

MANGANESE-ACTIVATED CATHODOLUMINESCENCE OF SELECTED CARBONATE MINERALS.

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Cathodoluminescence (CL) microscopy is a routine tool in the investigation of geological materials. This technique is particularly sensitive to minute amounts of trace elements and other defects. In trigonal calcite-group (*R3c*) and orthorhombic aragonite-group (*Pmcn*) minerals, Mn²⁺ and/or Rare Earth Elements (REE) are generally referred to as activators, aside from crystal-lattice defects, whereas Fe²⁺ is considered as a main quencher element of the CL in carbonates.

One major advantage of cathodoluminescence imaging lies in the visualization of internal textures, e.g., complex zonations displaying the growth history of carbonate crystals in cements and fossils. The interpretation of cement generations and the stratigraphic correlation are based mainly on the Mn²⁺ luminescence of their carbonate constituents [1–4]. Recently published results on the Mn²⁺ luminescence of various calcite- and aragonite-group carbonates [5,6], however, are controversial; perhaps due to misassignment of narrow-band REE as complex Mn emission.

We have studied a broad range of naturally grown trigonal and orthorhombic carbonates using CL spectroscopy and imaging. Calcite-group minerals are commonly characterized by an intense Mn²⁺ luminescence band, which occurs as broad-band emission in the orange to red range (Fig. 2). The broadness of the emission is explained by strong interaction of 3d ions with the surrounding crystal field, which is strongly affected by lattice and atomistic vibrations of the ligands. By contrast, Mn²⁺ luminescence is rarely observed in aragonite-type carbonates (due to generally low Mn concentrations in these minerals); it is only common in biogenic aragonite [7]. We found, however, characteristic REE luminescence emissions in several of the aragonite and strontianite samples studied. These emissions are similar to those observed by [5,6]. Synthetic REE-free, Mn-doped aragonite was found to show one single, broad Mn²⁺ band near 560–565 nm wavelength.

References: [1] Meyers W. J. (1974) *J. Sediment. Res.*, 44 (3), 837–861. [2] Bruckschen P. et al. (1992) *Sediment. Geol.*, 81, 195–214. [3] Habermann D. et al. (1998) *Sediment. Geol.*, 116, 13–24. [4] Richter D. et al. (2003) *Miner. Petrol.*, 79, 127–166. [5] Calderon T. et al. (1996) *Radiat. Meas.*, 26, 719–731. [6] Del Castillo H. C. et al. (2006) *Nucl. Instr. Meth. B*, 249, 217–220. [7] Götze T. and Richter D. (2009) *Sedimentology*, 56, 483–492.

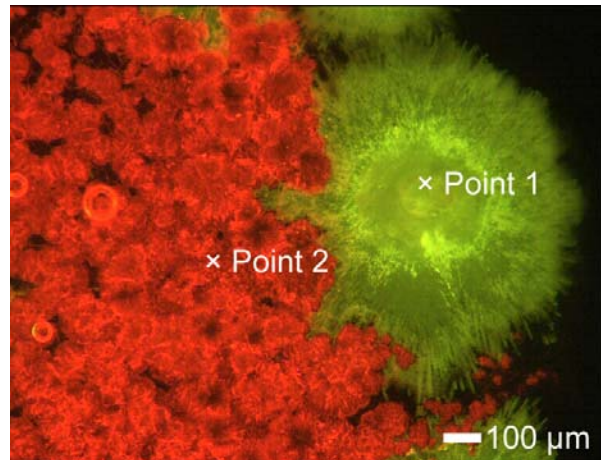


Fig. 1: Cathodoluminescence image (OM-CL) of synthetic Mn-doped aragonite (0.004 apfu Mn) overgrowing Mg-calcite (0.066 apfu Mn; 0.134 apfu Mg). The Mn²⁺ causes green CL in aragonite whereas the Mg-calcite shows bright red Mn²⁺ luminescence.

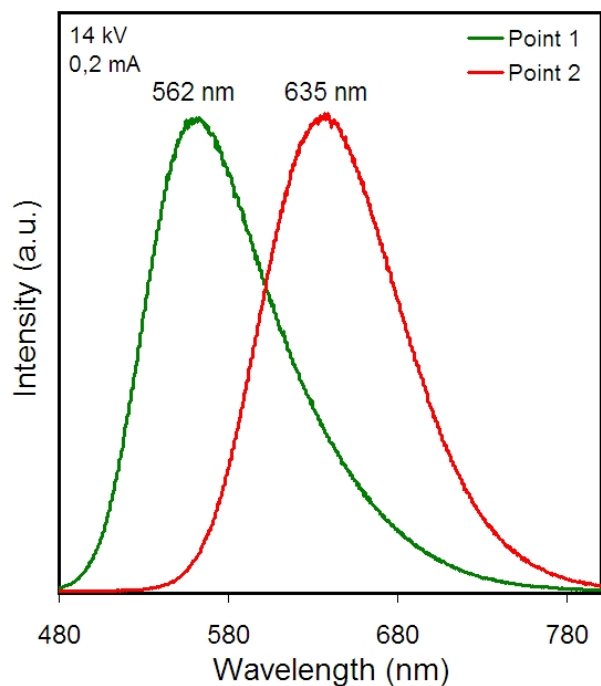


Fig. 2: Cathodoluminescence spectra of synthetic Mn-doped aragonite and Mn-doped magnesian-calcite (analysis points refer to Fig. 1). Both minerals show a broad luminescence band caused by Mn²⁺.