

Uranium minerals from the San Marcos District, Chihuahua, Mexico

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Abstract

The mineralogy of the two uranium deposits (Victorino and San Marcos I) of Sierra San Marcos, located 30 km northwest of Chihuahua City, Mexico, was studied by optical microscopy, powder X-ray diffraction with Rietveld analysis, scanning electron microscopy with energy dispersive X-ray analysis, inductively coupled plasma spectrometry, and gamma spectrometry. At the San Marcos I deposit, uranophane $\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_7 \cdot 6(\text{H}_2\text{O})$ (the dominant mineral at both deposits) and metatyuyamunite $\text{Ca}(\text{UO}_2)(\text{V}_2\text{O}_8) \cdot 3(\text{H}_2\text{O})$ were observed. Uranophane, uraninite (UO_{2+x}), masuyite $\text{Pb}(\text{UO}_2)_3\text{O}_3(\text{OH}) \cdot 3(\text{H}_2\text{O})$, and becquerelite $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot (8\text{H}_2\text{O})$ are present at the Victorino deposit. Field observations, coupled with analytical data, suggest the following sequence of mineralization: (1) deposition of uraninite, (2) alteration of uraninite to masuyite, (3) deposition of uranophane, (4) microfracturing, (5) calcite deposition in the micro-fractures, and (6) formation of becquerelite. The investigated deposits were formed by high-to low-temperature hydrothermal activity during post-orogenic evolution of Sierra San Marcos. The secondary mineralization occurred through a combination of hydrothermal and supergene alteration events. Becquerelite was formed in situ by reaction of uraninite with geothermal carbonated solutions, which led to almost complete dissolution of the precursor uraninite. The Victorino deposit represents the second known occurrence of becquerelite in Mexico, the other being the uranium deposits at Peña Blanca in Chihuahua State.

Introduction

In Chihuahua State, Mexico, there are about 30 known uranium anomalies; almost all of which are located in the vicinity of Chihuahua City, the state capital. Two major deposits are Victorino and San Marcos I, both in the San Marcos area NW of the capital. Deposits in this area are comparable to the well known Peña Blanca deposit, NE of the capital. (Calas 1977; Goodell 1985; Pearcy et al. 1994; Prikryl 2009).

According to Gascoyne (1992), uranium occurs as a trace element in igneous rocks, particularly in silicic rocks, at concentrations of about 6 ppm. In the San Marcos area (Fig. 1), 20 anomalies, where the concentration of uranium exceeds 30 ppm, have been identified (Chávez et al. 1981).

In the San Marcos area, hydrothermal processes led to the deposition of U(IV) minerals in rocks of rhyolitic composition. Subsequently, this uranium was remobilized by convecting geothermal fluids and deposited as U(VI) minerals. These features and the presence of argillized quartz-feldspar aggregates are similar to the deposits of Peña Blanca, Chihuahua (Goodell 1985; Pearcy et al. 1994). It is possible that the San Marcos deposits are associated with a caldera (Ferríz 1985).

The Upper Volcanic Series of the Sierra Madre Occidental consists mainly of rhyolitic tuffs and some Upper Cenozoic intermediate volcanic sequences. Uranium anomalies are located in this Series in the San Marcos area (Fig. 1), specifically in the Unidad Quintas, which was originally described as the Quintas Victorino Formation (TVq) by Spruill (1976). Ferríz (1985) described the lower member of this unit as the Victorino Formation at Cerro La Tinaja. According to Ferríz (1985), the Victorino formation consists of a moderately consolidated rhyolitic welded tuff that reaches

thicknesses of more than 250 m without its lower contact being exposed. The thickness of the Victorino formation would indicate an intracaldera facies. The superior member, called Quintas Ignimbrite (TQ) (Spruill 1976) and Formación Cumbres (Chávez et al. 1981) outcrops in the vicinity of the Las Quintas ranch and consists of welded rhyolitic tuff, with a thickness of more than 200 m.

