

MN²⁺- AND REE³⁺-ACTIVATED LUMINESCENCE OF SEDIMENTARY ARAGONITE: A GEOCHEMICAL AND EXPERIMENTAL APPROACH

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Aragonite is a very common mineral especially in Mg-rich marine and terrestrial sedimentary systems and in biogens, although calcite is the stable CaCO₃-modification at the earth's surface. Aragonite commonly has a complex trace element composition with numerous cations being incorporated on the Ca²⁺-site in the crystal lattice. Anorganic crystals of different meteoric, marine, and evaporitic origin as well as biogen skeletons have been investigated in this study by trace element analysis (proton microprobe) and cathodoluminescence spectroscopy (HRS-CL) and compared to synthetic aragonite doped with Mn²⁺ and REE³⁺.

Pure aragonite show dark greenish blue luminescence colours which originate from intrinsic emission bands at 440 nm and 540 nm. Detailed information on the point defects which are responsible for this luminescence have been lacking up to now. Mn²⁺ has been found to be the most important activator element in the freshwater biogens and in meteoric aragonite which contain up to 600 ppm Mn. Mn²⁺-activation results in a greenish yellow luminescence commonly observed in aragonite (Sommer, 1972). In contrast, no Mn was detected by proton microprobe analyses in the marine biogens and the luminescence is generally weak. The broad emission band centred at 575 nm to 580 nm which is commonly detected in the CL-spectra can be attributed to the ⁴T_{1g} → ⁶A_{1g}-transition in a Mn²⁺-centre. The maximum emission is shifted towards lower wavelength compared to the corresponding band in calcite due to different kation-oxygen-distances in the crystal lattice. The luminescence intensity shows a linear correlation with the Mn-content in synthetic aragonite doped with 400 to 2000 ppm Mn and in natural samples containing <10 to 600 ppm Mn. Above 2000 ppm Mn, selfquenching effects depress the luminescence intensity. Similar to the CL of trigonal carbonate (Richter et al., 2003), Fe²⁺ seems to be the most im-

portant quencher in aragonite causing a depression of the luminescence, if more than approx. 2500 ppm Fe²⁺ are present. Other trace elements like Sr²⁺ do not affect the CL-intensity.

Rare earth elements, which are common trace elements in hydrothermal aragonite and might also be important CL-activators (Mariano, 1989), have only been found in evaporitic aragonite from the *locus typicus* (Aragonia/Spain). Yellowish orange to greenish colours were found depending on the predominant activated element. Sm³⁺-activation result in orange colours, while Dy³⁺ generally shows greenish luminescence. Changes in the REE-pattern may result in zonation which is mapped by the luminescence. In the CL-spectra, narrow bands of Dy³⁺ at 480 nm, 575 nm, 660 nm and 760 nm and of Sm³⁺ at 560 nm, 605 nm, 645 nm and 705 nm are the dominating peaks. Emission lines of Tb³⁺ at 490 nm and 550 nm, Eu³⁺ at 615nm and Pr³⁺ at 600 nm may occur subordinately. Quantification of the REE³⁺ from the CL-spectra is difficult, because energy transfer between different ions and elements is very effective.

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