HIGH RESOLUTION CATHODOLUMINESCENCE OF CARBONATES FROM THE COLD BOKKEVELD CM2 CHONDRITE: IN PREPARATION FOR STUDY OF OSIRIS-REX ASTEROID SAMPLES. V. Guigoz[1] , A. Seret[2], M. Portail[1], G. Libourel[2], H. C. Connolly Jr[3,4,5], and D. S. Lauretta[4], [1]Université Côte d'Azur, CNRS, CRHEA, Rue Bernard Grégory, 06560 Valbonne, France, [2]Université Côte d'Azur, Observatoire de la Côte d'Azur, CNRS, Laboratoire Lagrange, Boulevard de l'Observatoire, CS 34229, 06304 Nice Cedex 4, France, [3]Department of Geology, Rowan University, Glassboro, NJ, USA, [4]Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, USA, [5]Department of Earth and Planetary Science, American Museum of Natural History, New York, NY, USA.

Introduction: Recent observations of near-Earth asteroid Bennu by the OSIRIS-REx mission revealed spectral evidence of widespread carbonates, as well as high-reflectance, centimeters-thick, meter-long linear features within boulders interpreted as hydrothermally deposited carbonate veins [1]. Given the extent of carbonates and the size of veins on Bennu, the samples of this asteroid that OSIRIS-REx will soon deliver [2] are likely to contain carbonates, telling us more about carbonaceous asteroids and their past hydrothermal activities.

To evaluate whether the returned sample chemistry is distinct from that of our corpus of meteorites, we have launched a high-resolution cathodoluminescence (HR-CL) survey of carbonates in several carbonaceous chondrites. Cathodoluminescence, the emission of photons (ultraviolet to near-infrared) following injection of high-voltage electrons, has long been recognized as a powerful technique to explore many fundamental properties of matter (including insights into crystal growth, zonation, deformation, trace elements, and defect structure) as well as its modes and its physico-chemical conditions of formation. The luminescence of carbonate minerals depends mainly on the abundance of Mn^{2+} activators, whereas the presence of Fe^{2+} has a fundamental role as quencher due to its capability in suppressing luminescence. More specifically, the different types of luminescence in $CaCO_3$ are caused by: (i) substitutions of Mn^{2+} for Ca^{2+}; (ii) substitutions of rare earth elements (REE) for Ca^{2+}; (iii) dislocations of the $[CO_3]^{2-}$ fraction; (iv) oxygen vacancies and broken Ca-O bonds [3, 4].

Here we report HR-CL results obtained from carbonates, mainly calcites of the Cold Bokkeveld CM2 carbonaceous chondrite. Cold Bokkeveld is classified as CM2.1–2.7 and is an impact regolith breccia that shows significant inter- and intrasample mineralogical heterogeneity [5]. Because its clasts experienced various degrees of aqueous alteration, it was chosen as an appropriate training meteorite for this study.

Experiment: The general overview of Cold Bokkeveld thin section NHMV-O1128 with coupled backscattered electron (BSE) images and energy-dispersive X-ray (EDX) spectroscopy chemical maps was acquired at CEMEF Mines ParisTech-Nice (France) with a MEB FEI XL30 ESEM LaB6 operated at 20 kV and 200 nA beam current, equipped with a BRUKER Quantax 655 detector with XFlash 6|30 technology silicon drift 10 mm² at 129 eV (100 kcps). BRUKER Microanalysor QUANTAX was associated with the software ESPRIT (semi-quantitative analyses without standard by P/B-ZAF method).

The high-resolution CL facility consists of a MonoCL4 GATAN monochromator equipped with both a high-sensitivity array detector and a high-sensitivity photomultiplier mounted on a field emission gun scaning electron microscope (FEB-SEM; JEOL JSM700F at CRHEA, Nice, France) and suitable both for hyperspectral analyses and panchromatic imaging. The electron beam current used in the study ranges typically from 1 to 4 nA and the voltage beam is fixed at 5 keV. For hyperspectral analysis, the extracted luminescence is directed towards a 300 mm focal length monochromator equipped with a 150 grooves/mm grating blazed at 500 nm; the entrance slit has been fixed to 300 µm, which gives a spectral resolution better than 3 nm. Dispersed light is collected as a whole using a CCD detector with a sensitivity range from 250 to 900 nm. Acquisition time is fixed to 10 sec/pixel.

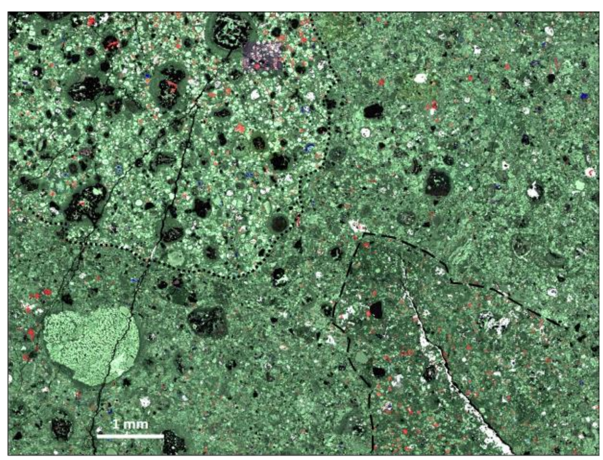

Fig. 1: X-ray map of part of the Cold Bokkeveld CM chondrite, overlaid on a BSE image, showing brecciated textures with various clasts, here delineated by dashed lines. Red, Ca; blue, Al; green: Fe; coral-colored specks are calcite.

