

Annealing and radiation effects on cathodoluminescence of zircon

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Cathodoluminescence (CL) analysis provides useful information on the existence and distribution of defects and trace elements in materials, which are related to genetic conditions such as formation temperature, metamorphic process and geochronological situation. U-Pb zircon dating (e.g., SHRIMP) is an important tool to determine geological age of a micro-ordered zircon, where CL image has been used for observation of internal zones and domains with different chemical compositions and structural disorder at spatial high resolution. CL of zircon is caused by various types of emission centers, which are divided into two groups: extrinsic center such as rare earth element (REE) and intrinsic center such as lattice defects. Above all, CL of zircon is closely related to metamorphic process and radiation from contained radionuclides. Most zircon has yellow emission, which seems to be assigned to radiation-induced defect or UO₂ centers. According to Nasdala et al. (2002) and Hancher and Hoskin (2003), the yellow emission band has been recognized to be eliminated by heat treatment. Therefore, the radiation effects on zircon CL have been studied for He⁺ ion-implanted samples annealed at various temperatures to clarify radiation-induced defect centers involved with yellow CL emission in zircon.

A single crystal of zircon from Malawi (MZ) was selected for annealing and He⁺ ion implantation experiments. The sliced samples were cut perpendicular to c- and a- axes, and annealed at 100 to 1400 deg. C for 12 hours. Zircon crystals in Takidani granodiorite (TZ) and Kurobegawa granite (KZ), and the sliced MZ were implanted by He⁺ ion at 4.0 MeV corresponding to energy of alpha particle from ²³⁸U and ²³²Th. The radiation dose was set at 4.77 x 10⁻⁴ and 5.11 x 10⁻⁵ C/cm². CL spectra in the range from 300 to 800 nm with 1 nm step were measured by a scanning electron microscopy-cathodoluminescence (SEM-CL). The operating condition was set at 15 kV accelerating voltage and 0.1 nA beam current. All CL spectra were corrected for the total instrumental response.

CL spectra of untreated and annealed zircon almost show emission bands at ~370 nm assigned to intrinsic defect center and at ~480, ~580 and ~760 nm to Dy³⁺ impurity centers [Cesbron et al, 1995; Gaft et al, 2005]. Yellow CL emissions have been undetected in annealing zircons above 700 deg. C, where an elimination of radiation-induced defect centers may be appeared due to recrystallization of the structure suggested by Nasdala et al (2002). Blue CL intensity at ~370 nm gradually increases with an increase in annealing temperature, which may be responsible for a formation of intrinsic defect center due to a recovery of the framework structure from metamict by heating. CL spectra of MZ show an increase in the yellow emission intensity with an increase in radiation dose of He⁺ ion implantation as well as the emission related to the impurity centers (REE), though He⁺ ion implantation reduces the intensity of impurity centers. Yellow emission intensity has a tendency to depend on radiation dose of He⁺ ion implantation. TZ and KZ, with young formation ages of 1.93-1.20 Ma and 1.7-0.9 Ma, respectively [Harayama,1994; Harayama et al., 2010], show dull yellow CL emission attributed to radiation-induced defect center, suggesting relatively low radiation dose of alpha radiation from ²³⁸U and ²³²Th on them. If the component of yellow emission could be deconvoluted from the CL spectra in zircon, the intensity of yellow emission should be used for an indicator to evaluate total exposure doses on it during geological age.

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