

Naica's "cueva de los cristales": Synchrotron radiation characterization of the wall-crystal interface

B. Pérez-Cázares^a, M. E. Fuentes-Montero^{a,*}, L. E. Fuentes-Cobas^b, I. Castillo-Sandoval^b,
I. J. A. Carreño-Márquez^{b,†}, H. E. Esparza-Ponce^b, D. Eichert^c, R. Loredo-Portales^d, J. Canche-Tello^b,
J. M. Nápoles-Duarte^a, L. Muñoz-Castellanos^a, G. González-Sánchez^b, I. A. Reyes-Cortés^a, and M. E. Montero-Cabrera^{b,*}

^aUniversidad Autónoma de Chihuahua, Campus Universitario #2,
Circuito Universitario, 31125, Chihuahua, Chih. México.

^bCentro de Investigación en Materiales Avanzados,
Miguel de Cervantes 120, Complejo Industrial Chihuahua, 31109, Chihuahua, Chih. México.

* e-mail: mfuentes@uach.mx; elena.montero@cimav.edu.mx.

^cElettra Sincrotrone-Trieste, S.C.p.A.,

AREA Science Park, 34149 Basovizza (Trieste) Italy.

^dCONACYT-Universidad Nacional Autónoma de México,
Av. Luis D. Colosio M. esq. Madrid s/n, 83000, Hermosillo, Sonora, México.

Received 30 September 2021; accepted 23 December 2021

Naica's "Cueva de los Cristales" was discovered in 2000, and it has been considered particularly interesting for its beauty and the challenges it poses to crystallography. This article focuses on the study of the wall-selenite interface by various techniques, particularly X-ray diffraction (XRD), scanning electron microscopy (SEM), with emphasis on micro-X-ray fluorescence (μ -XRF) and micro-X-ray absorption near edge structure (μ -XANES). The main phases calcite, quartz, goethite and montmorillonite were identified by XRD, as well as the association of crystalline and amorphous minor and trace phases of Zn, Mn, Cu, As and Pb. The latter were identified in μ -XRF maps and μ -XANES spectra. The results for the morphology and the chemical description of the crystal-wall interface may contribute to propose a nucleation and growth mechanism for Naica megacrystals.

Keywords: Naica's Cueva de los Cristales; μ -XRF; μ -XANES.

DOI: <https://doi.org/10.31349/RevMexFis.3.010604>

1. Introduction

The Naica mine is located in a semi-desert region in the south-central part of the state of Chihuahua (Mexico). The "Cueva de los Cristales" (Cave of the Crystals) was discovered by miners in 2000. Its galleries have been celebrated worldwide due to the purity and the 10 - 11 meter dimensions of the gypsum megacrystals they house [1-6]. Its crystals are a system of large structures, type "rosette", called "blocky", and shaped like beams, which cross the cave from wall to



FIGURE 1. Naica's "Cueva de los Cristales", showing several beam-like crystals with diameters of 0.5 – 1 m and some blocky type crystals. All crystals grow from the wall.

ceiling or floor to wall. The main chamber has a temperature of $\approx 50^\circ\text{C}$ and relative humidity near to 100%. The view of a section of the Cueva de los Cristales is shown in Fig. 1.

This study presents the mineralogy of the rock-crystal interface obtained by powder X-ray diffraction (XRD), micro-X-ray fluorescence (μ -XRF) and micro-X-ray absorption near edge fine structure (μ -XANES).

2. Materials and methods

2.1. Samples description

All the study samples were sections of a single blocky gypsum crystal torn from the Cueva de los Cristales wall, specially donated by Industrias Peñoles for the present study (Fig. 2). The image of the crystal surface shown in Fig. 2 includes a brownish layer of variable thickness, which corresponds to the wall on which the blocky crystal was attached. The mentioned layer of the blocky crystal thus represents the wall-crystal interface, the object of this study.

