Cathodoluminescence of barytocalcite CaBa(CO₃)₂

M. MAKIO¹, H. NISHIDO², N. KUSANO² AND K. NINAGAWA²

¹Graduate School of Social and Cultural Studies, Kyushu University, 744 Motooka, Nishid-ku, Fukuoka, 819-0395, Japan

² Department of Biosphere-Geosphere Science, Okayama University of Science, 1-1 Ridai-cho, Okayama 700-0005, Japan (correspondence: nishido@rins.ous.ac.jp)

Anhydrous double salts of $CaCO_3$ and $BaCO_3$ have not been investigated with respect to CL properties up to date. In this study we have characterized CL emissions in barytocalcite $CaBa(CO_3)_2$, of which structure is different from rhombohedral-calcite type.

Single crystals of three barytocalcite (Blagill, UK; Fosters, UK; Langban, Sweden) were selected for CL spectral measurements at various temperatures.

CL spectra of barytocalcite at room temperature have a pronounced emission peak at around 600 nm in red region. It can be assigned to an impurity center of divalent Mn ion (4G-6S) as an activator, which occupies Ca site in barytocalcite structure, where the centered wavelength is appreciably smaller than the value of calcite (620 nm) due to different crystal field. Barytocalcite has aragonite-like structural configuration rather than calcite-like one. Therefore, various types of Ca sites substituted with Mn ions can be suggested for this Ca-Ba series carbonates, which might modify the strength of crystal field around activated Mn ions. Temperature controlled CL measurements reveal that the CL intensity of Mn activated emission in barytocalcite decreases in an increase of sample temperature, suggesting a temperature quenching effect especially pronounced in the range of -50~25 °C. The intensity at -189 °C is twice as much as that at room temperature. Furthermore, an increasing temperature results in a shift of the emission peak to shorter wavelengths, which might be attributed to an increase in the distance between Mn ion and adjacent ligand.

Hematite scalenohedra –ancient jewelry and a problem of sedimentary mineralogy

 $\begin{array}{c} \mbox{Emil Makovicky}, \mbox{Matteo Parisatto and} \\ \mbox{Flemming H} \mbox{Mulund}^{123} \end{array}$

¹Institute for Geoscience and Natural Resource Management, University of Copenhagen, Østervoldgade 10, 1350 Copenhagen, Denmark, emilm@geo.ku.dk

²Department of Geosciences, University of Padova, Via Gradenigo 6, 35131 Padova, Italy, matteo.parisatto@unipd.it

³Moesgaard Museum, Moesgaard Allé 20, 8270 Højbjerg, Denmark, farkfh@hum.au.dk

In 1964 a scalenohedron of hematite was found in archaeological excavations of the bronze-age layer (1980-2020 BC) of the Tell of Qala'at al-Bahrain on the shores of the Persian Gulf, together with faience and carnelian beads. We subjected the scalenohedron to X-ray tomographic investigation using a Bruker microCT-Skyscan 1172 high resolution scanner. The system has a polychromatic microfocus X-ray source with a tungsten anode; it was run at 100 kV and 10 W. 2000 radiographs were acquired over 360°, 9 radiographs were averaged for each angular position.

Scanning revealed considerable internal porosity of the 'crystal', with a preferential concentration of small pores in the central portions and with larger, elongated pores in the subsurface portions. The internal structure reveals that it is a pseudomorph after a scalenohedral carbonate, composed of an intergrowth of hematite tablets and grains. Its geometry coincides with that of calcite {21-34} scalenohedron, with minor presence of {10-10} and {02-24}.

Mineral trade knows such 'hematite scalenohedra' from the Arzanah and Hormuz Islands in the Persian Gulf. Both are top portions of tall salt diapirs occluding fragments of Precambrian Hormuz Formation: blocks of various volcanic rocks, sediments and even iron ore, forming a jumbled mass. Specularite is reported in geological descriptions but not the hematite pseudomorphs which look very much like our specimen. Our research revealed an extensive replacement of well-crystallized carbonates by hematite (may-be in relation to the formation of large hematite masses which in this pre-ironage society were polished into hematite weights) but it leaves open the question at which geological stage the evaporite sequence produced perfect carbonate crystals and when were they pseudomorphosed by hematite. This may have practical importance, a number of these diapirs being connected with the Gulf gas and oil occurences.