Radioactive mineral samples from the northwest of Chihuahua City, Mexico

M. Reyes-Cortés, M. E. Montero-Cabrera, M. Rentería-Villalobos, L. Fuentes-Cobas, E.F. Herrera-Peraza, and H. Esparza-Ponce.

Abstract

The Chihuahua-Sacramento valley is an area of 6 km wide by about 32 km in length, it is located from north to south. In the area, at least two zones exist that may have rocks with radioactive minerals: The Pastor´ıas zone at the SW and the Majalca-San Marcos zone to the NW. The latter, was the object of the present investigation. By studying the geologic conditions and the processes of alteration in the San Marcos deposits, its hydrothermal origin and the different (at least two) alteration stages that has transformed the alkaline rhyolitic rock into per-alkaline were determined, to do more favorable the conditions for the hexavalent uranium minerals deposits. In the mineralogical characterization the following radioactive species were identified: uranofane, metatyuyamunite and uraninite. These minerals were found also with secondary quartz-feldspar mineralization, with abundant hematization and an advanced process of argillization. The XRD, SEM and optical microscopy analyses of samples were very important for the accomplishment of the present investigation.

Keywords: Radioactive minerals; petrographic microscopy; X-ray diffraction; scanning electron microscopy; uranium deposits.

El valle Chihuahua-Sacramento es un área de 6 km de ancho por unos 32 km de largo, dirigido de norte a sur. Existen en el área al menos dos zonas con posibilidades de aportar rocas con minerales radiactivos; la zona de Pastorías al suroeste y la de

Majalca-San Marcos al noroeste. Ésta última, fue el objeto del presente trabajo. Mediante el estudio de las condiciones geológicas y los procesos de alteración en los yacimientos de San Marcos, se determinó su origen hidrotermal y las diferentes (por los menos dos) etapas de alteración que transformaron a la roca riolítica alcalina en peralcalina, para hacer más favorables las condiciones del depósito de minerales de uranio hexavalente. En la caracterización mineralógica se identificaron las siguientes especies radiactivas: uranofano, metatyuyamunita y uraninita acompañadas por mineralización secundaria cuarzo-feldespática, con abundante hematización y un avanzado proceso de argilización. Los análisis no destructivos por DRX, MEB y microscopía óptica, fueron decisivos para la realización del presente trabajo.

Descriptores: Minerales radiactivos, petrografía, difracción de rayos X: microscopía electrónica de barrido; depósito de uranio.

Introduction

The state of Chihuahua is a semi desert area. Most of the urban area of Chihuahua City (671,790 inhabitants) is located in the denominated Chihuahua-Sacramento valley. This is an area of 6 km wide by 32 km in length located from North to South . Alluvial deposits of 220 m thickness have been determined on a clay base of the Tertiary age [1]. The recent investigation of Rodriguez Pineda et al. [2] proposes that the sediments of Chihuahua-Sacramento reach more than 3,500 m depth. Nevertheless, for the North region the depth could be smaller. In the area, at least two zones exist that may have rocks with radioactive minerals: The Pastor´ıas zone at the SW and the Majalca-San Marcos zone at theNW. A great part of those sediments and alluvial fans has been eroded from the hills of the San Marcos-Majalca area, where there have been located about 30 radiometric anomalies [3].

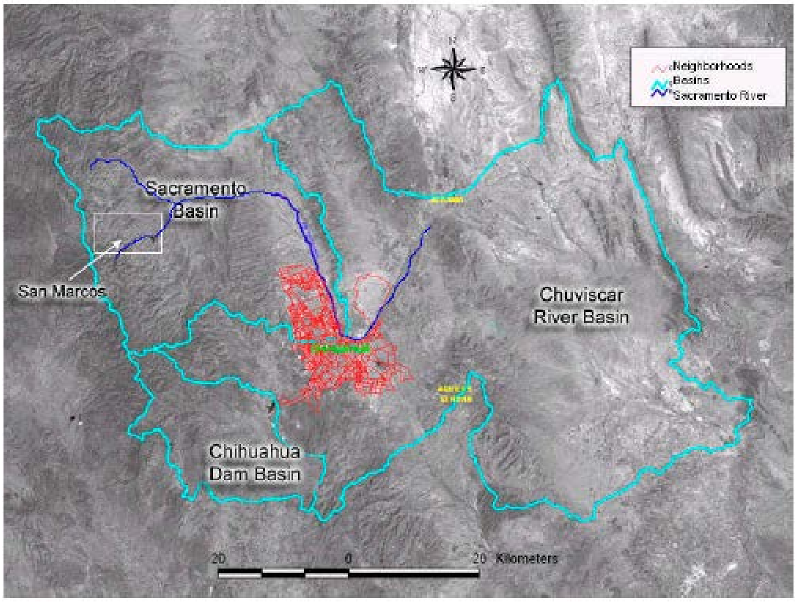

FIGURE 1. Location of the study area in the state of Chihuahua, Mexico.

