

# Cathodoluminescence microcharacterization of ballen silica in impactites

T. Okumura<sup>a</sup>, A. Gucsik<sup>b</sup>, H. Nishido<sup>c</sup>, K. Ninagawa<sup>a</sup>, and S. Toyoda<sup>a</sup>,

<sup>a</sup>*Department of Applied Physics, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama 700-0005, Japan*

<sup>b</sup>*Max Planck Institute for Chemistry, P. O. Box 3060, D-55020 Mainz, Germany*

<sup>c</sup>*Research Institute of Natural Sciences, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama 700-0005, Japan*

**Abstract.** The ballen silica shows fairly weak (faint) CL with homogeneous feature in its grain exhibiting almost same spectral pattern with two broad band peaks at around 390 and 650 nm, which might be assigned to self-trapped excitons (STE) or an intrinsic and nonbridging oxygen hole centers (NBOHC), respectively, recognized in amorphous and crystalline silica. In addition, ballen silica from Lappajärvi crater shows bright and heterogeneous CL with a broad band centered at around 410 nm, presumably attributed to  $[\text{AlO}_4/\text{M}]^0$  centers or self-trapped excitons (STE). Micro-Raman and micro-XRD analyses show that fairly homogeneous CL part is  $\alpha$ -quartz and heterogeneous CL part is composed of  $\alpha$ -cristobalite and  $\alpha$ -quartz. These indicate that ballen silica could be formed in the quenching process from relatively high temperature.

**Keywords:** ballen silica,  $\alpha$ -quartz,  $\alpha$ -cristobalite, shock metamorphism, terrestrial impact structures.

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## INTRODUCTION

The physical state of silica is a very useful index for shock-metamorphism [1]. In this study, we used cathodoluminescence (CL) microscopy and spectroscopy to characterize ballen silica structure. "Ballen silica", characterized by bubble-wall texture under a petrological microscope, has been observed in impactites [2-4]. Bischoff and Stöffler [3] found that ballen silica represents recrystallized diaplectic glass that had undergone the transition to cristobalite and then to  $\alpha$ -quartz.

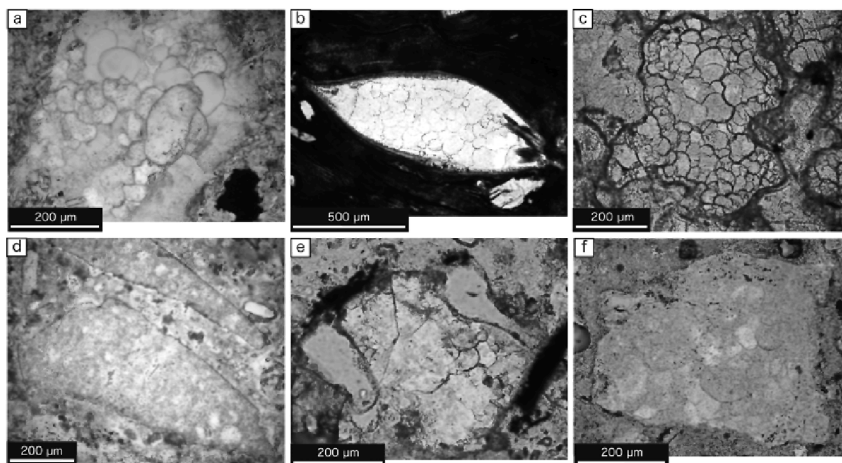
## SAMPLES AND EXPERIMENTAL PROCEDURE

The ballen silica samples were obtained from six well-known terrestrial impact craters; Dellen, Mien (both in Sweden), Lappajärvi (Finland), Rochechouart (France), Terny (Ukraine), and Ries (Germany) and investigated by standard optical microscopy. Optical microscopic properties of the selected ballen silica samples are shown in Figure 1. High-resolution CL images and spectra were acquired using a Jeol JSM-5410LV scanning electron microscope (SEM) equipped with an Oxford Instruments MonoCL2 grating-type monochromator, SEM-CL system at Okayama University of Science. The CL emission was collected using a retractable parabolic aluminum mirror positioned directly above the

