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Analysis by PIXE of Underground Water from Ixtacxochitla, Puebla

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Abstract. The *Sierra Negra* mountain range is located in the Southeast of Puebla, Mexico. This area is part of the Papaloapan basin, the third in importance in Mexico due to its water volume. According to some estimation, the local annual precipitation is around 4000 mm. At the same time, *Sierra Negra* is a very rich karstic zone. In the present work, the contents of heavy metals in water in karst streams in the site of Ixtacxochitla, was investigated for its potential use as an indicator of pollution. In a preliminary study, four points were chosen for sampling; they were selected at different stratigraphic levels in the cave. Concentrations of the elements Fe, Ni, Cu, Zn, and Zr were determined using particle induced X-ray emission (PIXE). The amount of trace elements bound to each sampling point may give insight of its availability and geochemical dependence. Metal amounts quantified in this study remained below the critical values established by Mexican drinking water regulations, although Cu concentration appears to be high in one of the sites. The most relevant result of the analysis is that toxic elements in water cave samples were below detection limits.

Keywords: Cave water, PIXE, Metal concentration.

INTRODUCTION

Underground water is a very important resource. Around 20 % of the Mexico territory is covered by limestone [1], which has the potential for cave formation. There are works on analyzing the elemental composition of underground water, more specifically on metals [2], but as far as we know, there are not reports on elemental analysis by PIXE on underground water of a cave. It is relevant to know the degree of resource conservation, in particular, levels of purity of the water of this area which belongs to the third basin in importance in Mexico. Research on potential contamination by colloids has been reported [3, 4]. Colloids have a large specific area and are considered charged species, and they show a high chemical reactivity which explains their ability to transport contaminants, such as heavy metals. In areas with dense vegetation, the abundant organic matter could act like a source of colloids, as is the case of the Ixtacxochitla zone. Moreover, an accelerated process of deforestation, including wood cutting and burning may be modifying the physicochemical properties of the soil. This process implies an increase in the contaminants, in particular metals, which leach into the cave and then dissolve in the water superficial streams. Although it is necessary to prove the hypothesis, this report is an initial attempt to systematize the information about the heavy metal contents in the underground water cave.

Site Description

Site Location

Ixtacxochitla is located in the *Sierra Negra* mountain range in the Southeast of Puebla, Mexico at approximately 300 km from Mexico City, or more precisely around 50 km East from Tehuacán. The boundary of the caves exploration zone is defined by an irregular polyhedron. The limits are: at the east Zoquitlán, at the southeast Coyomeapan, at the south the Zizintépetl mountain, at the north east Oxtopulco, and at the center Ixtacxochitla. The altitude ranges from 800 m up to 3250 m (Fig. 1) [5].

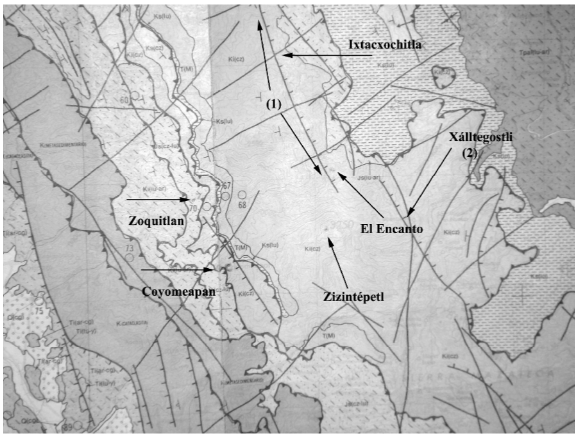

FIGURE 1. Geological map and sampling location. (1) *El Encanto* normal fault. (2) The hypothetical resurgence Xálltegostli. The arrows indicate the precise location for important sites.

The average rainfall, over the last years, was about 3000 mm/year, as shown in Fig. 2. The collector of this cave exploration zone is El Encanto system, which has at least four entrances. At this time the depth of the cave is around 320 m, considering its most elevated entrance and the exploration edge. This is the system where the water samples were taken. El Encanto normal fault, the collector area, is represented by (1). The hypothetical resurgence is the system Xalltegoxtli (2). More than one hundred entrance caves have been positioned in the exploration zone.

Geological Setting

During the Cretacic, 65 million years ago, almost all the surface of Mexico was under the sea. Thus, sediments associated to reefs were deposited practically in all the Mexican territory, mainly formed by calcium carbonate, which had their origin in the corals, the shell of rudistids, molluscs and other marine organisms. At the beginning of the Tertiary, these sediments transformed in limestone, were folded and broken to form the eastern *Sierra Madre del Sur*. The *Sierra Negra* is part of that. The *Sierra Madre del Sur* is structurally very complex. It has many tectonic domains, each one above the next. A compression phase at the end of the Mesozoic, which continued to the Tertiary, is responsible of many folds and horses. They have an important effect on the limestone of the *Sierra Negra*. The normal faults are associated with a set of horst and graben, resulting of a decompression phase during the Quaternary.