TABLE I. Optical properties of uranium minerals, observed in San Marcos area.

MACROSCOPIC ASPECT	URANOPHANE	TYUYAMUNITE	METATYUYAMUNITE	URANINITE	PITCHBLENDE
SYSTEM	X	X	X	X	X
FORM OR HABIT	Veins, powdery masses prismatic to acicular	Veins, botryoidally powdery masses	Veins, Crystalline aggregates	Veins	Veins
COLOR	Orange-yellow	Yellowish green	Yellowish green	Black	Black
STREAK	Yellow	Yellow	Yellow	Black	Black
LUSTER	Pearly	Adamantine	Powdery	Submetallic	Submetallic
FLUORESCENCE	Pale green	X	X	Olive green	X
H	2	2	2	5	5
G	3.7	3.5	3.7	9	8
MICROSCOPIC ASPECT					
SYSTEM	Monoclinic	Orthorhombic	Orthorhombic	Isometric	Amorphous
FORM OR HABIT	Prismatic	Radial, aggregates	Radial acicular	Botryoidal	Botryoidal
COLOR	Yellow	Green	Green	Black	Black
PLEOCHROISM	Yellow	Yellow	Yellow	X	X
REFRACTION INDICE	n = 1.65	n = 1.90	n = 1.90	X	X
EXTINCTIÓN ANGLE	Parallel	Parallel	Parallel	X	X
INTERFERENCE FIGURE	Biaxial (-)	Biaxial (-)	Biaxial (-)	X	X
2V	35°	30°	45°	X	X

This zone was the objective of the present investigation (Fig. 1). The intention is to characterize the minerals that are the primary sources of water radioactivity in the zone and to give an explanation of the processes that generated the mineral deposits.

U and Th are lithophile elements; they are strongly partitioned in the continental crust and their average content varies as a function of rock type. Usually acidic rocks contain more Th and U than mafic rocks. These elements are likely to be more concentrated in argillaceous deposits than in sandstone and limestone when located in sedimentary rocks. Both U and Th exist in the +4 and +6 oxidation states in most geologic environments. In the weathering environment the U is much more soluble and mobile than Th in oxic natural waters. U tends to form strong associations mainly with organic material and with dissolved phosphates. Under arid conditions, U forms several relatively stable compounds (e.g. oxides, carbonates, phosphates, vanadates, and arsenates) [4].

The volcanic rock uranium deposits are commonly associated with Mo, F and Th and they can be found at felsic rocks from subalkaline to potassium peralkanine, where the uranium can be concentrated. The host-rock generally has been albitised, argillized, hematized and/or altered by carbonation. Gandhi and Bell [5] assert “Type examples include the rhyolite-hosted Michelin in Labrador, Canada, the trachytehosted Rexpar deposits, British Columbia, Canada, and the ignimbrite-hosted Peña Blanca deposits in Chihuahua, Mexico.”

The purpose of this research is to demonstrate that the San Marcos area had a primary hydrothermal deposition of tetravalent uranium on acid or neutral environment. This uranium was reactivated by geothermal processes that involved convection of groundwater for redeposits uranium in hexavalent state, on a peralkalin environment; this was done in a similar way to the one done to the deposits of Peña Blanca, Chihuahua [6-7].

Materials and methods

The samples studied by the scanning electron microscope (SEM) and by x-rays diffraction (XRD) were selected accordingly to the petrographic analyses performed to them. All the samples sent for study of x-rays diffraction were carefully scraped from the matrix rocks. The diffractometer Philips X'Pert MPD was used in XRD. This technique provided important information about the mineral structure by phase analysis.

The morphologic characterization, like relief, porosity and microscopic spaces of the dissolution were performed with the SEM Jeol JSM-5800 LV. The electron microprobe associated to the microscope was used in order to determine the elemental composition of crystals and grains. Doing this, the exact position of the radioactive elements among other minerals was determined.

