

CATHODOLUMINESCENCE MICROSCOPY AND SPECTROSCOPY OF SHOCKED ZIRCON FROM THE VREDEFORT IMPACT STRUCTURE, SOUTH AFRICA. A. Gucsik¹, ¹Max Planck Institute for Chemistry, Dept. of Geochemistry, Joh.-J.-Becherweg 27, D-55128, Mainz, Germany (E-mail: gucsik@mpch-mainz.mpg.de)

Introduction: Zircon is a highly refractory and weathering-resistant mineral that has proven useful as an indicator of shock metamorphism in the study of impact structures and formations (e.g., [1-6]). Zircon has advantages compared to quartz or other shock-metamorphosed rock-forming minerals that have been widely used as impact indicators, but are far less refractory than zircon. The purpose of this investigation is to further investigate the capability of the SEM-CL technique to document shock deformation and to determine whether specific CL effects in zircon can be utilized to determine particular shock pressure stages.

Samples and Experimental Procedure: The Vredefort (South Africa) samples were first examined under a petrographic microscope. Digital optical images were stored without further computer enhancement. The samples were then examined with an Oxford Mono-CL system attached to a JEOL JSM 6400 scanning electron microscope (SEM). Operating conditions for all SEM-CL investigations (at Natural History Museum of Vienna, Austria) were 15 kV accelerating voltage and 1.2 nA beam current; backscattered-electron (BSE) and cathodoluminescence (CL) images were obtained. The BSE and CL images were captured digitally. CL spectra were recorded in the wavelength range of 200-800 nm, with 1 nm resolution. The grating of the monochromator was 1200 lines/mm.

Results

Backscattered-electron (BSE) and cathodoluminescence (CL) image observations: Planar Fractures (PFs) associated with the irregular fracture system are observable in an optical micrograph, BSE (Fig. 1a) and CL images (Fig. 1b) of zircon grains from the Vredefort impact structures (South Africa). In general, a high density of micro-lamellar feature system occurred in two orientations can be discernible in BSE and CL images showing dark lines (Figs. 1a and b). The widths of individual microstructures vary from 3 to 10 μm . This observation indicates the presence of Planar Deformation Features (PDFs) corresponding to relatively high shock pressure in between 20-30 GPa [6]. Some of the grains show an inverse relationship between BSE and CL brightness.

Cathodoluminescence spectrometry: Five Vredefort zircon samples were selected for the CL

spectroscopical analysis. Compared to CL properties of Ries samples, zircon grains from the Vredefort crater exhibit similar CL spectral features as follows. Narrow emission peaks centered at 314, 406, 475-484, 580, and 628 nm with relatively high peak intensities are superimposed on a broad band. The doublet peak at 475-484 dominates CL spectra of all samples (Fig. 2).

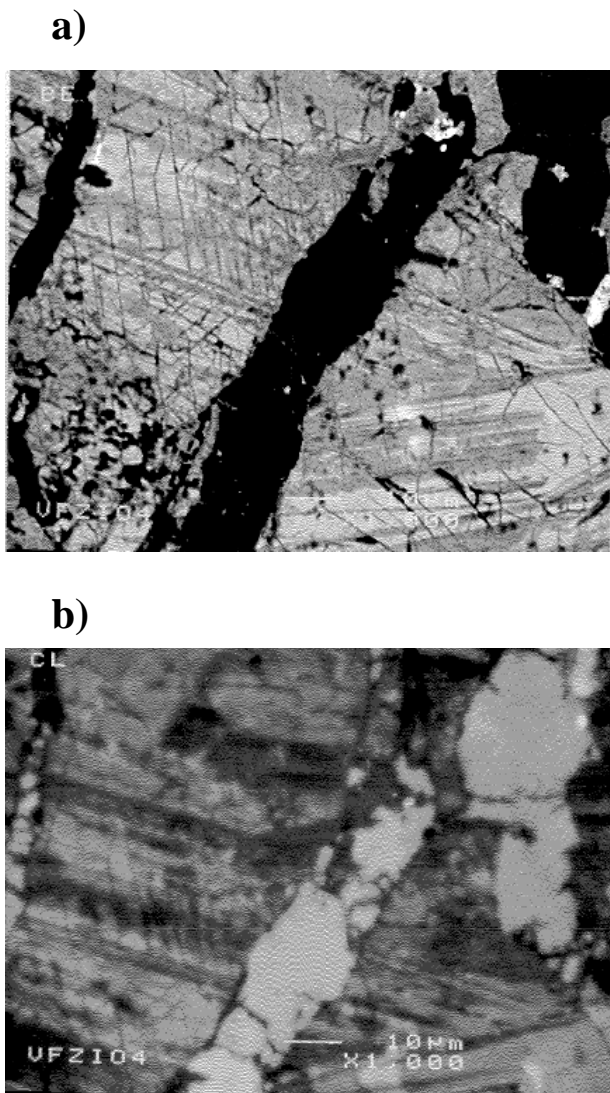


Figure 1. BSE (a) and CL (b) images of Planar Deformation Features (PDFs).

