Characterization of gypsum crystals exposed to a high CO_2 concentration fog using x-ray

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In Chihuahua State, a little town called Naica has the largest gypsum single crystals in the world. The growth of these structures has been described as a long and stable process developed over thousands of years. Due to the change in the environmental conditions, these crystals could suffer alterations on their surface. In this project we study the cause of possible deterioration of the giant crystals and intend to suggest measures for their preservation. For this sake, our first experiment consists on several gypsum crystals that have been subjected in a climate chamber to a fog at high CO_2 concentration and 51 °C for a period of time of six months, extracting two crystals every 15 days. Then the crystals have been characterized through Grazing Incidence X-Ray Diffraction using a diffractometer PanAlytical X'PertPro with two different detectors; Xe-filled proportional detector and a Pixel 3D detector. The results were compared to determine which technique is the most suitable to study the degradation of gypsum single crystals. In the two cases, we have identified only the gypsum phase, but with different crystal plane orientations.

Naica is a small mining town located in the southeast of the state of Chihuahua, Mexico. Nowadays “IndustriasPeñoles” is the owner of the extraction rights in the zone, becoming the main source of lead in the country and one of the more important for silver and zinc. In the year 2000 there was discovered a new cave with giant formations of gypsum crystals, and even if other locations around the world enclose similar formations[1,2], giant crystals in Naica are the most magnificent example known by humankind. From the geological point of view, the structural complexity that the zone had to offer has been studied for a long time; Naica is formed by three minor mountain chains that produced a large dome in direction NW-SE. Its coordinates are 27°51′3″N and 105°29′47″W. This dome contains a series of fractures and caves flooded with heated water by an intrusive body, where the single crystals have had the possibility of grow and prosper, becoming worldwide famous.

Due to the fact that underground gypsum formations in the mining zone of Naica are probably the largest crystalline structures reported in the world, several researches have tried to determine the genesis and evolution of these structures as well as the potential contamination in them. The heavy extraction activity performed *in situ* have induced that the water that flooded the caverns is being constantly extracted by powerful pumps, exposing the giant crystals to an unconventional environment; these changes have the potential to trigger a series of both chemical and physical processes in a plausible detriment of the integrity of these wonderful structures. Literature considers as independent phenomena the inclusion of strange materials over the crystal due to natural causes and the depositions of new compounds by the interaction with some substances. For example, Badino *et al.* in 2011[3] and Forti in 2007 argue that the carbon dioxide dissolved in water can cause the formation of a thin layer of calcium carbonate on the surface of the selenite crystals [3,4]. Gypsum is a soft mineral with the chemical formula $CaSO4 \cdot 2H2O$ that due to the crystallization conditions can form several crystal varieties including alabaster, gypsite and selenite among others. These varieties usually differ in color and shape being the colorless gypsum variety *selenite*, named after the Greek goddess of the moon, the type which is found in Naica. According to the mechanism proposed by the Spanish researcher Juan Manuel García-Ruiz, the gypsum crystals grew from low concentration dissolution with an isotopic composition commensurable with the sulfate from native anhydrite dissolution in the mine. At 54 °C it would take more than a million years to the Naica gypsum mega crystals to reach their actual size[5]. Even if the grow mechanism is comprehensible nowadays, it is not clear if some crystals will have *a posteriori* contaminants on their surface. The aim of this work is to clarify this question.

The temperature of the hydrological bodies in the Naica mine have decreased gradually over the millennia. For continuous growth of the gypsum the anhydrite must dissolve. These phenomena, at temperatures under 58 °C, supplies Ca2+ and SO 2ions, over-saturate the waters with gypsum and cause its crystallization. The minimal difference in the solubility of gypsum and anhydrite is the driving force needed to contribute calcium and sulfate ions to this very stable mechanism. The combination of unusual geological conditions resulted in a self-sustained mechanism based in a slow and delicate phase equilibrium [5]. The conditions at which the structures have developed have been analyzed by several research groups, emphasizing on the fact that this unique conditions are not likely to repeat somewhere around the world [6]. In addition, new structures like a candle shaped ones, have been described derived from the novel hydric conditions of the caves [7].