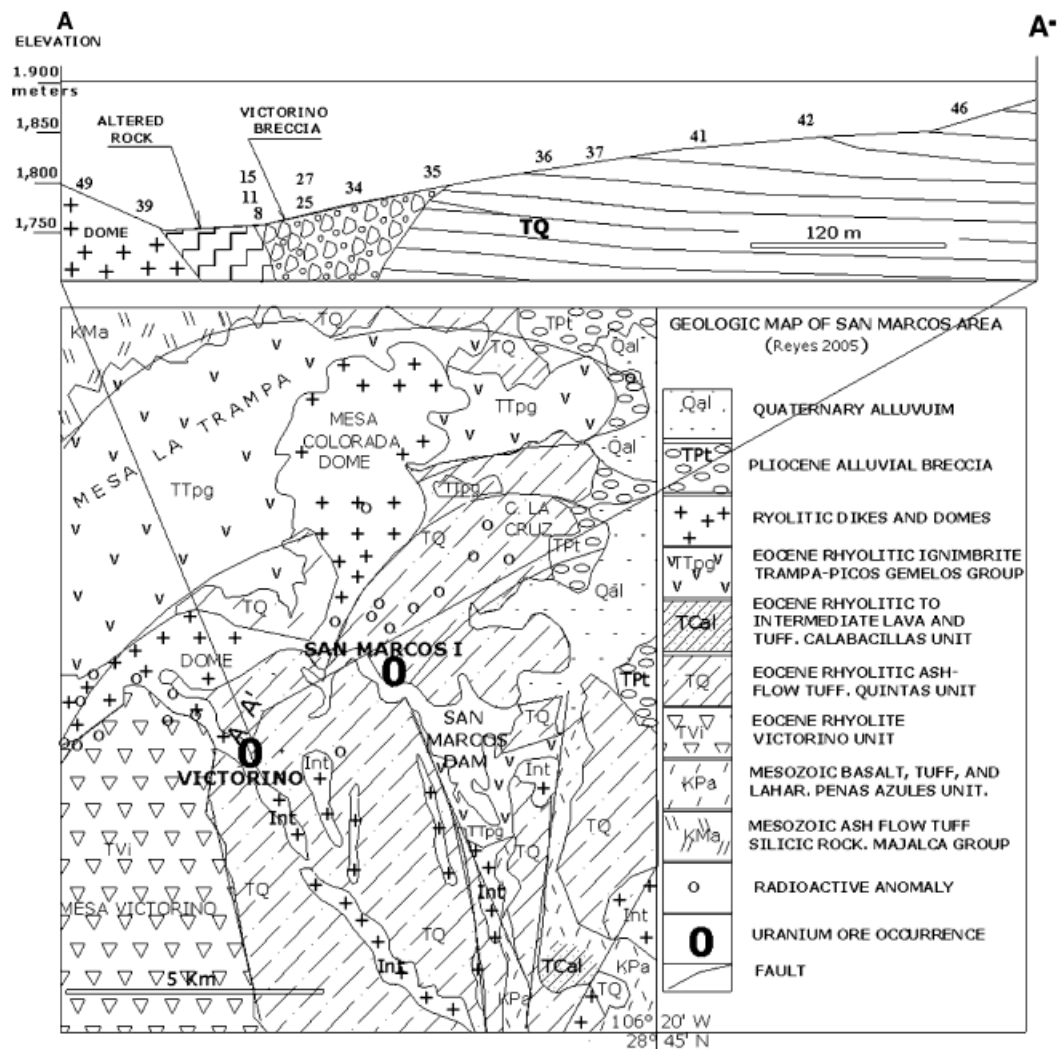


Fig. 1 Geology of San Marcos area showing the location of the Victorino and San Marcos I deposits, as well as other radiometric anomalies. Also shown are the idealized cross-section of the mineralized breccia and the Victorino sampling locations

The uranium deposit in Victorino is part of a collapse breccia in Unidad Quintas. In contrast, the San Marcos I rocks show only micro fracturing. The host rock for both

deposits is the Unidad Quintas. In addition, there are different dikes and rhyolitic domes with strongly distorted vertical flow structures, which can sometimes be confused with this unit.

The purposes of the present study are to identify the minerals of the Victorino and San Marcos I uranium deposits and to establish their paragenetic sequence.