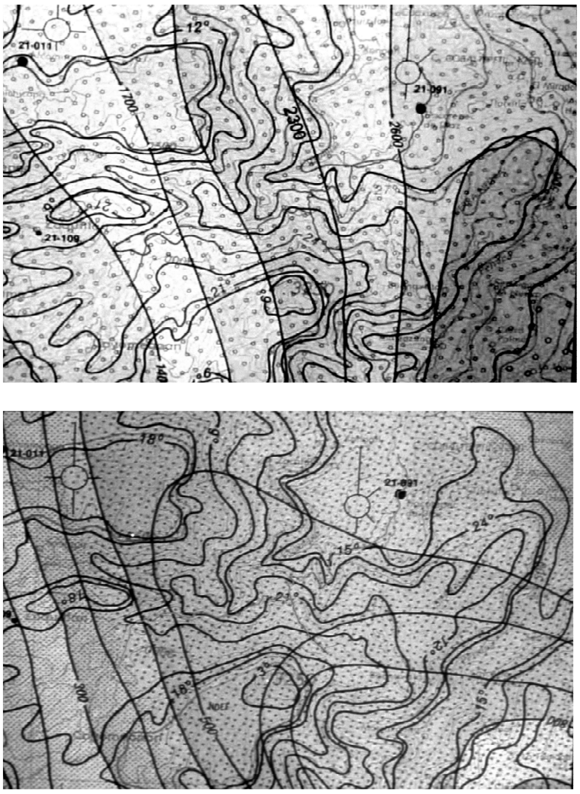

FIGURE 2. Pluvial and temperature maps for the wet (up) and dry (low) season. Numbers represent the rainfall in mm.

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The two phases described above, particularly the first one, gave the structure of its general orientation in a direction 150º-330º. This is particularly visible from the east, in the limits of *Presa Miguel Alemán*. Then, the foldings have a direct relationship with the morphology of the zone.

With regard to the stratigraphy of the exploration zone, it is possible to say that in the sequence base there is the Miahuatepec formation of the Aptian. It is characterized by grey and folded limestone, very brittle, with fractures filled with calcite. After this formation, the Morelos Formation is found from the Albian-Cenomanian, with a gray and massive limestone fossilized with gasteropodous, rudistids and micro-fossils [5].

Finally, the karstification of the exploration zone must be described. Over the land, the relieve is the result of a normal fault, called *El Encanto*. Almost all the entrance caves are aligned along this fault, which is expected because fractures and faults are the axes for the developing of the karst.

EXPERIMENTAL

Samples were taken at three different levels and settings in *El Encanto* cave system (Fig. 3). They were labeled according to sequence S1 to S3. One more sampling location was at the Xalltégoxtli cave system, based on the hypothesis that it is just here where *El Encanto* resurges (See Fig. 1). This location was labeled as (2) in Fig. 1: According to our notation, it was the sampling point S4. The sampling amount for each point was 1L. Pre-concentration of elements in the sample with carbamates was carried out with the following method: 500 mL of an aqueous solution were adjusted to pH 3.5-4. After this, 300 mg of APTC, 300 mg ascorbic acid (Merck), 20 mg of Cupferron (Merck), 15 mg of bisulfite (sodium salt dissolved in 5-mL deionized water), and 30 mg of oxine (Merck) previously dissolved in 2 mL of propanol, were added. Following the formation of carbamates, a 100-μL aliquot of ultra pure Pd (1 g/kg) (Merck) was added to co-precipitate the elements as carbamates. After a 5 min agitation and decanting for 30 min, the carbamates were deposited by filtration onto a polycarbonate Nucleopore™ 0.45 μm pore size filter. The elemental composition was determined by Particle Induced X-ray Emission (PIXE) at the Pelletron Accelerator, Instituto de Física, Universidad Nacional Autónoma de México [6]. The dried filters were irradiated under vacuum using a 3.0 MeV proton beam, where two semiconductor detectors (a Si PIN and an HPGe), with different efficiencies as a function of the X-ray energy emission, were used to collect the radiation. A thin (38 μm) Al foil was located in front of the HPGe detector to minimize background interference from lower energy X-ray emission. The GUPIX computer code [7] was used to simulate PIXE spectrum and to determine the elemental compositions.

RESULTS

Table 1 shows the element concentration for the metals found in the underground water of each sampling location, as well as the limit of detection of these metals. Concerning the toxic elements, the limits of detection for Co and Pb they were 0.037 and 0.063 μg/L respectively. Although the limit of detection for Co should be taken cautiously due to the overlapping of Co_{K_α} and Fe_{K_β} lines.

In Table 2, the measured metal concentrations are compared to the maximum concentration allowed for the Mexican Official Standard (NOM-127-SSA1-1994 modified in 2000) [8], for drinking water. The purity of the underground water of *El Encanto* is apparent, as the levels are two or three orders of magnitude below the allowed limits. However, the concentrations may vary, because the sampling was made in a rainy season, when probably more water goes to the underground system, giving lower values for the metal content in water. To date, we have water samples from the dry season, to be compared with those obtained in the present study. The presence of Cu and Zn may be associated to the presence of these elements in carbonates. On the other hand, the soils in the exploration zone are rich in iron, being the natural source for this element.