Under normal circumstances selenite crystals are diaphanous, nevertheless nowadays some opacity can be appreciated in the surface of the crystals, being the anthropogenic activity developed the last years the main candidate to cause this condition. Water extraction and explosions performed for the mine exploration produce several gases such as carbon oxides (COx) and nitrogen oxides (NOx) that mixed with water produce acidic solutions that may contribute to the dissolution of the crystals. At the same time the CO2 produced by combustion and human breathing may cause the deposition of other compounds on the surface of the crystals[8,9].

The crystals of Naica are a Mexican and mankind treasure. As a research topic they have already generated a variety of publications that approach the problem of the nucleation and growth. The objective of this study is to simulate in a climatic chamber a plausible environment, in a reasonable time, the possible effects of dangerous agents for the crystals. The simulation was realized in a climate chamber were it was introduced a mixture of water and CO2at saturation forming fog. The experiment went on for about six months and the main propose was to evaluate the effect of CO2 over the gypsum crystals. Grazing Incidence X-Ray Diffraction (GI-XRD) analysis has been employed for testing changes in composition on crystal surfaces using two types of detectors to corroborate the effectiveness of the characterization.

Materials and Methods

Climate simulation

Accelerated weathering test of materials in climatic chambers is a procedure well established for studies of corrosion diagnosis and prevention of alloys, building materials and aircraft parts [10]. Its application is based on the hypothesis of the capability of reproducing weathering conditions with laboratory-controlled parameters. In engineering practice, accelerated weathering leads to standardized technical criteria, applicable in manageable time intervals, linked with economyand safety-linked important decisions. Temperature, concentration of chemical agents and exposure time are representative of acting agents to be established and controlled.

The application of the accelerated weathering test to similar-to-gypsum materials has been adopted a long time ago [11]. The problem of characterizing the corrosion in the crystals of Naica in their new environment (not flooded and surrounded by gas) is new and original.

The experimental procedure was executed on gypsum crystals, similar to the ones that can be found in the "Cueva de los cristales gigantes". These samples were introduced in a Singleton custom-made climatic chamber where the atmospheric composition, temperature and humidity were controlled. The samples sizes were approximately 2x2 cm and can be appreciated in Figure 1

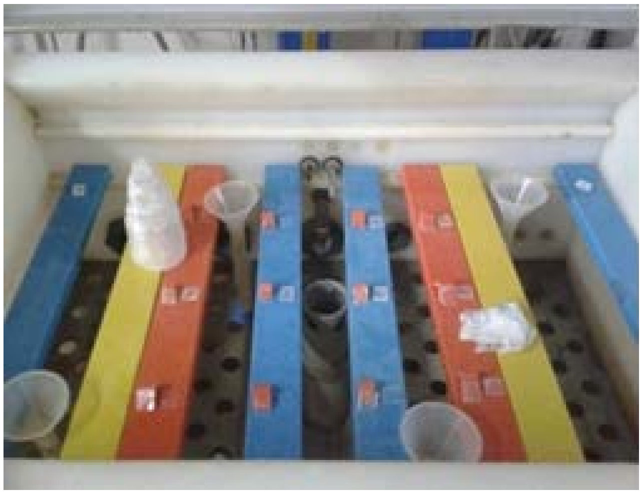

FIGURE 1. Arrangement of gypsum samples inside the climatic chamber.

Grazing Incidence X-Ray Diffraction

The GI-XRD measurements were performed in a Panalytical X'Pert Pro Powder Diffractometer with two different detectors: Xe-filled proportional detector (so-called 0D or point detector) and PIXcel 3D (2D or plane image detector). The Xefilled proportional detector is a wave-length sensitive detector, capable of selecting and integrating the intensity of the reflected $k_{\alpha 1}$ Cu line, while the PIXcel 3D is an area detector with small pixel size of 55x55 μm that delivers a higher resolution and a high speed data collection. The incident angle was 0.5° and the measurement was from 2θ = 10 to 60° with a step of 0.01°, with step intervals of 7 second for the Proportional Detector Xe and 0.3seconds for the PIXcel 3D. The critical incident angle for selenite is 0.22° while for calcite and aragonite the critical incident angle is 0.24° and 0.25° respectively, to ensure the possible detection of superficial substances in the crystals the incident angle was fixed at 0.5°, this angle allows the X rays to penetrate about 1.46 μm into the sample.