From this unique gypsum crystal specimen, it was possible to prepare four different types of samples (Fig. 2): 1) "LMS" - wall rock limestone; 2) "A" - a wall-crystal interface layer on gypsum single crystal, related to the nucleation process; 3) "B" - a section of the wall-crystal interface on the bulk crystal, related to the growth process; 4) "C" - red

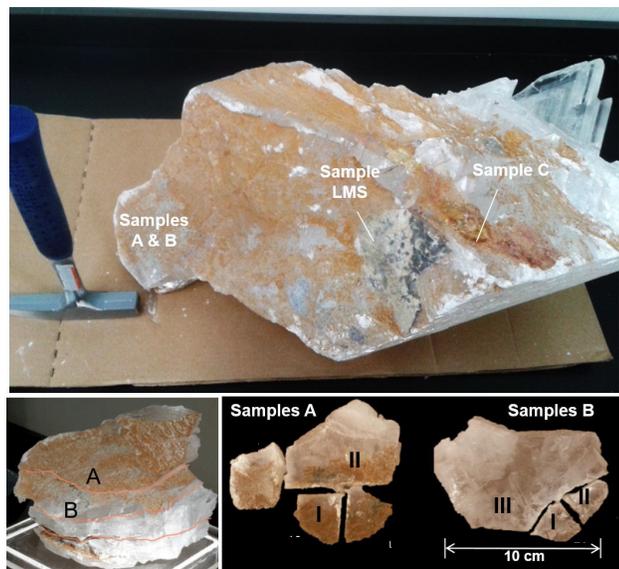


FIGURE 2. Top: Wall-crystal interface of the blocky crystal, showing the limestone section (LMS), the samples A and B, and the brownish overlay attached to the crystal base (C). The brownish surface constitutes the wall-crystal interface. At the upper right the cleavage planes (0,1,0) of the sample are appreciated. Bottom: Left: samples A and B, stacked after their extraction from the blocky crystal. Right: representative images of the A and B samples, showing crystal faces and dimensions.

mineral coating extracted from the crystal surface. A total of 11 samples were analyzed. The LMS sample was sectioned for petrographic observation, and the remaining volume was finely ground to obtain several representative aliquots for chemical and phase analyses. Two sections of sample A and three sections of sample B were obtained along the cleavage plane (0,1,0).

2.2. Characterization methods of the wall-crystal interface

The nature of the mineral aggregates found in the wall-crystal interface samples was characterized by the following techniques. Shapes and dimensions were obtained by confocal differential interference contrast microscopy (LCM-DIM), performed with a LSM 700 (Zeiss, Jena) system. Petrographic and mineragraphic observations complemented the mentioned analysis. Chemical composition was studied in an ICP-OES Thermo Jarrell Ash, IRIS AP/Duo, and by secondary and backscattering electron images, using a scanning electron microscope Hitachi SU3500 (SEM-EDS). Mineral phases and formation environment were obtained as a result of applying powder XRD patterns, performed in a PANalytical X'Pert Pro diffractometer in Bragg-Brentano geometry, with a PIXcel3D detector using Cu $K\alpha$ radiation, by SEM-EDS, μ -XRF and μ -XANES methods. The last two methods, for most samples, were performed at Stanford Synchrotron Radiation Lightsource (SSRL), beamline 2-3. Other μ -XRF maps and μ -XANES were acquired at the XRF beamline 10.1, at Elettra - Sincrotrone Trieste (ELETTRA). In this

work, we present the morphology and describe the results of chemical composition and mineral phases obtained by optical microscopy, and of applying XRD, SEM-EDS, μ -XRF and μ -XANES methods.

3. Results and discussions

Sample A, taking advantage of LCM-DIM, provided a three-dimensional view of the wall-crystal interface (Fig. 3). In this method, the light goes through the transparent gypsum and emits a shadow when light intercepts an opaque object. It was observed that individual particles form microscopic aggregates. Also, they present irregular shape, being separated by empty spaces and defining a layer of 30 to 60 μ m thick on the wall-crystal interface. The arrangement of these particles follows the cleavage planes.