In the deposits of Peña Blanca, to the east of San Marcos, it has been radiometrically dated the tetravalent uranium deposits with a very erratic age of 9 ± 4 my. In addition an age of 2 my has been proposed for the hexavalent uranium deposits [7]. This information is useful to interpret the events of mineralization of the San Marcos zone. A manual gamma ray scintillation detector was used for the location in the field of radioactive rocks, therefore allowing the finding of areas with greater uranium content. The location of some uranium deposits in the area of San Marcos was already reported [8], making easier to locate three points with anomalies, from which, the samples for the research were obtained.

Results

Radioactive minerals optical study: The samples collected in the three different deposits from the San Marcos area, were carefully prepared for their study at the polarizing microscope. After their petrographic examination the most representative samples were analyzed by XRD. Table I shows the radioactive minerals identified with optical microscopy technique. Tyuyamunite was not reported by XRD. The main macroscopic and microscopic characteristics observed are listed in Table I.

All the species were found forming veins (Fig. 2), in thin threads inside the rock fractures or forming small nuclei inside the leached feldspars spaces. Whereas statistically, the uranophane occupies more spaces in feldspars, the metatyuyamunite appeared more scattered in the argillized vitreous matrix. The uraninite and pitchblende were found only in an intensively oxidized breach.

Agreeing with the observations done directly in the outcrops in the field, a sequence of events can be confirmed in Fig. 3. First, by means of the microscope, in this sample it is observed a feldspar crystal leached by some solution, which also altered the matrix that surrounds it. The silified and hematized matrix indicates that all these solutions loaded with different ions Si^{+4} and Fe^{+3} were attacking the feldspar crystal and the matrix. The environment that was generated then could be more favourable. Next, the mineralization of tetravalent uranium in form of uraninite and pitchblende was deposited in the leached feldspar cavities (the black colour fraction at the center of the crystal observed at Fig. 3). In third place, with the pH change caused by the feldsparization (K+), hexavalent uranium was precipitaded as silicate (uranophane).

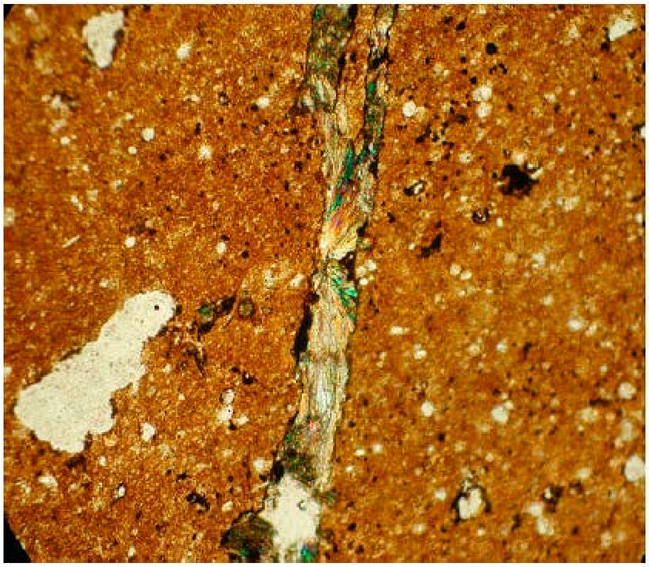

FIGURE 2. Micrograph, non polarized light. Metatyuyamunite with pitchblende vein filling up ignimbritic rock fractures of the Quintas unit. Width 3 mm.

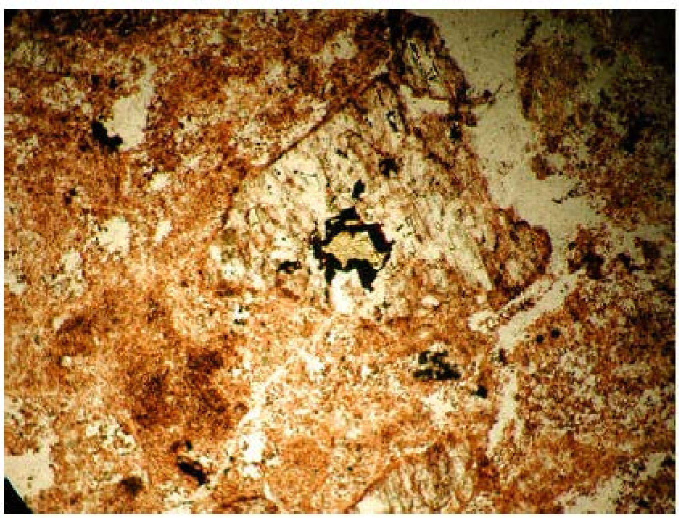

FIGURE 3. Micrograph. Rhyolitic ignimbrite of the Victorino Unit, it shows a phenocrystal of feldspar in a strongly silicified vitreous matrix. At center of feldespar crystal there are pitchblende (black) and uranophane (light). Width 5 mm.