With the Xe-filled proportional detector the measurements were made over large sample areas, compared to the PIXcel 3D, since for the last detector, one should focus the incident beam on the desired spot. For the first detector there was no selection of the irradiated area on the sample, while with PIXcel 3D detector different small sample areas were chosen, such as opaque spots, fractures and plane zones.

Results and Discussion

Following the procedure described above, the gypsum samples were extracted from the chamber, were dried and weighted. The most evident result of the simulation in the climatic chamber was the apparent dissolution of the crystals. To confirm this perception a comparison of the initial and final weight was done, showing that there is a mass loss of 1-3%, as seen on Table 1 in the Appendix. Literature reports solubility between 0.18 and 0.20% in a range of temperature where the temperature used in this work is located [12]. Figure 2 shows the behavior of different samples in horizontal position that represents an average dissolution rate of 0.015% per day while in Figure 3 the dissolution rate is 0.0067% per day for samples placed in a 45° angle. The relative uncertainty of the variation is estimated about 15%, due to the inherent instabilities of an experiment conducted in such a long time so the fitted behavior is shown in the a black line. The pressure, temperature, relative humidity and CO2 were fixed, as explained above, along the measurements. In a visual examination, it becomes evident that the crystals were introduced into the chamber with a diaphanous appearance, while after being removed from the chamber, some of the samples become a little opaque and presented more evident fractures and shape (Figure 4).