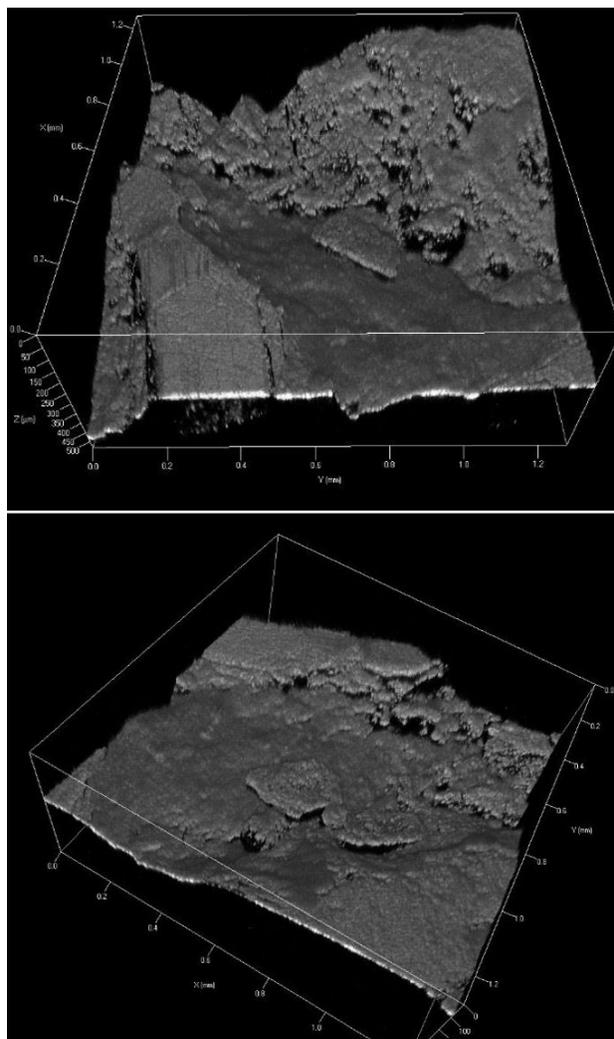


FIGURE 3. LCM-DIM 3D image views of the A-I sample interface. The greyish sandy material corresponds to the mineral aggregates of the interface. The black areas correspond to the transparent gypsum crystal, which is not visible because it transmits light.

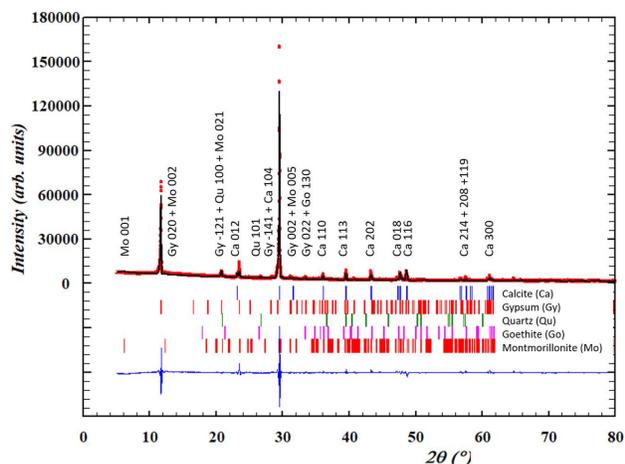


FIGURE 4. Observed and calculated XRD patterns for sample C-III. Representative diffraction peaks from identified phases are indexed.

3.1. Mineral phases

The phase composition of the mineral aggregates was determined by powder XRD. For sample C-III (brownish coating, Fig. 4), in addition to the intense reflections of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Gy, resulting from the scraping of the wall-crystal interface) and calcite (CaCO_3 , Ca), weak signals from quartz (SiO_2 , Qu), goethite [$\text{FeO}(\text{OH})_2$, Go] and montmorillonite [$(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, Mo] were detected.

