Origin of surface impurities on the Cave of Swords selenite crystals at Naica

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The Cave of Swords was discovered in 1910 at Naica mine, Chihuahua, Mexico. Its name refers to the look of the 1-2 m long crystals the cave had when it was discovered. Currently the crystals are 0.1-0.3 m long. The crystals surface is opaque and ocher. For over 100 years these crystals continue to amaze and give us clues about their formation. This work is part of a research aimed at the conservation of the Naica Giant Crystals. Thirteen samples from the Cave of Swords were analyzed by Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), Confocal Laser Microscopy with Differential Interference Contrast (LCM-DIM) and Transmission Electron Microscopy (TEM). X-Ray Fluorescence (μ-XRF) together with X-ray Absorption Near Edge Structure (μ-XANES) and X-ray Photoelectron Spectroscopy (XPS) were employed for elemental analysis. For phase analysis, X-ray diffraction (XRD) in both symmetric and grazing incidence geometries (GI-XRD) and Micro electron diffraction at TEM were used. Impurities on crystals surfaces show a heterogeneous distribution of the present elements. The thickness of impurities ranges from 120 nm to 150 μm. The phases identified were (see figure) gypsum (1, 2, 3, 6, 9, 10, 13), hematite (4, 7, 8), sphalerite (14), chalcopyrite (11), cuprite (15), galena (5), alabandite (12), halite, fluorite and amorphous Pb and Mn oxy-hydroxides. Al, C, Ca, Cl, Cu, F, Fe, Mg, Mn, Na, O, Pb, S, Si and Zn elements were identified. A model for the origin of impurities follows: Selenite stopped growing when the solution became sub-saturated. Then, hematite was deposited as the main phase, which was dissolved or suspended in the solution. Hematite matrix served for the adsorption of other crystalline and amorphous phases. We concluded that humans have not produced the impurities, which are witnesses of the gypsum crystals formation. Acknowledgment: Stanford Synchrotron Radiation Lightsource, Harvard Museum of Natural History and CONACYT CB-183706.