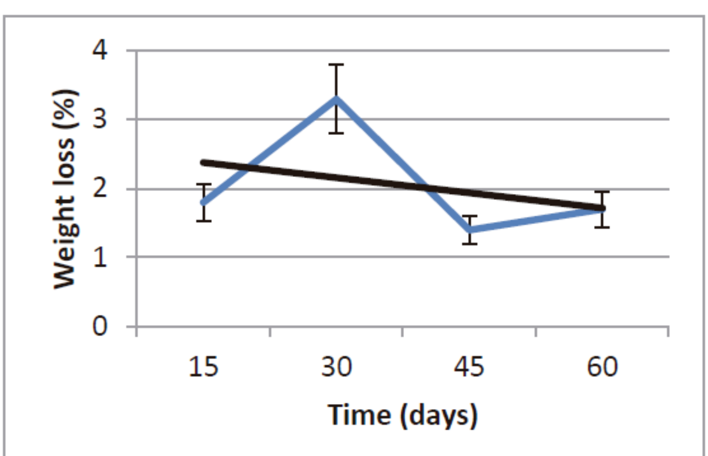

FIGURE 2. Weight loss (%) for samples set in a horizontal configuration

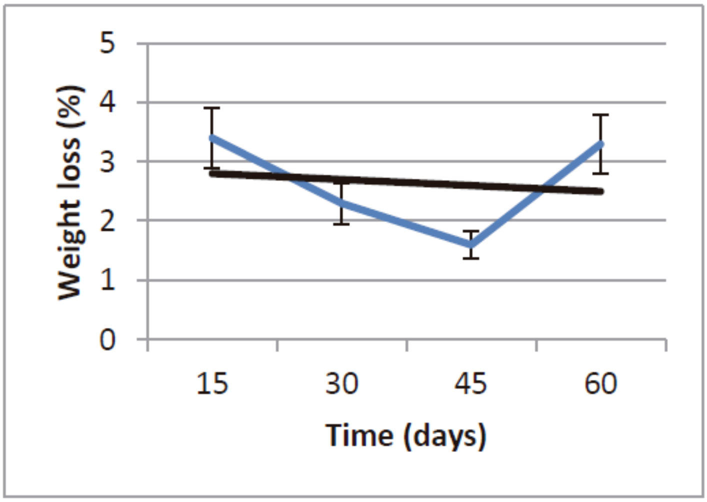

FIGURE 3. Weight loss (%) for samples set in a 45° configuration

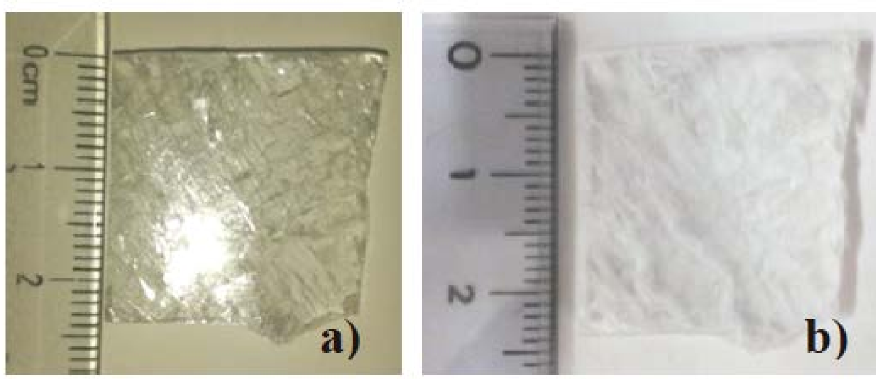

FIGURE 4.Morphology of the crystals a) before and b) after the climatic chamber exposure.

Inside the climatic chamber, the condensed fog becomes the water that is discharged to the drain. This water contains 2 to 3 mg / L of sulfates, fact that provides confirmation of the dissolution of the gypsum crystals.

After weighting, the samples were measured by GI-XRD, with the PIXcel 3D detector and the Xe-filled proportional detector. The only phase detected was gypsum, presenting a mosaic microstructure. In the Figure 5 is shown a characteristic morphology after the crystal is broken, the crystal has the same composition but the crystal orientation changes. This feature was concluded by the observation of few reflections, most of them corresponding to low angles of incidence on the gypsum crystal planes. No calcium carbonate was detected. In both detectors, the main peak observed was the reflection of the plane (020) of gypsum. Other peaks emerged depending on the sample and the detector. In Figure 6 a) the measurement obtained with PIXcel 3D detector can be appreciated and in 6 b) the one obtained with the Xe-filled proportional detector. This sample corresponds to a 75 days residence in the climatic chamber and, as can be seen, a better definition is obtained using the PIXcel 3D detector. The rest of the measured samples show the same behavior. It is important to remark that one of the main differences between detectors is the fact that the incident beam can be manipulated more precisely with the PIXcel 3D set up, that gives us the opportunity of studying regions of interest.

It is known that selenite crystals assemble, in some cases, is composed by two or more single crystals growing together with orientations related by a subset of the crystal symmetry group. The Naica single crystals are {100} contact twins, formed by two single crystals growing side by side separated by a {100} surface. This effect can cause the diffraction peaks to appear in an unexpected angular position [4].