sample and its intensity is measured using a Hamamatsu R2228 multi-alkali photomultiplier with a wavelength range of 300-900 nm. The system configuration has been described in Okumura et al [5]. Beam current for CL imaging and CL spectroscopy in this study was set 1.5 nA at room temperature. CL images were collected in the panchromatic mode. To prevent the change in CL emission during SEM operation, the adjustment of CL measurement was carried out with a non-irradiated sample. CL spectra were recorded in the wavelength range of 300-800 nm with 1 nm spectral resolution and a dwell time of 1 second per step by photon counting. The total system response is a smoothly varying function of wavelength between 300 and 800 nm, and the features have Wood anomaly at  $\sim 450$  and  $\sim 720$  nm [6]. Spectra were collected over the wavelength range from 350 to 750 nm where the CL intensity was sufficient to ensure that uncertainties in the low intensity quartz CL were not magnified by the instrument response corrections. All spectra were corrected for monochromator dispersion and total instrument response.

Raman measurements were performed on a JASCO NRS-2100 laser Raman spectrometer system equipped with an integrated confocal microscope at Kyoto University. Spectra were excited with the 514.5 nm line of an argon ion laser with 400 mW power. Spectra were recorded in the frequency range from 100 to 800  $\text{cm}^{-1}$  with a 60 s acquisition time.

X-ray diffraction (XRD) measurement was performed by using a Rigaku RINT-2500V micro beam X-ray diffractometer PSpC-MDG with a total diffraction collimator of 30  $\mu\text{m}$  in diameter at 40 kV and 200 mA at the Okayama University of Science.

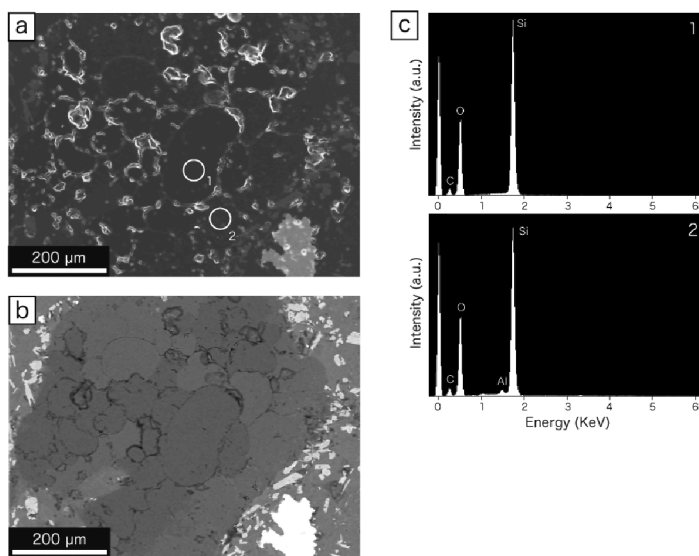


**FIGURE 1.** Microphotographs of ballen silica from various impactites. (a) ballen in impact melt rock from Lappajarvi, Finland. (b) ballen in suevite from Dellen, Sweden. (c) ballen in impact melt rock from Mien, Sweden. (d) ballen in impact melt rock from Rochechouart, France. (e) ballen in impact metamorphosed granite from Ries, Germany. (f) ballen in impact melt rock from Terny, Ukraine.