Sample C-III permitted correlating these phases with both chemical and optical results obtained in C-I and C-II samples. Some of the minerals were previously identified by Gázquez *et al.*, [7] in the phreatic zones of the walls of the Naica caves. The phases of the aggregates already identified by XRD were confirmed and complemented by SEM-EDS, μ -XRF and μ -XANES analysis, unraveling minor or trace elements and phases composition. A standard two-step procedure was followed for synchrotron radiation experiments: μ -XRF mapping (Fig. 5) allocated regions of interest (ROI) where elements As and Pb spatially overlap. Then, they were chosen for the speciation of a few elements with μ -XANES.

Some representative μ -XRF maps with their corresponding μ -XANES spectra, acquired at the Mn, Zn and Fe edges on sample A-II, are presented in Fig. 6.

In the μ -XRF maps, there was a positive correlation among Zn, Fe, and As signal intensities. Also, in the μ -XRF maps of the four samples, Pb and Mn signals showed spatial correlations. By the analysis of μ -XANES Fe K-edge spectra, the presence of goethite ($\alpha\text{-Fe}^{3+}\text{O}(\text{OH})$) in all samples can be established [8]. Copper was detected only in sample B, allowing the identification of μ -XANES spectra of cuprite (Cu_2O) and chalcocite (Cu_2S) [9,10]. A Mn_2O_3 content [11,12] was observed on sample A, while on sample B, the coronadite $\text{Pb}(\text{Mn}^{+4}, \text{Mn}^{+2})_8\text{O}_{16}$ was identified [13]. Some samples presented a low content of lead, which was probably amorphous. As μ -XRF maps also showed that Pb and Zn spatially coincide, some μ -XANES Pb L_3 -edge spectra identification of larsenite was suggested in areas studied on

