

Cathodoluminescence of calcite decomposed from dolomite in high-temperature skarn

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Purple luminescent calcite associated with periclase has been found from the high-temperature skarn in Kanehira mine located in the eastern part of Hiroshima Prefecture. Calcite usually emits red to orange in cathodoluminescence (CL), but scarcely purple to blue. In this study we have conducted to clarify the emission center related to purple luminescence by using CL spectral analysis and the origin of the calcite during skarn mineralization.

The specimens collected from the skarn zone in the limestone contacted with intrusive granodiorite in the outcrop of the pit-tunnel. The polished thin sections of the selected samples were employed for optical observation and CL measurements. Color CL images were obtained using a cold-cathode type Luminoscope with a cooled-CCD camera. CL spectroscopy was made by a SEM-CL system, which is comprised of SEM (JEOL: JSM-5410LV) combined with a grating monochromator (OXFORD: Mono CL2). The CL emitted from the samples was dispersed by a grating monochromator (1200 grooves/mm), and recorded by a photon counting method using a photomultiplier tube. All CL spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp.

Color CL imaging reveals two types of CL emission, red and purple, in calcite closely associated with spotted periclase. The CL spectra of both calcite show a broad emission band at 620 nm in a red region, which is assigned to an impurity center derived from an activator of divalent Mn ion substituted for Ca, where the intensity of red CL is higher than that of purple CL. Furthermore, the calcite with purple calcite exhibits a broad emission band at 400-500 nm in a blue region, which might be related to a defect center such as "back-ground blue" found in low-Mn activated calcite.

The calcite with purple CL is accompanied by spotted periclase grains, which is usually found as a component of metamorphosed dolomitic limestone. If the hydrate condition would be presumed during its formation, periclase could easily hydrate and alter to brucite and other magnesium minerals by action of the humidity. According to the results of heating experiments of dolomite, dolomite decomposes to calcite and periclase at around 750 °C, whereas calcite causes its decarbonation above around 850 °C. It implies that the calcite with purple CL might be persisting after the decomposition of dolomite under a dry condition at relatively high-temperature near 800 °C, and leave the defects in the calcite structure during thermal decomposition of dolomite, which can be assigned to the component of an emission band in a blue region.