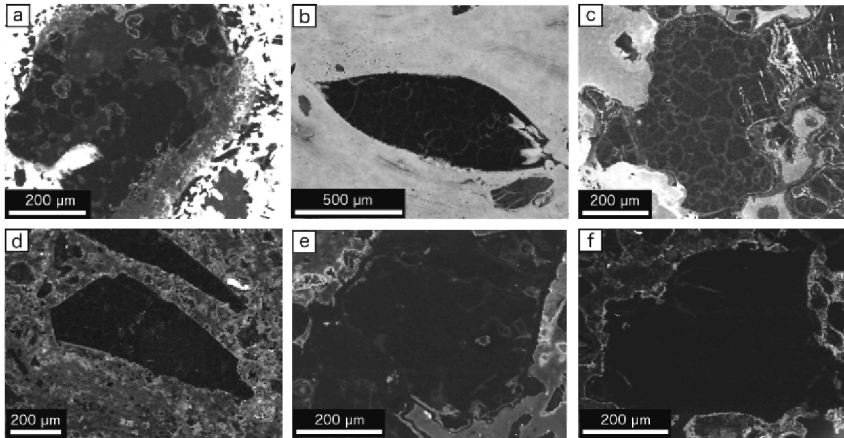
## RESULTS

### Scanning Electron and Backscattered Electron (SEM) and Cathodoluminescence (CL) Microscopic Observations

A representative sample from the Lappajarvi impact crater was selected to the SEM study. The Secondary Electron (SE) image shows that individual ballen are homogeneous in composition (Fig. 2a). However, Backscattered Electron (BSE) exhibits a shade of gray (Fig. 2b). The bright area contains aluminum-rich shown by energy-dispersive X-ray (EDX) microanalysis (Fig. 2c). In general, the ballen silica shows fairly weak CL with homogeneous feature in all ballen samples (Fig. 3). In addition, ballen from Lappajarvi, Finland shows bright and heterogeneous CL (Fig. 3a).



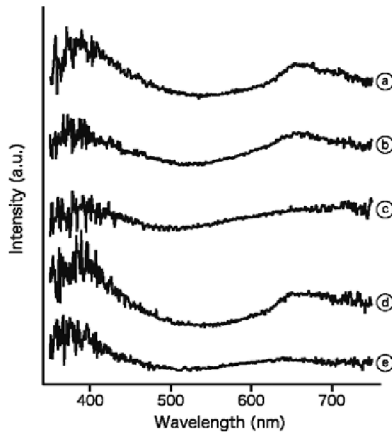
**FIGURE 2.** Secondary electron (a) and backscattered electron (b) images of ballen silica from Lappajarvi, Finland. Energy dispersive X-ray (EDX) spectra of area 1 and 2 in SE image (c).



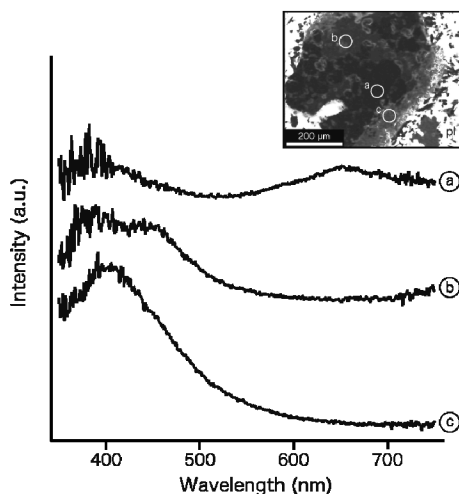
**FIGURE 3.** CL images of ballen silica from various impactites. (a) ballen in impact melt rock from Lappajärvi, Finland. (b) ballen in suevite from Dellen, Sweden. (c) ballen in impact melt rock from Mien, Sweden. (d) ballen in impact melt rock from Rochechouart, France. (e) ballen in impact metamorphosed granite from Ries, Germany. (f) ballen in impact melt rock from Terny, Ukraine.

### CL Spectral Analysis

CL spectra of ballen in all samples exhibit almost same spectral pattern with two broad peaks at around 395 and 650 nm (Fig. 4). On the other hand, bright CL areas of ballen from Lappajärvi, Finland have a broad band centered at around 410 nm and two peaks centered at around 395 and 650 nm (Fig. 5).



**FIGURE 4.** CL spectra of ballen silica from various impactites. (a) ballen in suevite from Dellen, Sweden. (b) ballen in impact melt rock from Mien, Sweden. (c) ballen in impact melt rock from Rochechouart, France. (d) ballen in impact metamorphosed granite from Ries, Germany. (e) ballen in impact melt rock from Terny, Ukraine.



