cretaceous boundary). They studied patterns of variable-intensity CL including e.g. zoning, healed fractures, complex fractures, complex shears and planar microdeformations from a variety of sources rocks by using SEM-CL fabric-analysis technique. Ramseyer et al. [11] reported CL luminescence changes of quartz and feldspar from the granitic rocks of the Siljan impact structure, Sweden and related their findings to describe complicated alteration of the above mentioned minerals during post-impact effects.

Shock-induced microdeformations: Planar deformation features (PDFs), which are well-known shock metamorphic indicators in the other rock forming minerals, appear as dark, nonluminescent lines in the CL images [3]. The nonluminescent nature of PDFs could be explained due to several causes. PDFs are filled by amorphous (glassy) material, which shows absence of traps (no photon emission), may not contain suitable activators (recombination centers), and traps are closely spaced (phonon emission) [3]. Reidite as a scheelite-type high pressure polymorph of zircon and zircon remnants at high shock pressures (i.e. 40 GPa) were also identified by high-resolution CL imaging by Gucsik et al. [12,13]

Impact-derived glasses: The first cathodoluminescence data on Lybian Desert Glass by Piacenza [14] were interpreted to show evidence for a granular structure and the presence of lechatelierite. Microphotographs were used by Cipriani et al. [15] in the determination of a possible extraterrestrial body signature in LDG. They concluded that the luminescence of Libyan Desert Glass is intrinsic, not induced by particle damage as in the case of amorphous silica. More recently, in a study of Gucsik et al., most samples show an inverse relationship between backscaterred electron (BSE) brightness and CL intensities, which seems to be related to the presence of activators, such as Al, Li, Na, Fe. The Muong Nong-type tektite has a homogeneous appearance in both BSE and CL images, indicating that it was subjected to a high temperature; the Aouelloul impact glass preserves remnants of a texture in both BSE and CL images, showing a relatively low formation temperature, and the Libyan Desert Glass preserves a flow texture that is only visible in the CL images, indicating a medium temperature.

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