Results and discussion: The X-ray map of the studied thin section confirms the occurrence of various clasts characterized by different mineralogy and chemistry in the Cold Bokkeveld chondrite (Fig. 1). Despite lithological heterogeneity, carbonates, mainly calcite, are ubiquitous. Their modal abundances, however, vary greatly from clast to clast. Image processing of X-ray maps of the bulk thin section give an estimate of 0.8 ± 0.1% for calcite modal proportions, consistent with those calculated by XRD on bulk, i.e., ≈ 1% [5].

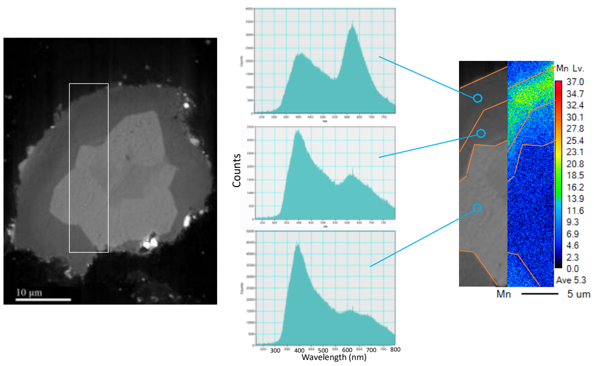

Fig. 2: HR-CL panchromatic image of a zoned calcite grain (left) from Cold Bokkeveld with its spectral analyses (center) and the Mn element corresponding map acquired by EMPA (right; 0.1< MnO wt% < 0.43).

Panchromatic HR-CL images and representative spectra from calcites of Cold Bokkeveld are displayed in Figs. 2 and 3. All samples exhibit one emission band peaking at 620 (±10) nm (orange-red), and most of them also show a second emission band peaking in the range 375–425 (±10) nm (violet-blue). The CL of calcite-based materials can be linked to two luminescence centers, namely (i) Mn^{2+} substituting for Ca^{2+} (orange-red), as shown by the covariation of the 620 (±10) nm emission band intensity and the Mn concentration measured by electron microprobe analysis (EMPA) (Fig. 2), and (ii) intrinsic structural defects due to lattice distortions (violet-blue) with, possibly, the presence of non-bridging oxygen hole centers [3,4].

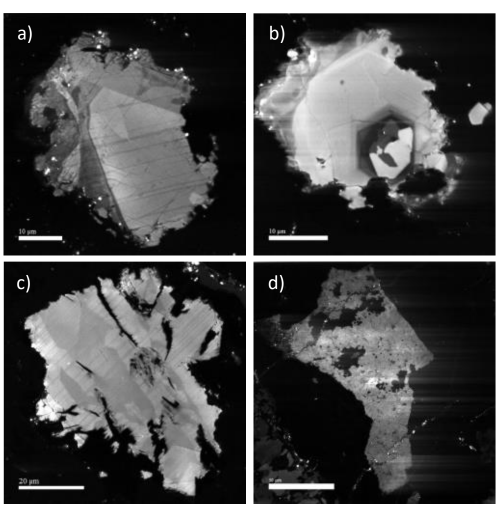

Fig. 3: HR-CL panchromatic images of different calcite grains showing euhedral cores with complex CL edge (a) and core (b), complex interfingering between calcite and Fe–S-rich serpentine/tochilinite (c), or homogeneous CL intensity area (d).

The high sensitivity of our CL detector to these two spectral luminescence centers, coupled with the high-spatial resolution of a FEG-SEM on the other hand allow us to resolve petrographic and compositional features that would otherwise have remained invisible at the sub-micrometer scale. More than 80 calcite grains have hence been probed in the different clasts of the studied section of Cold Bokkeveld (Fig. 1). In agreement with a recent study [7], our panchromatic HR-CL images revealed the existence of a variety of carbonate displaying petrographic features (Fig. 3) that are more complex and distinct from those of type 1 (T1) and type 2 (T2) carbonates commonly observed in CM2 meteorites. The T1 calcites are characterized by small grain sizes and are always mantled by a rim composed of phyllosilicates and tochilinite. The T2 calcites are larger, multi-grain aggregates that lack rims but are commonly associated with sulfide grains. If these CL zonations suggest complex conditions of formation, our survey also indicates that each clast is hosting calcite grains characterized by a specific petrographic feature (Fig. 3).

Conclusion: Is the presence of carbonates displaying various petrographic features indicatives of several generations of fluids (T, Eh, pH) on each clast parent body? Or, did they result from the compositional evolution of fluids on a single parent body? Can temperature variations deduced from isotopic analyses constrain these complex carbonates? Based on our results, HR-CL promises to help answer these questions and decipher the crystallization history of carbonates and the corresponding type of hydrothermal activity in the parent body.

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