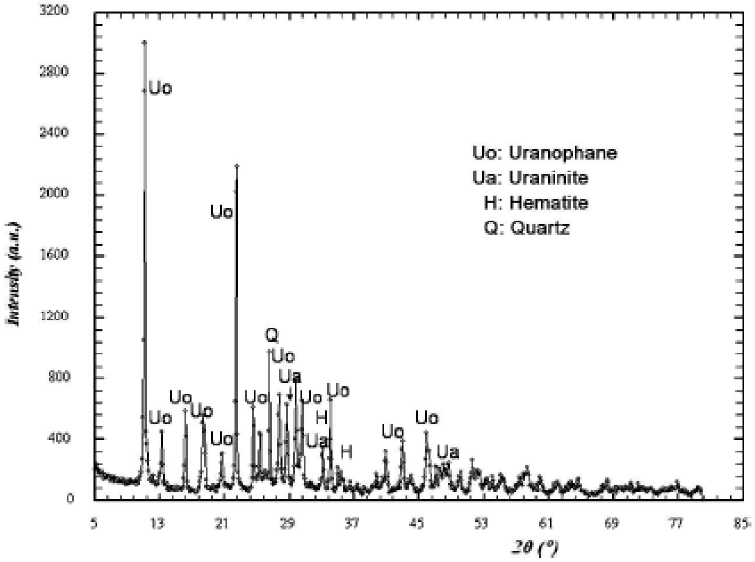

FIGURE 4. Diffraction pattern of a San Marcos's sample, showing uranophane as the main mineral in the rock, accompanied with hematite, uraninite and quartz.

X-ray diffraction: Figure 4 shows the diffraction pattern of a collected sample in the San Marcos deposit. The sample is characterized by a reddish coloration due to intense oxidation undergone by hydrothermal solutions. The diffraction pattern evidently shows uranophane as the main mineral. The presence of hematite and quartz appears because it was not possible to completely separate them from the uranium mineral at the rock matrix. As observed in the micrographs of Fig. 3, hematite and quartz are included in the rock matrix.

Another representative sample was collected in the Victorino-Tinajas area. It is a breach of a rhyolitic ignimbrite rock with its fractures filled by a black mineral, submetallic color, surrounded by yellow mineral. In this sample, the diffraction pattern indicates the presence of uraninite, metatyuyamunite and uranophane. It is presumed that most of the black mineral could be pitchblende. Using the optical microscope, this mineral seems to have an amorphous constitution. The crystallized portion produced a very representative XRD pattern of uraninite, with relatively broad peaks, due to small crystallites sizes.

Scanning electron microscope results: The model on the origin of the uraniferous deposits became consolidated while the laboratory analyses advanced and agreed with the field observations. From the geologic point of view, it was established that after the deposit of the last lithologic unit and the location of the dikes and resurgent domes in the zone of the caldera of San Marcos, the introduction of hydrothermal solutions showed in at least two different stages.

The hydrothermal solutions loaded with iron and potassium altered the original rock and formed the favorable niche for the deposition of the uranium mineral. The results of the scanning electron microprobe, supported the chemical elements and mineral association with the paragenesis of the uraniferous deposit. It was possible to verify that the uranium mineral had been deposited in a peralcaline area (with abnormal potassium presence on the rhyolitic rock). For this particular case the original rock didn't contain potassium in excess, but it was acquired due to the contribution of the hydrothermal solutions.

Figure 5 is the spectrum of a sample collected in the San Marcos zone where the presence of potassium accompanying uranium is observed. This run was made on the sample with minerals "in situ". A thin section of the polished surface of the rock was taken from the zone where a mineral nucleus was located (Fig. 6).

The elemental distribution (mapping) is observed in Fig. 7 where the concentration in the same zone of uranium and potassium matches. Here, the uranium mineral has been determined previously by analysis of x-rays diffraction, turning out to be uranophane. This mineral does not contain potassium and therefore, the potassium that reports the microprobe must be surrounding the uranophane. It is suggested that potassium was deposited before the arrival of the uranium mineral and the potassium worked as “preparing” material of the hexavalent uranium.