Sampling area and analytical techniques

Figure 1 shows the geology and stratigraphy of the San Marcos area, (Reyes-Cortes et al. 2007), as well as the various points where radiometric anomalies have been found, including the Victorino and San Marcos I deposits. The insert in Fig. 1 is an idealized cross-section of the Victorino deposit showing the brecciated zone, contact with a rhyolitic dome and sampling points. Table 1 presents the association of collected samples with their respective geologic formations, as well as the different types of analyses that were carried out.

Mineral identification was carried out using optical microscopy (OM) using an OLIMPUS SZH-10 polarizing microscope and an OLIMPUS AX-70 stereographic microscope. Based on the OM results, representative samples were selected for study by X-ray diffractometry (XRD) using a PHILLIPS X'PERT MPD equipped with a Cu-K α source. Rietveld analysis of XRD data was performed using the Fullprof code (Rodríguez-Carvajal 2001). Samples were also studied by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) using a JEOL JSM-5800 LV scanning electron microscope operated at 15 kV. Elemental analysis was performed by inductively coupled plasma spectrometry (ICP) using a Thermo Jarrel Ash IRIS/AP spectrometer and by gravimetric methods. Gamma spectrometry (GS) was

used to determine uranium, thorium and potassium concentrations using a 10×10 cm NaI (TI) detector, coupled to a CANBERRA spectrometer. The computer programs GENIE 2000 and Standard Stripping (Valenzuela Hernández 2006) were used to interpret the gamma spectra.

Petrography

Hand-specimen observations and OM examination showed that the Unidad Quintas is a massive, welded rhyolitic tuff, with a eutaxitic vitro-crystal-lithic texture, containing abundant lithic and deformed pumice fragments. It contains (by volume) 20% to 25% of lithic fragments and 20% to 25% of quartz phenocrysts, sanidine, andesine-oligoclase and biotite. Other minerals present in amounts less than 1% include hornblende, albite, spherulitic orthoclase, riebeckite, ilmenite, zircon, titanite, magnetite and possibly apatite.

In the Victorino deposit area, all of these minerals occur in a glassy matrix that underwent partial devitrification, chloritization, hematization, argillization and pyritization. Recrystallization of spherulitic orthoclase replacing glassy matrix is often observed. The ignimbrite contains kaolinized and argillized feldspar phenocrysts refilled with uraninite and uranophane crystals (Fig. 2). This texture suggests that hydrothermal solutions caused kaolinization and partial leaching of the crystal. The glassy matrix has been partially replaced by adularia-type orthoclase and represents the product of recrystallization of spherulitic orthoclase. Goethite, hematite and pyrite pseudo morphs, produced by chemical weathering of pyrite, occur as filling in micro-fractures. The concentrations of these minerals decrease with distance from the deposit. The Victorino deposit occurs in an intensely brecciated zone that outcrops in an area of approximately

3,000 m² also in contact with a rhyolitic dome (Fig. 1). The matrix of the breccia is made up of uranium minerals (Fig. 3).

The extent of alteration of the rocks in the San Marcos I area increases with uranium mineralization. Quartz phenocrysts, microcrystalline chalcedony, opal and hematite–limonite veinlets were observed. Hematite also occurs as spots in the mineralized zone. Some feldspars show intense kaolinization and argillization. Hydrothermal solutions cause the breakdown of the feldspars by loss of sodium, potassium and, to some extent, silica. This process eventually led to the formation of argillic alteration products. Occasionally, feldspars are completely leached out, leaving only the crystal mold. Hydrothermal processes resulted in dissolution of ironbearing sulfides and corrosion of primary uranium minerals. These processes led, respectively, to the formation of iron oxy-hydroxides and uranyl oxide hydrates. In comparison with the Victorino area, alteration by argillization is more intense in the San Marcos I area.

