Cathodoluminescence properties and trace element signature of hydrothermal quartz: A fingerprint of growth dynamics

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ABSTRACT

Relationships between cathodoluminescence spectra and trace element contents of hydrothermal α-quartz including hydrogen species are characterized for crystals from Gigerwald (Switzerland) and Rohdenhaus (West Germany) grown under highly different physico-chemical conditions and related to growth fabrics visualized by classical cathodoluminescence microscopy.

Distinct emission bands at 395, 448, 503, 569, and 648 nm determine the spectral characteristics of cathodoluminescence images. Aluminum, Li, and H are the most important trace elements as determined by LA-ICP-MS and IR spectroscopy, reaching up to 6000 µmol/mol Al4+, 3300 µmol/mol Li+, and 5000 µmol/mol H+. Germanium, B, and Na are present at less than a few µmol/mol concentrations. A large amount of H is present in structurally bound water. AlOH-defects are also common, whereas LiOH- and SiOH-defects play only a minor role.

Fast grown zones contain Li+ and H+ concentrations too low to compensate the charge deficit if all measured Al substitutes for Si4+ in the quartz structure. This indicates the occurrence of intrinsic defects such as oxygen deficiency centers, which are assumed to affect the luminescence properties. Lithium abundances correspond to [AlO4][Li]-defects, correlated to the unstable intensity at 395 nm, but the correlation is different for both localities. This is inconsistent with a simple causal relationship between Al-Li centers and the emission at 395 nm. Conversion of [AlO4][Li]-defects to [AlO4]-defects by natural irradiation is a possible explanation for this discrepancy. The increase of the intensity at 648 nm is not proportional to SiOH concentration as suggested in the literature, indicating that other precursor defects such as peroxy-linkages are more important. The decay of the intensity at 395 nm is much more rapid than the increase at 648 nm, excluding a coupling between these processes.

Trace element incorporation in slowly grown hydrothermal quartz crystals is a direct function of fluid chemistry and temperature for a specific growth sector. Because quartz grows during extended periods of hydrothermal activity, changes in trace element inventory as visualized by cathodoluminescence may identify significant changes in growth conditions, which likely remain unrecognized during sample characterization with conventional microscopy.

Keywords: Dynamics of quartz growth, trace elements: Al, Li, H in quartz, electron microscopy, cathodoluminescence of quartz, IR spectroscopy, quartz

INTRODUCTION

Quartz is among the most important hydrothermal minerals, often crystallizing during extended periods in the lifetime of hydrothermal systems. Quartz, with its fluid and solid inclusion inventory has been used to constrain the physico-chemical evolution during crystallization ever since the pioneering work of Sorby (1858). Quartz growth zoning is only rarely visible in transmitted light microscopy in thin section and trace element contents are commonly too low to allow for back-scattered electron (BSE) imaging of growth zones. Cathodoluminescence (CL) microscopy or charge contrast imaging (CCI) is capable to visualize growth zoning (Lehmann et al. 2009), providing the basis for a much more straightforward interpretation of fluid and solid inclusion data, e.g., from hydrothermal ore deposits. This in turn allows one to more reliably constrain their genesis (e.g., Landtwing et al. 2005; Klemm et al. 2008).

The details on what causes different responses in CL or CCI has remained only poorly understood despite the broad consensus that the CL-properties of quartz depend on the physico-chemical conditions during crystallization and subsequent evolution (Götzte 2000). Fluid composition, the extent of fluid saturation with respect to quartz, pH, and temperature significantly influence the growth dynamics and trace element composition, and thus likely the CL properties of hydrothermal quartz. Hydrothermal quartz is often idiomorphic and zoned and may exhibit discontinuous internal fabrics, suggesting episodically changing growth conditions. In addition to such growth inhomogeneities the trace element composition and defect structure of quartz...