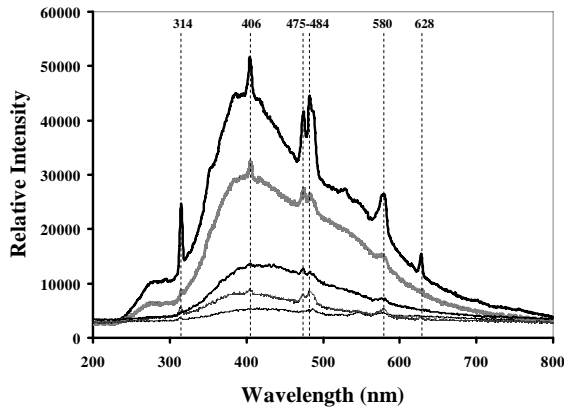


Figure 2. Cathodoluminescence spectra of the shocked Vredefort zircon samples.

Discussion: The inverse relationship between BSE and CL brightness might be explained as follows. According to Remond et al. [7], backscattered electrons (BSE) are primary beam electrons that leave the specimen as a result of a single large-angle scattering event or multiple small angle scattering processes. The fraction of primary beam electrons, which leave the specimen, $\eta = I_{\text{BSE}}/I_{\text{B}}$, increases with the mean atomic number of the specimen, where I_{B} is the beam current entering the sample and I_{BSE} is the BSE current leaving the specimen. This dependence of backscattered-electron yield on mean atomic number allows for the compositional imaging of flat surfaces with submicrometer resolution, which provides better spatial resolution and microcompositional information than standard optical methods.

The BSE contrast is sensitive to changes of average atomic number, i.e., higher Z causes bright BSE yield and lower Z leads to the dark BSE brightness. In the case of natural zircon, the inverse relationship between BSE and CL brightness might be caused by high concentrations of Hf, Y, Yb, U, and Th, corresponding to high BSE intensities. The CL images of naturally shock-deformed zircon crystals from the Ries and Vredefort impact structures also exhibit an inverse relationship between BSE and CL brightness, which indicates that the spatial distribution or abundance of the above-mentioned elements causes low (dark CL) and high (bright CL) intensities.

The luminescence properties are mostly the result of luminescence-activating ions, such as transition metals, rare-earth elements, or actinides. According to Remond et al. [7] the trivalent rare-earth element (REE) radiative recombination centers are characterized by sharp visible and near-infrared (NIR) emission peaks in the spectrum. The luminescence results from electronic transitions between the partially filled 4f shells, which are well shielded (screened)

from the lattice by outer shell electrons. Broad intrinsic emission generally results from self-trapped excitons (STE), which are highly localised excitons trapped by their own self-induced lattice distortion. Self-trapped excitons are generally produced in crystals with a deformable lattice (e.g., SiO_2), which are characterised by strong electron-phonon coupling.

The emission energy of the STE is usually much lower than the band gap of the material due to energy lost by phonon emission during the electronic transition. In the present study, CL luminescence centers are dominated by Dy^{3+} indicated by the relatively strongest peaks at 478-491 and 573-586 nm in the visible light range. According to Blanc et al. [8], a weak emission line at around 630 nm might be assigned to Gd^{3+} . The weak bands at 406 and 548 nm might be related to Tb^{3+} [8].

Summary and Conclusions: For all shocked samples from Vredefort impact crater, an inverse relationship between the brightness of the backscattered electron (BSE) signal and the corresponding cathodoluminescence intensity of the zonation patterns was observed. The CL spectra of unshocked and experimentally shock-deformed specimens and naturally shock-metamorphosed zircon samples are characterized by narrow emission lines and broad bands in the region of visible light and in the near-ultraviolet range. The emission lines result from rare earth element activators and the broad bands might be associated with lattice defects.

Consequently, the combination of BSE and CL imaging and CL spectroscopy is a potentially useful tool that can be used to characterize the shock stage of zircons from impactites. Our results also give new insight into the structural changes that occur in zircons during shock metamorphism, and the pressures associated with these changes.

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