CONCLUSIONS

The underground water in *El Encanto* system at Ixtacxochitla is of relatively good quality, with heavy metals below the Mexican regulations for drinking water. The most relevant result of the analysis is that toxic elements in water cave samples were below detection limits. Finally, it must be pointed out that this work demonstrates the high sensitivity of PIXE to measure the very low concentrations of metals in the underground water.

TABLE 1. Element concentration for each sampling point, including Pd as internal standard, and the concentration range for the elements detected.

Element concentration [μg/L]	S1	S2	S3	S4	Limit of detection [μg/L]	range
Fe	2.4	7.1	2.7	2.1	0.053	2.1 a 7.1
Ni	0.64			0.98	0.04	0.6 a 0.9
Cu	7.8	1.02	1.51	1.50	0.03	1.0 a 7.8
Zn	ND*	0.093	ND	0.699	0.067	0.1 a 0.7
Zr	0.413	1.250	0.369	ND	-	0.4 a 1.2
Pd	200	200	200	200		

*Not detected

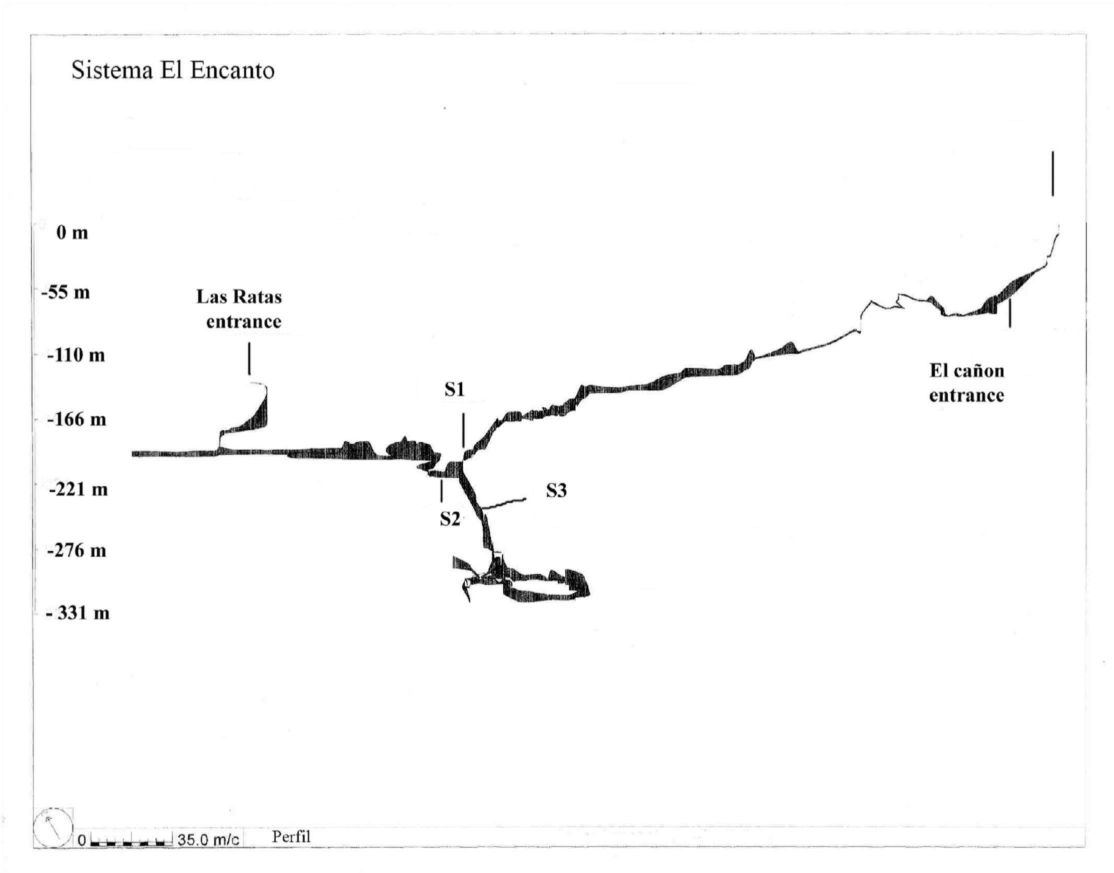

FIGURE 3. Cross section topography of *El Encanto* cave. S1, S2 and S3 correspond to the sampling points. The topography was performed by conventional topographical techniques by *Grupo de Espeleología Asociación de Montañismo*, UNAM.

TABLE 2. Metal concentrations measured in *El Encanto* cave and those set by the Mexican official standard.

Element	Experimental Range (μg/L)	NOM (mg/L)
Fe	2.1 a 7.1	0.3
Ni	0.6 a 0.9	NS*
Cu	0.1 a 7.8	2.0
Zn	0.1-0.7	5.0
Zr	0.4- 1.2	NS

*Not specified.

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