**FIGURE 5.** CL spectra of ballen silica in impact melt rock from Lappäjarvi, Finland. Each spectrum was obtained at area 1-3 in SEM-CL image included. pl: plagioclase

### Raman Spectroscopy and XRD Analysis

Raman spectra from Lappäjarvi, Finland are shown in Figure 6. Raman spectra of  $\alpha$ -quartz and  $\alpha$ -cristobalite have detected. Dark CL area shows several peaks at 124, 201, 260, 351, 393, 462 and 694  $\text{cm}^{-1}$  (Fig. 6a). Their peaks are for typical  $\alpha$ -quartz. Raman spectra of  $\alpha$ -cristobalite and  $\alpha$ -quartz are exhibited in bright CL area (Fig. 6b). The brightest CL of ballen shows four peaks at 111, 227, 414 and 780  $\text{cm}^{-1}$  for  $\alpha$ -cristobalite (Fig. 6c) [4]. In addition, we confirmed the existence of  $\alpha$ -quartz and  $\alpha$ -cristobalite in bright CL area by micro-XRD analysis (Fig. 7).

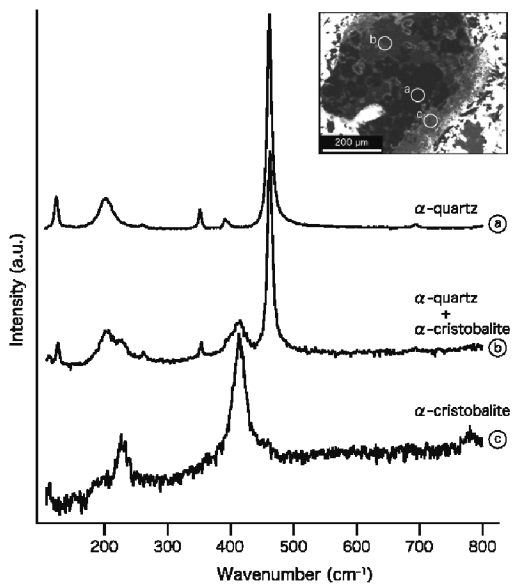


FIGURE 6. Micro-Raman spectra of ballen silica in impact melt rock from Lappajarvi, Finland. Each spectrum was obtained at area 1-3 in SEM-CL image included.

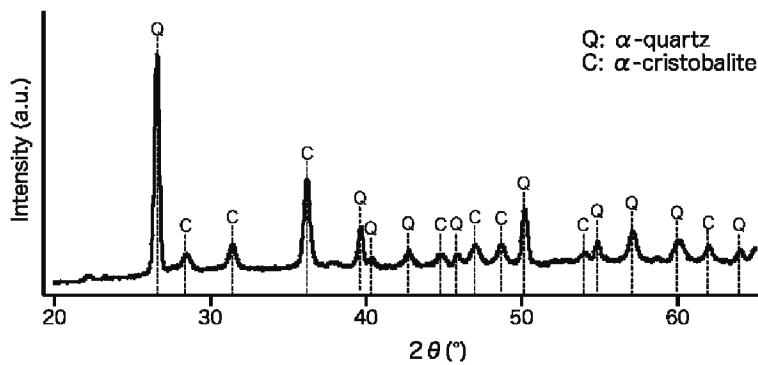


FIGURE 7. XRD pattern of ballen silica in impact melt rock from Lappajarvi, Finland.

## DISCUSSION

Two CL spectral peaks at around 395 and 650 nm obtained in all ballen quartz are assigned to self-trapped excitons (STE) or intrinsic defects and nonbridging oxygen hole centers (NBOHC), respectively [7,8]. In ballen silica in impact melt rock from Lappäjarvi, Finland, the existence of Al in  $\alpha$ -cristobalite exhibited bright CL was confirmed by EDX analysis. The bright CL emission of  $\alpha$ -cristobalite is presumably attributed to  $[\text{AlO}_4/\text{M}^+]^0$  centers (M:  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) or STE localized to  $[\text{AlO}_4/\text{M}^+]^0$  centers [6,9]. The fact probably indicate that  $[\text{AlO}_4/\text{M}^+]^0$  centers were created by migration of monovalent cations (e.g.,  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) associated with exchanged aluminum in the tetrahedral by shocked metamorphism. Therefore, ballen silica could be formed in the quenching process from relatively high temperature.

Consequently, CL microscopy and spectroscopy are an easy and powerful technique for identifying silica polymorphs in ballen, and CL investigation provides a new knowledge due to clarify the formation mechanism of ballen silica.

## ACKNOWLEDGEMENTS

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