Do the Naica Giant Crystals Deteriorate by Human Action?


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Abstract. Located in Chihuahua State, at Naica mine, lay two famous caverns: The Cave of Swords, which was discovered in 1910 and the Cave of Giant Crystals, which was found in the year 2000. The last referred cave contains the largest gypsum single crystals in the world. A multidisciplinary research is presented with the results of experimental simulations and the study of existing surface impurities, in which conventional laboratory, synchrotron radiation techniques and numerical modeling have been used. The most important conclusions are summarized in that the gaseous environment is the most dangerous for the conservation of crystals and that the origin of most surface impurities is natural.

Key words: Naica giant crystals; 2D-GI-X-ray diffraction; micro-X-ray absorption near edge structure.

The giant crystals of Naica have dazzled crystallographers around the world since 1912, when the first publication [1] appeared that described the crystals discovered in the so-called "Maravilla Mine" in the "Cave of Swords". In the same mine in 2000 the "Cueva de los Cristales" was discovered, which houses gorgeous crystals of selenite (CaCO₃·2H₂O) of more than 11 m in length. Some crystals show darkening impurities on their surfaces. A multidisciplinary team from Chihuahua, with international collaboration, accomplished a project to study the origin of observed surface impurities and their possible link with the human action inside the Naica caves. The performed investigation entailed two components: a) the detailed chemico-structural characterization of the detected impurities and b) the experimental simulation of possible deterioration.

a) Surface impurities of 30 samples from Cueva de las Espadas and 40 samples from Cueva de los Cristales were studied. Conventional techniques of petrography, optical and electronic microscopy, as well as laboratory X-ray diffraction were employed. The synchrotron radiation techniques of 2D grazing incidence X-ray diffraction (2D GI-XRD), micro-X-ray fluorescence (μ-XRF) and micro-X-ray absorption near edge structure (μ-XANES) played an important role in the identification of the phases of the impurities. The results were as follows. Twenty-eight crystalline phases and two amorphous phases were determined. The determined chemical elements are: B, Na, K, Mg, Al, Cd, Cr, Si, O, S, Fe, Mn, V, Cu, Ti, Ca, Zn, Sr, As, Pb. The elements Sr, Cu, Fe, Ti, Mn, Pb, and As were observed in the impurities in higher concentrations. The determined phases are consistent with the minerals present in the mine and the walls of the caves. Hematite and iron oxyhydroxides predominate among crystalline impurities.
Manganese and lead oxides are the most frequent amorphous phases. Among the impurities, calcium carbonate product of incongruent dissolution was not detected. For the first time the saturation index was numerically modeled, which determines the solubility, equilibrium or precipitation of the phases present in the impurities, between the temperatures 44 °C and 60 °C, with a pH range of 6.5 to 8.5. The numerical modeling allowed to complete the geochemical model on conceptual and physicochemical bases. The paragenesis shows that surface impurities were deposited in the late stage of gypsum crystal growth, as a result of the fluctuations of the water table in the Cueva de las Espadas and after the Cueva de los Cristales emptied due to the descent of the extraction cone of water from the mine. Subsequently, the impurities have evolved with the environment of high relative humidity and possible condensations produced when the cave is opened. In this sense, human intervention was a factor [2, 3].

b) The effects of various microclimatic conditions were simulated to predict their impact in different potential scenarios. Experiment in microclimatic chamber: The effect of the condensation of water saturated in CO₂ was explored, to simulate acceleratedly the action of opening the door and causing the deposition of dew on the crystals. Microclimatic simulation: Separately, the action of four types of atmospheres was tested: air, methane (CH₄), carbon dioxide (CO₂) and nitrogen oxides (NOₓ) in reactors at a controlled temperature of 25 and 60 °C. Each reactor housed crystals submerged in water and in contact with a gaseous atmosphere. A relative humidity of 85% was maintained. The residence times of the crystals inside the reactor were 1, 3, 6 and 12 months.

In the experiments of the microclimatic chamber the formation of carbonates on the surface of the crystals was not detected, and the dissolution of the crystals was observed, between 1 and 4% by weight, caused by the combination of high concentration of CO₂ and permanent fog. In the microclimatic simulation it was concluded that the modification of the appearance of the crystals predominates in short exposure times. In long exposure times, surface defects tend to disappear by the establishment of chemical equilibria that dissolve and recrystallize calcium sulfate. The formation of bassanite is the result of dehydration of the gypsum phase. The appearance of bassanite was more likely observed in a gaseous environment. The atmospheres of air and CO₂ were those that presented greater bassanite proportions [4, 5].

The general conclusions of the investigation are:
- The origin of most surface impurities is natural. There are some impurities of clays mechanically deposited by man.
- The greatest damage produced by man are the extraction of water from caves and theft.

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References


