Quantitative application of cathodoluminescence microscopy and spectroscopy to earth and planetary sciences

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Introduction

Cathodoluminescence (CL) microscopy and spectroscopy provide valuable information on the existence and distribution of lattice defects and trace elements in minerals with a spatial resolution of a few micrometers. This information is otherwise quite difficult to obtain using other analytical methods. The CL properties such as color, intensity and spectral peak features depend on the nature of defect and impurity centers, their concentrations, chemical composition and structure of host crystal, and the crystal fields in materials, which are closely related to crystallization temperature, pressure and temperature conditions during metamorphism or impact event, radioactive exposure from decay of natural nuclides, and geological age. CL of minerals, therefore, has been used as an important tool in many disciplines of earth and planetary sciences, e.g., interpretation of mineral genesis, observation of zonal patterns and microtextures, visualization of radiation halo, clarification of hydrothermal alteration and identification of mineral polymorphs. Although recent scientific interests in earth and planetary sciences focus on the CL of minerals such as silica, feldspar, zircon and carbonate, there have been a few quantitative application of CL microscopy and spectroscopy, e.g. geodosimetry, geochronometry, thermometry and barometry in spite of the usage of thermoluminescence and optically stimulated luminescence for these applications. Here, we propose a new approach of CL spectral deconvolution method to quantitative applications for earth and planetary sciences.

Samples and methods

Scanning electron microscopy-cathodoluminescence (SEM-CL: SEM of JEOL: JSM-5410 combined with a grating monochromator of Oxford Mono CL2) was used to obtain CL images and spectra with operating conditions of 15 kV and 2.0 to 50 nA in scanning mode with a 110 × 93 μm scanning area or ~1 μm spot. The dispersed CL was recorded by a photon-counting method using a photomultiplier tube (Hamamatsu: R2228). The beam condition was established based on the preliminary CL spectroscopy for the prevention of electron irradiation damage and enhancement of the signal/noise (S/N) ratio. All CL spectra were obtained in the range from 300 to 800 nm in 1 nm steps and were corrected for the total instrumental response using a calibrated standard lamp (Eppley Laboratory: Quartz Halogen Lamp). This correction prevents errors in the peak position of emission bands and allows a quantitative evaluation of CL intensity. The corrected CL spectra in energy units were deconvoluted into the Gaussian components corresponding to each emission centre using the peak-fitting software (peak analyser) implemented in OriginPro8J SR2. The number of Gaussian components was determined by chi-square test for each CL spectral datum of measured samples fitted with the smallest margin of standard error.

1. Geodosimetry and geochronometry

Color CL images of cross-sections of He^+ ion-implanted K-feldspar and Na-rich plagioclase show a bright luminescent halo extending from the implanted surface to a depth of 12–14 µm. CL spectra of these feldspars have a yellow-red emission from 500 to 650 nm, which is assigned to a radiation-induced defect centers. Deconvolution of the CL spectra can successfully separate this emission band into a Gaussian component at 2.09 eV for the K-feldspars and 1.86 eV for the Na-rich plagioclase, both of which intensities positively correlate with radiation dose. Taken together these results indicate that these emission intensities may be used for quantitative determination of α radiation dose from natural radionuclides that feldspars have experienced.

2. Shock barometer

CL spectra of these shocked sanidine and albite have emissions at ~330, ~380 and 400–420 nm of which intensities increase with an increase in shock pressure. Similar UV-blue emissions were found in the feldspar and maskelynite in Martian, lunar and condorite meteorite, and impactites. The deconvolution of these CL spectra provides the emission component at 2.95 eV assigned to shock-induced defect center, where this intensity correlates linearly with the peak shock-induced pressure with little dependence on composition and structure. The correlation allow us to quantitatively estimate the shock pressures experienced by the feldspar in the meteorites and impactites, of which values are concordant with those obtained from reflective index method and the paragenetic assembly of the high-pressure phases. The CL intensity of feldspar, therefore, has a potential for a universal shock barometer with high spatial resolution and in a wide pressure range. This leads to a breakthrough in understanding the impact histories on solar planet and asteroid.

3. Identification of post-stishovite

Transmission electron microscopy and Raman spectroscopy have been attempted to identify post-stishovite phase, whereas it was not successful to determine the structure due to potential vitrification or transition into other phase by the irradiation. Only XRD analysis gives its structural information, where silica minerals are excavated with a focused ion beam system from the meteorite. Therefore, it is necessary for identification of micron-order high-pressure silica polymorphs in precious extraterrestrial materials to develop a new method with high spatial resolution analysis without slight damage. CL spectra of synthetic and meteoritic seifertite show emission bands at 330 and 380 nm, which can be deconvoluted into emission components centered at 3.79 and 3.25 eV assigned to pressure-induced defect center. The peak wavelengths are distinct from those obtained from other silica polymorphs. The emission intensities of the components appear to depend on the inferred shock pressure on the meteorites reported by previous studies. Therefore, CL spectroscopy enables identification of silica polymorphs with high-spatial resolution and without destruction, and provides a constraint of impact condition in lunar meteorite and rocks returned from the spacecraft.

Further applications

We have further attempted to the progressive CL applications as follows; geochronometry using yellow emission of zircon, estimation of mylonitization by blue and red emissions of quartz, provenance-tracing for a single quartz grain using the assembly of the emission components, clarification of impact history in meteorite and impactite based on the activation energy of CL in quartz and diamond, and others.