Table 1 Summary of samples analyzed, provenance, and analysis methods

Sample	Deposit	Host rock type	Analytical methods
SMV 8	Victorino	Brecciated welded tuff	OM, XRD
SMV 11	Victorino	Brecciated welded tuff	OM, XRD
SMV 15	Victorino	Brecciated welded tuff	OM, XRD
SMV 25	Victorino	Brecciated welded tuff	OM, XRD, SEM/EDS
SMV 27	Victorino	Uranium mineral	OM, SEM/EDS
SMV 34	Victorino	Brecciated welded tuff	SEM/EDS, GS, ICP
SMV 35	Victorino	Brecciated welded tuff	SEM, GS, ICP
SMV 37	Victorino	Rhyolitic welded tuff	OM, GS, ICP
SMV 41	Victorino	Rhyolitic welded tuff	OM
SMV 42	Victorino	Rhyolitic welded tuff	OM, GS, ICP
SMV 46	Victorino	Rhyolitic welded tuff	OM
SMV 49	Victorino	Rhyolitic welded tuff	OM, GS, ICP
SM 53	San Marcos I	Rhyolitic welded tuff	OM, XRD, GS
SM 56	San Marcos I	Rhyolitic welded tuff	OM, GS, ICP
SM 60	San Marcos I	Rhyolitic welded tuff	OM, XRD
SM 64	San Marcos I	Rhyolitic welded tuff	OM, GS, ICP
SM 67	San Marcos I	Uranium mineral vein	OM, XRD, GS, ICP
SM 70	San Marcos I	Rhyolitic welded tuff	OM, GS

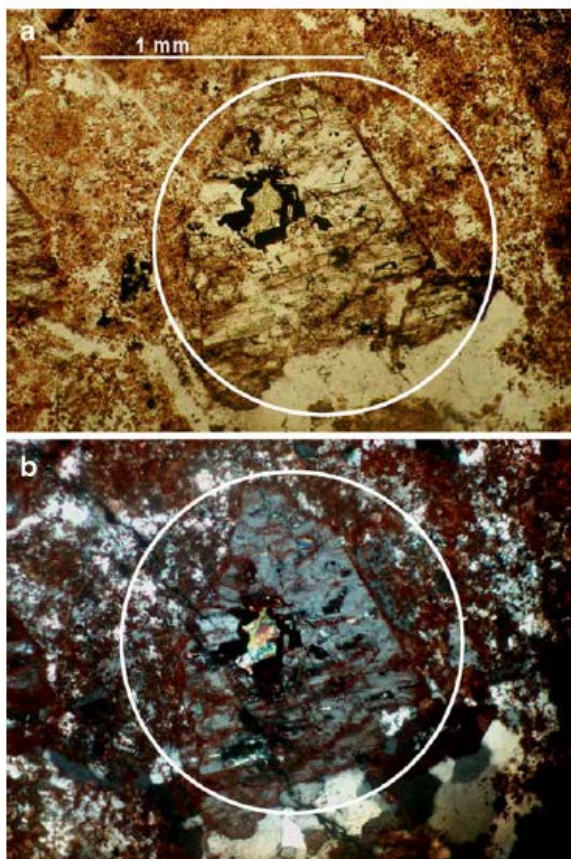


Fig. 2 Optical micrographs of Victorino sample SMV-35, which consists of a kaolinized feldspar phenocryst (*circled*) in a glassy matrix that has been argillized, silicified and partially replaced by spherulitic orthoclase. The leached core of the feldspar phenocryst consists of black uraninite and yellow uranophane. a Plane-polarized light and b crossed polars

Compositional analyses of mineralized and unaltered rocks

Samples of mineralized and unaltered rock from the Victorino and San Marcos I deposits were analyzed by ICP. Samples SMV-34 and SMV-35 were collected in the Victorino mineralized zone and samples SMV-37, SMV-42 and SMV-49 were collected outside the Victorino deposit (Fig. 1). The mineralized samples show a molar fraction ratio $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3 > 1$ and the ones collected from the fresh rock show a ratio less than 1. The altered rock from the Victorino breccia is slightly more alkaline than the

rock that was not altered and the brecciated rock is highly argillized and hematized, but there is no significant change in the elemental composition (Table 2).

At the San Marcos I deposit, uranium mineralization was only observed in the most intensely altered rock. Sample SM-67 was collected in the mineralized zone of San Marcos I, the rest of the samples labeled “SM” were collected outside the deposit. The low sodium content observed in the mineralized sample SM-67 (Table 2), when compared to mineralized samples from the Victorino deposit, can be explained by the more intense argillic alteration in the San Marcos I area.