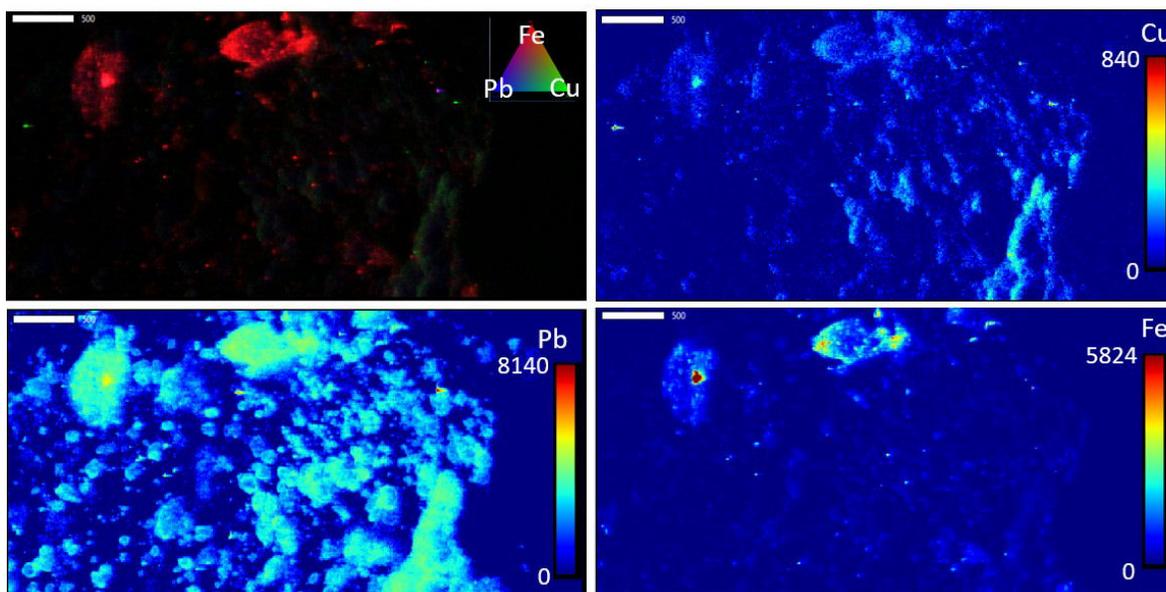


FIGURE 5. μ -XRF maps of an area of sample B-I, excited by a $3 \times 5 \mu\text{m}^2$ beam of 13200 eV. The total scanned area was $4.7 \text{ mm} \times 2.3 \text{ mm}$, with a step size of $10 \mu\text{m}$ in both scan directions, and 250 ms dwell time. The areas of highest intensities were chosen for acquiring μ -XANES spectra. Top-left: Tricolor map: The intensity of the colors red, green and blue correspond to the intensity of the signals of the fluorescent emissions Fe K_{α} 6405 eV, Cu K_{α} 8048 eV, and overlapping As K_{α} 10 543 eV and Pb L_{α} 10 551 eV. Top-right: Rainbow intensity of Cu signal. Bottom-left: Rainbow intensity of Pb-As signals. Bottom-right: Rainbow intensity of Fe signal. BL2-3 (SSRL).