In another location, to the north of San Marcos, at the Cerro de la Cruz, two samples were collected, one close to the deposit and the other at the mineralized breach. The first sample does not report uranium, but it reports a 32% of weight in iron, which is quite anomalous for a rhyolitic rock. It is suggested that the rock presents an intense hematization as consequence of hydrothermal solutions. These liquids surely acted as the first event of alteration, after the setting of the dikes and domes present in the region and, of course, previous to the deposition of uranium. The second sample shows almost no iron but it appears to contain vanadium, uranium and calcium. These elements are constituent of the metatyuyamunite, reported by x-rays diffraction, for the same sample. In the SEM uranium mapping, calcium and vanadium match in position. They belong to the metatyuyamunite mineral. In addition the concentration of potassium appears in the same place even though, it does not belong to the mineral.

Discussion: uranium mineralization

In events with participation of hydrothermal solutions it should be emphasized that not much information exists about the fractionation of the elements that belong to the uranium radioactive series [9]. That is why only conceptual considerations are exposed here.

At Victorino unit, located at the San Marcos area, an uranium deposit was found in rhyolitic ignimbrite rocks. The uranium deposits are part of a hydrothermal phenomenon composed at least by two events of alteration previous to the mineralization of uranium. At the beginning, the introduction of quartz and feldspar caused numerous veins formation; then, an intense argillitic alteration with hematization occurred. Both events help the conditions of the site to be able to carry the deposit of the uranium mineral. The radioactive anomalies are aligned throughout several parallel fractures. The hematized and argillized fractures almost took a course E-W in the unit Quintas and they continued for more than 300 m until cutting a rhyodacitic dike at the West area. This indicates that the fracture is subsequent to the dike. The analyzed samples with the highest uranium mineral content were obtained from one of these fractures.

The quartz veins with feldspar and hematite are extremely thin, not greater than 3 cm of thickness. They contain more amount of quartz than of potassic feldspars. In addition, they contain cristobalite and tridymite. Opal incrustations appear in some cases. Normally, the hematite and goethite appear scattered in the argillized matrix of the rock. The hematization is evident when the original feldspars are totally or partially kaolinized. In some cases, only feldomolds and a relict texture are observed.

The argillitic alterations of deposits act mainly replacing the rock matrix by a quartzfeldspatic aggregate micro to cryptocrystalline with chalcedony and tridymite. In addition, where the density of the fractures is high, the rock is more altered by kaolinization and silication. The uranophane appears filling up thin fractures and forming veins. The cryptocrystalline uraniferous material is incrusted into the walls of the fractures as fine dust. This cryptocrystalline uraniferous material also replaces, partially or totally, the kaolinized feldspar and occupies the tabular form of the original molds of sanidine crystals.

At La Tinaja area, a sample of an amorphous material, from shining to opaque black color and highly radioactive, was collected. The XRD studies showed the presence of uraninite. This material was obtained from the fractures of a rhyolitic outcrop at the field. In one hand, the alteration in the samples of San Marcos presents quartz veins and sanidine with hematite, suggests that the fluid responsible for the early alteration had a relatively high content of K. In addition the recrystallization and the dissolution of the structures in the ignimbrite suggest that the alteration took place at high temperatures. On the other hand, another stage with the fluids responsible for the argillization has occurred. The strong hematization that is observed can indicate that the fluids were relatively low in temperature but high in oxygen fugacity.

Furthermore, the alteration stages of quartz-feldspar and hematite do not seem to be directly associated with the uranium mineralization. It seems that it increased the potassium feldspar and quartz content on the rock, which helped the tetravalent uranium deposit. Besides, the space coincidence between the hematization and the argillization as well as the filling up of the feldspar molds with kaolinite could attract or absorb the precipitation of hexavalent uranium. It is possible that low temperature fluids, including ground waters in supergenic conditions, were responsible of the argillization, uranium distribution and their mineralogical characteristics.

Conclusion

In accordance with the classification of the uranium deposits of the IAEA [10], San Marcos deposit is placed within the deposits type “Igneous with acid volcanic rock association". The deposits are formed by hydrothermal activity from high to low temperatures. The volcanic uranium deposits, according to Gandhi and Bell [5], happened mainly on formed volcanic rocks during a post orogenic period. The uranium is concentrated normally on potassium alkaline rocks. There are at least three uranium minerals that would be object of study by phase analysis and crystalline structures: Metatyuyamunite, Uranophane and Uraninite.

This investigation is the first characterization of radioactive minerals in the San Marcos area. The study of this area has both fundamental and practical significance. It will be possible to correlate San Marcos with other areas, mainly with Peña Blanca. It will be interesting to know if both areas have the same origin and structure, that means, they may be underground connected. Furthermore, ground and superficial water at the North of the Chihuahua-Sacramento valley could have uranium content, high enough to be a public health concern induced by the presence of the San Marcos uranium deposits.

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