X-ray diffraction of uranium minerals

A concentrated powder from the black fraction of Victorino sample SMV-8 was analyzed by XRD. The diffraction pattern shows the presence of uraninite, accompanied by significant amounts of uranophane, calcite and quartz. A separate from the yellow portion of the same sample was also examined by XRD. Uranophane was found to be the dominant mineral in this separate and was accompanied by small amounts of uraninite, hematite and quartz.

The most abundant uranium mineral in the San Marcos I deposit is uranophane. However, in sample SM-67, a calcite veinlet containing yellow–green areas showed the presence of metatyuyamunite. Phase analysis of a homogenized sample SM-67 showed the presence of quartz, orthoclase, uranophane, metatyuyamunite, nontronite and albite.



Fig. 3 Photograph of Victorino sample SMV-8, which consists of brecciated ignimbrite. Fragments are set in a matrix made up of (1) black uraninite (2) yellow uranophane and (3) becquerelite (in the white frame)

Table 2 Analyses of mineralized and non-mineralized samples, in weigh percents

Major oxides ^a	SMV 34	SMV 35	SMV 37	SMV 42	SMV 49	SM 56	SM 64	SM 67
SiO ₂	68.81	70.36	72.91	72.93	72.48	72.87	70.63	69.72
Al ₂ O ₃	10.67	11.06	12.40	12.27	12.20	12.26	13.05	12.08
K ₂ O	5.11	4.89	5.20	4.68	5.07	4.88	5.14	6.53
Na ₂ O	3.15	3.82	3.51	3.53	2.91	4.11	4.09	0.90
CaO	0.57	0.25	0.15	0.15	0.13	0.88	0.35	0.49
FeO ^b	1.89	1.51	1.78	1.32	0.80	0.79	0.91	0.75
MgO	0.07	0.10	0.05	0.02	0.07	0.12	0.17	0.28
MnO	0.07	0.11	0.02	N.D	N.D	0.06	0.08	0.22
TiO ₂	0.09	0.12	0.11	0.11	0.15	0.10	0.37	0.16
P ₂ O ₅	0.04	0.11	0.09	0.11	0.11	0.02	0.05	0.00
UO ₂	7.03	6.92	0.01	0.01	0.01	0.00	0.00	6.10
LOI	0.75	0.70	1.35	0.98	4.08	1.85	3.15	2.54
Total ^c	98.25	99.95	97.58	96.11	98.01	97.94	97.99	99.77
Na+K/Al ^d	1.00	1.04	0.92	0.88	0.84	0.98	0.94	0.71

SMV; Victorino area

SM; San Marcos I area

^a Major oxides normalized on a volatile-free basis

^b Total Fe as FeO

^c Total before normalization to 100% anhydrous

^d Na+K/Al = mol(Na₂O+K₂O)/Al₂O₃

Evidence for the presence of becquerelite in the Victorino deposit was found in several samples. Figure 4 shows the XRD pattern of an orange-colored powder that was carefully separated from sample SMV-8 (Fig. 3) using a needle probe. In spite of the care taken, incorporation of certain amounts of impurities in the separate was unavoidable. Rietveld analysis of the pattern in Fig. 4 showed the presence of about 5%

of becquerelite $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8 (\text{H}_2\text{O})$. Other phases identified in this sample include calcite (81.5%), uranophane (7%), microcline (5%) and masuyite (1%).

The XRD pattern of Fig. 4 shows at $2\theta \approx 12.5^\circ$ a peak that coincides with the most intense diffraction maximum of some U-Pb oxy-hydroxides (masuyite, fourmarierite and vandendriesscheite). The diffraction patterns of these minerals are very similar to each other, with comparable intense peaks in similar positions. When analysis of selected samples is performed, with comparison of modeled versus measured diffraction intensities, it is observed that the best profile-fitting results are achieved with masuyite. The hydrated U-Pb oxy-hydroxide in question is thus presumed to be masuyite.