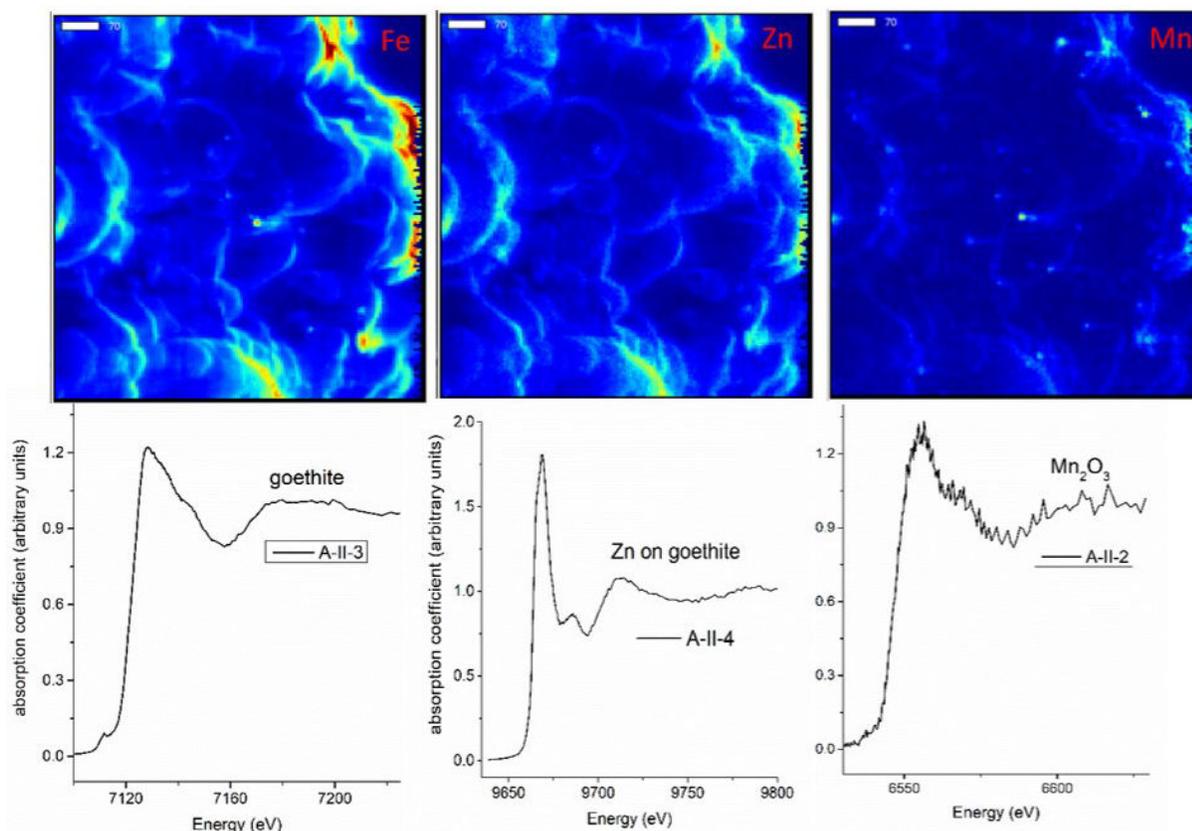


FIGURE 6. μ -XRF maps of Fe, Zn and Mn intensities of an area of sample A-II, excited by a $3 \times 5 \mu\text{m}^2$ beam of 13200 eV. μ -XANES spectra were acquired in the ROIs taken on the zone of high intensities, at the Fe (left), Zn (center) and Mn (right) K-edges. BL2-3 (SSRL).

samples A and B. The impurities of Zn and As should be adsorbed on hematite Fe_2O_3 , goethite, and ferrihydrite $(\text{Fe}^{3+})_{4-5}(\text{OH},\text{O})_{12}$ [14,15]. Conversely, other Pb spectra from samples B have been identified as cerussite (PbCO_3) [16-20].

4. Conclusions

Synchrotron light spectroscopy techniques (μ -XRF and μ -XANES), together with electron microscopy and XRD, were used to identify the minerals involved in the nucleation and growth process of the gypsum blocky crystal. Calcite, silica and minor phases gave the Fe, Mn, Zn, Cu, As and Pb particulate substrate on which these processes took place. These findings support the hypothesis of heterogeneous nucleation, with few initial nuclei, as the first step of formation history.

Acknowledgments

The support given by Consejo Nacional de Ciencia y Tecnología Project No. 183706 is acknowledged. The support of Industrias Peñoles for providing the main sample of all experiments is accredited. The authors are also thankful to the National Nanotechnology Laboratory in CIMAV Chihuahua, México. μ -XRF and μ -XAS spectra were measured (as part of Proposal No. 3939) at the Stanford Synchrotron Radiation Lightsource (SSRL), a Directorate of SLAC National Accelerator Laboratory, and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University. The support provided by International Centre for Theoretical Physics (ICTP), and Elettra Sincrotrone Trieste under proposal 20165205 is acknowledged.

1. P.S. Garofalo *et al.*, Climatic control on the growth of gigantic gypsum crystals within hypogenic caves (Naica mine, Mexico). *Earth Planet. Sci. Lett.* **289** (2010) 560, [nurlfhttps://doi.org/10.1016/j.epsl.2009.11.057g](https://doi.org/10.1016/j.epsl.2009.11.057g).
2. A. E. S. Van Driessche *et al.*, Ultraslow growth rates of giant gypsum crystals. *Proc. Nat. Acad. Sci.*, **108** (2011) 15721, <https://doi.org/10.1073/pnas.1105233108>.
3. A.E. Van Driessche *et al.*, Unraveling the sulfate sources of (giant) gypsum crystals using gypsum isotope fractionation factors. *J. Geol.*, **124** (2016) 235, <https://doi.org/10.1086/684832>.
4. R. M. Marín Herrera, F. Vogel Gonzalez, and R. Echegoyén Guzman. Las megaselenitas del distrito minero de Naica, Chi-

