

CAUSES AND EMISSION OF LUMINESCENCE IN CALCITE AND DOLOMITE

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ABSTRACT: Luminescence in calcite and dolomite is governed by physical phenomena that are common to all oxygen-dominated crystalline substances, including other carbonates and silicates. Absorption of excitation energy, energy transfer, and emission involve predictable transitions between electronic energy levels. Strong emission in various colors is always caused by impurities which function as activators of luminescence. Visible luminescence is not expected from pure, undistorted insulators, including carbonates. However, a faint blue 'intrinsic' luminescence, with a broad emission peak (band) around 400 nm, presumably caused by lattice defects, occurs in pure calcite and dolomite, and even in some samples containing impurities.

The most important activators in carbonates are transition elements and rare earth elements. Luminescence spectra can be used for activator identification. These spectra are largely independent of the type of excitation, e.g., electron beam (cathodoluminescence = CL), photon (photoluminescence = PL), X-Ray (radioluminescence = RL) excitation, and others. Emission intensities depend on activator, sensitizer, and quencher concentrations, and on the method of excitation. At a given activator concentration, the luminescence intensity generally increases with an increase in excitation energy from PL (relatively weak) to CL (strong). Changes in visual luminescence color between different excitation methods are caused by relative changes in emission peak heights.

Mn²⁺ appears to be the most abundant and important activator in natural calcite and dolomite. Substituting for calcium in both minerals, its emission is orange-red to orange-yellow, with a fairly broad band between 570-640 nm (maximum between 590-620 nm). The emission band maximum of Mn²⁺ substituting for Mg²⁺ (in dolomite) is located around 640-680 nm. As little as 10-20 ppm Mn²⁺ in solid solution are sufficient to produce visually detectable luminescence, if total Fe contents are below about 150 ppm. Sm³⁺ activated luminescence can be visually indistinguishable from that activated by Mn²⁺. The spectrum of Sm³⁺ emission, however, is quite distinct from that of Mn²⁺ and consists of three narrow bands at 562 nm, 604 nm, and 652 nm. Tb³⁺ and Dy³⁺ activate green and cream-white luminescence, respectively. The main emission of Tb³⁺ is at 546 nm. The emission of Dy³⁺ consists of three bands, located at 484 nm, 578 nm, and 670 nm. Emission from Eu-containing calcite is red or blue. Narrow spectral bands of 590 nm, 614 nm, and 656 nm are caused by Eu³⁺ and correspond to the red emission. A broad emission spanning a large range of shorter wavelengths is caused by Eu²⁺ and corresponds to the blue emission. As in the case of Sm³⁺-activated luminescence, the red Eu³⁺ luminescence can be mistaken visually for Mn²⁺-activated luminescence. Visual luminescence detection limits for rare earths are on the order of 10 ppm.

Pb²⁺ is an activator, with an emission band around 480 nm, but it also is a sensitizer of Mn²⁺-activated luminescence in carbonates. Another recognized sensitizer for Mn²⁺ in carbonates is Ce³⁺. Sensitizers appear to be effective at concentrations as low as 10 ppm in calcite.

Quenchers of Mn²⁺-activated luminescence in carbonates are Fe²⁺, Co²⁺, Ni²⁺, and Fe³⁺. The concentrations at which quenchers appear to be effective may vary from element to element and with host mineralogy. Effective minimum concentrations as low as 30-35 ppm have been reported for calcite.

The interplay of Mn²⁺ and Fe²⁺, commonly regarded to be the most important activator and quencher, respectively, in determining the luminescence characteristics of natural carbonates is not well understood because the available data are partially inconsistent. The Mn/Fe ratio may exert a control on luminescence intensity. Mn and Fe concentrations at which 'bright' CL changes to 'dull' can be determined only semi-quantitatively. The available data on the concentration of Mn²⁺ at which quenching starts are partially inconsistent. Consequently, the Mn²⁺ concentration at which concentration extinction occurs has not been determined unequivocally.

The data presented and summarized in this paper can be used as a basis for the interpretation of luminescence of geological materials. In particular, knowledge of the possibilities and complexities of activation, sensitization, and quenching has great potential for the interpretation of diagenetic carbonate cements.

INTRODUCTION

Many minerals display luminescence when excited with different types of radiation, such as an electron beam (cathodoluminescence = CL), X-rays (radioluminescence = RL), visible or ultraviolet light (photoluminescence = PL), heat (thermoluminescence = TL), or an ion beam (ionoluminescence = IL). This paper will focus on CL with comparisons to PL because most carbonate geologists use these two excitation methods. Occasionally comparisons will be made to RL which is energetically intermediate between CL and PL.

Early reports of luminescing carbonates, particularly calcite, date back to the middle of the nineteenth century (Becquerel, 1859, 1867). The first extensive experimental data on carbonate luminescence were provided in the nineteen twenties (e.g., Tanaka, 1924; Nichols et al., 1928), at which time only solid state physicists appeared to be interested in carbonate luminescence. It was not

until the nineteen sixties that geologists began to utilize carbonate CL for petrographic studies (Long and Agrell, 1965; Smith and Stenstrom, 1965; Sippel and Glover, 1965). In the nineteen seventies, CL studies on zoned calcite cements led to the concept of 'cement stratigraphy' (Freeman, 1971; Meyers, 1974). In the nineteen eighties, CL had become a routine tool with a variety of applications to carbonate petrology (Richter and Zinkernagel, 1981; Machel, 1985; Marshall, 1988; and references therein). The use of PL, although not as widespread as CL among carbonate petrologists, has also increased significantly in the last ten years (Dravis and Yurewicz, 1985; Marshall, 1988; and references therein).

The most widespread use of CL is in studies of carbonate diagenesis. Most commonly, visual CL colors and intensities are correlated with Mn²⁺ and Fe²⁺ contents, as determined by wet-chemical or microprobe analysis. CL and Mn²⁺ and Fe²⁺ contents are then used, often in combination with stable isotope data, to interpret the diagenetic environment, i.e., salinity, temperature,