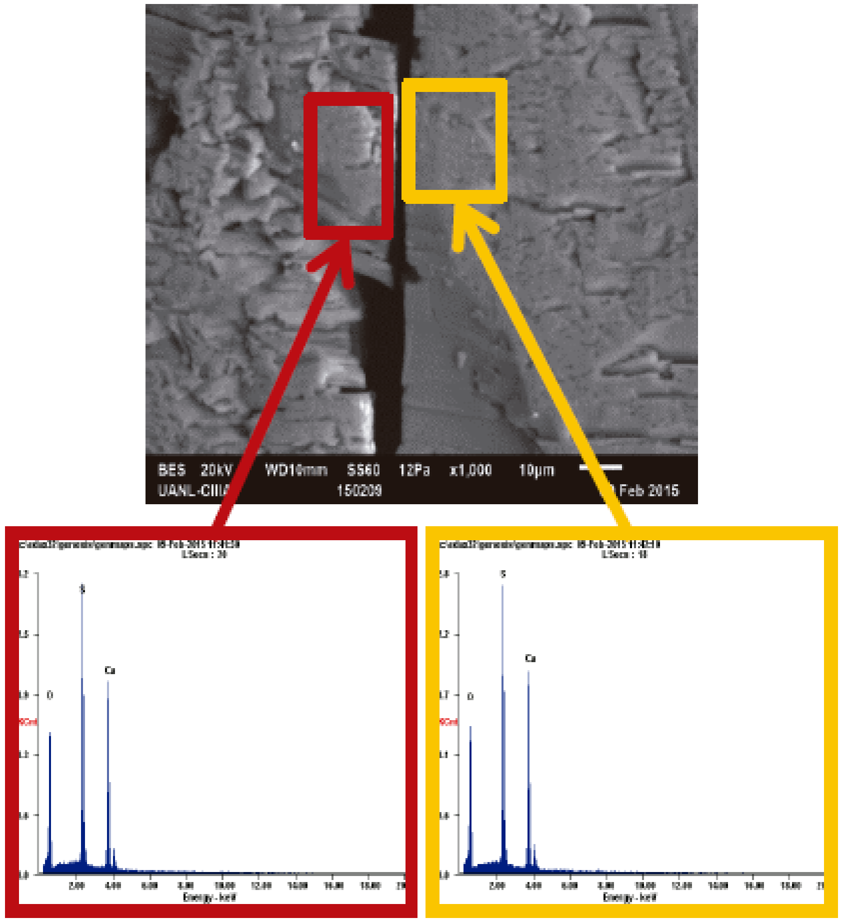

FIGURE 5. Morphology and composition by SEM and EDS of gypsum crystals.

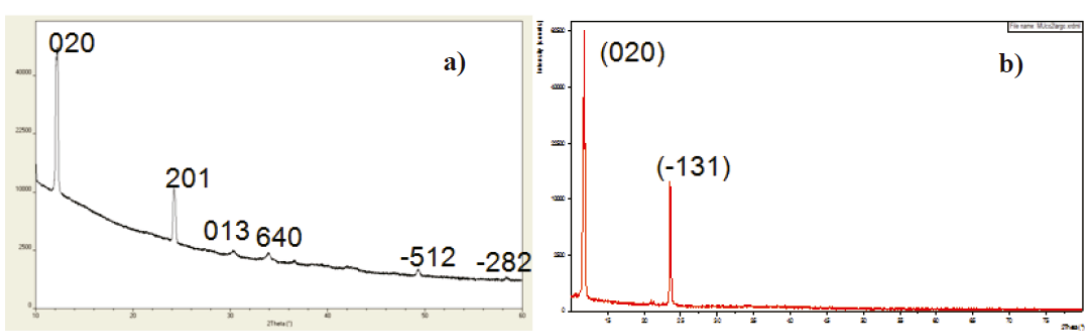

FIGURE 6. Diffraction patterns for a 75 days sample obtained by a) the PIXcel 3D detector and b) the Xe-filled proportional detector.

Conclusions

The analysis of the samples after their removing from the accelerated weathering, as indicated above, shows no evidence of the formation of calcium carbonate on the surface of the crystals. There is no evident correlation between the exposure time in the climatic chamber and the effect on the samples. The fractures and the opaque regions show different reflections by GI-XRD, no matter the residence time in the chamber.

It may be concluded that the accelerated weathering can produce anomalies in the crystal structure of gypsum, giving as result atypical diffraction peaks due to the twining phenomena. Nevertheless, the moisacity phenomena can be observed better with PIXcel3D detector than with the proportional detector. PIXcel3D provides better definition in reduced time intervals.

The effect of the water/CO_2 fog mixture consists only on the dissolution of gypsum. The addition of CO_2 by breathing and explosions probably do not affect the crystals more than the water absence will do on its own. With this study, regarding to CO_2, the crystals are safe.

Acknowledgments

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