- huahua, una ocurrencia mineralogica anomala. *Bol. Mineral.* **17** (2006) 139.
5. J. M. García-Ruiz *et al.*, Formation of natural gypsum megacrystals in Naica, Mexico. *Geology.* **35** (2007) 327, <https://doi.org/10.1130/G23393A.1>.
 6. P. Forti and L. Sanna, The Naica Project: A multidisciplinary study of the largest gypsum crystals of the world 3. *Episodes* **33** (2010) 23.
 7. F. Gázquez *et al.*, The Caves of Naica: a decade of research. *Bol. Geol. Minero.* **127** (2016) 147.
 8. M. Wilke *et al.*, Oxidation state and coordination of Fe in minerals: An FeK-XANES spectroscopic study. *Am. Mineral.* **86** (2001) 714, <https://doi.org/10.2138/am-2001-5-612g..>
 9. M. Salomé *et al.*, The ID21 Scanning X-ray Microscope at ESRF. *J. Phys.: Conf. Ser.* **425** (2013) 182004, <https://doi.org/10.1088/1742-6596/425/18/182004g..>
 10. J. Yang *et al.*, Speciation and distribution of copper in a mining soil using multiple synchrotron-based bulk and microscopic techniques. *Environ. Sci. Pollut. Res.* **21** (2014) 2943, <https://doi.org/10.1007/s11356-013-2214-8>.
 11. A. Carmona *et al.*, Environmental manganese compounds accumulate as Mn (ii) within the Golgi apparatus of dopamine cells: relationship between speciation, subcellular distribution, and cytotoxicity. *Metallomics* **6** (2014) 822, <https://doi.org/10.1039/c4mt00012a>.
 12. B.L. Stueben *et al.*, Manganese K-edge XANES studies of Mn speciation in Lac des Allemands as a function of depth. *Microchem. J* **76** (2004) 113, <https://doi.org/10.1016/j.microc.2003.11.011>.
 13. E. Chalmin, F. Farges, and G.E. Brown. A pre-edge analysis of Mn K-edge XANES spectra to help determine the speciation of manganese in minerals and glasses. *Contrib. Mineral. Petrol.* **157** (2009) 111, <https://doi.org/10.1007/s00410-008-0323-zg..>
 14. R. Loredó-Portales *et al.*, Zinc Speciation in Mine Dust and Soils in Mexico Trough Synchrotron Radiation. In. VIII Congreso Nacional de Cristalografía, II Reunión Latinoamericana de Cristalografía, VI Reunión de Usuarios de Luz Sincrotrón. Mérida, Yucatán, México (2016).
 15. R. Loredó-Portales *et al.*, Synchrotron based study of As mobility and speciation in tailings from a mining site in Mexico. *J. Environ. Chem. Eng.* **5** (2017) 1140, <https://doi.org/10.1016/j.jece.2017.01.019>.
 16. L.R. Baker *et al.*, Micro-X-ray fluorescence, micro-X-ray absorption spectroscopy, and micro-X-ray diffraction investigation of lead speciation after the addition of different phosphorus amendments to a smelter-contaminated soil. *J. Environ. Qual* **43** (2014) 488, <https://doi.org/10.2134/jeq2013.07.0281>.
 17. J. Dubrail *et al.*, Pb in naturally irradiated monazites and zircon. *In. J. Phys.: Conf. Ser.* **190** (2009) 012180, <https://doi.org/10.1088/1742-6596/190/1/012180g..>
 18. B. Saini-Eidukat *et al.*, Chemical Environment of Unusually Ge-and Pb-Rich Willemite, Tres Marias Mine, Mexico. *Minerals.* **6** (2016) 20, <https://doi.org/10.3390/min6010020g..>
 19. K. Funasaka *et al.*, Detection of Pb-LIII edge XANES spectra of urban atmospheric particles combined with simple acid extraction. *Sci. Total. Environ.* **403** (2008) 230, <https://doi.org/10.1016/j.scitotenv.2008.05.020>.
 20. J.E.S. Barrett *et al.*, Solid-Phase Speciation of Pb in Urban Road Dust Sediment: A XANES and EXAFS Study. *Environ. Sci. Technol.* **44** (2010) 2940, <https://doi.org/10.1021/es903737k>.