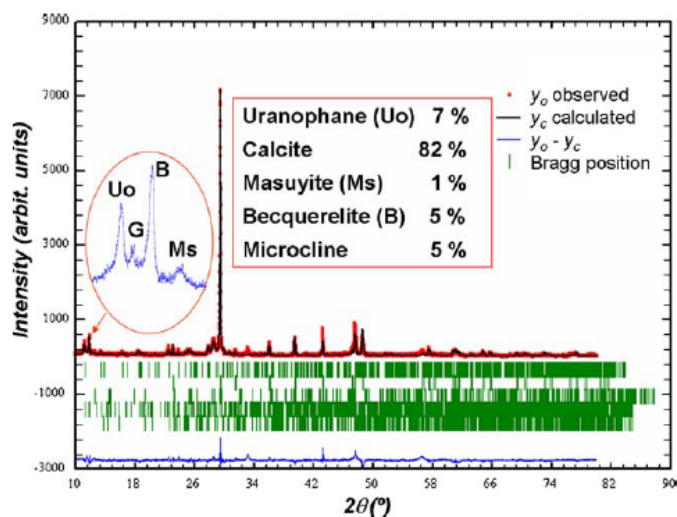


Fig. 4 XRD Rietveld analysis of sample SMV-8, representative of the Victorino deposit. The inset shows diffraction peaks characteristic of becquerelite and masuyite. Tick marks indicate the ideal positions of the Bragg reflections for the phases included in the refinement. The lower profile is the difference spectrum. The agreement factors for this

refinement are $R_p=15\%$ and $\chi^2=6$. The standard deviations of the concentrations are $\approx 1\%$. The weak peak denoted "G" has not been unambiguously identified. Its position coincides with the most intense peak of gypsum

Other minerals identified by XRD in most of the investigated mineralized samples are: quartz, sanidine, glass, spherulitic orthoclase, and hematite. Some samples contain calcite, albite and nontronite (SM-67). Microcline was identified in sample SMV-8.

Scanning electron microscopy/energy dispersive X-ray spectroscopy of uranium minerals

The metatyuyamunite in the San Marcos I sample (SM-67) was detected by XRD. Subsequent EDS analysis showed the presence of U, V, and Ca, which is consistent with the identification of this phase as metatyuyamunite. Elemental distribution maps obtained by SEM/EDS of sample SM-67, show the presence of K. Because metatyuyamunite does not contain K, the presence of K in the microprobe analysis of the same area where vanadium is present, suggests that it comes from the pre-existing partially leached feldspar.

The SEM micrograph of sample SMV-25 from the Victorino deposit (Fig. 5) shows the complex structure of a botryoidal aggregate of uraninite. Elemental distribution maps (by EDS) of Victorino sample SMV-25 show that the portion of the globular structure of uraninite is covered by a region with a slight increase in Pb concentration. Lead was identified mainly in the upper layers of the concentric structure (Fig. 5, area B). This area corresponds to uraninite, whereas Ca was detected in microfractures (Fig. 5, area D), where it is, presumably present in the form of calcite and becquerelite.

A more detailed SEM image of sample SMV-27 (Fig. 6) shows a globular grain of uraninite covered by a coating and containing some inclusions. Area A is massive microcrystalline uraninite, area B is botryoidal uraninite with inclusions of masuyite, and area C contains a crystal with elevated levels of both U and Pb, which suggests the presence of masuyite.

Uranium minerals

Uraninite (UO_{2+x}): In hand specimen, uraninite was observed in abundance. It has a massive texture and forms the matrix of fractured rock referred to as the Victorino breccia (Fig. 3). In thin section, it is characterized by a botryoidal habit consisting of radial lumps ranging from 1 to 10 mm in diameter (Fig. 7). Microcrystalline uraninite is easily recognized by XRD due to broadening of diffraction peaks arising from the very small size of its crystallites.



Uranophane is the prevalent mineral in both ore deposits. In San Marcos I, uranophane is accompanied by a small percentage of metatyuyamunite. The uranophane fills fractures and replaces part of the glassy matrix of the ignimbrite. In the Victorino deposit, uranophane occurs together with becquerelite and masuyite in the breccia and partially replaces feldspar and devitrified glassy matrix.



A small amount of becquerelite was identified in a fragment of the Victorino breccia consisting of a matrix filled with uranium ore (Fig. 8a). It was necessary to use concentrated samples of the uranium ore associated with this fragment to obtain representative diffraction patterns. Rietveld interpretation of the XRD patterns was performed and becquerelite concentrations of up to 5% were determined (samples SMV-8 and SMV-15).

This secondary mineral can be produced by oxidation of uraninite in situ (Wogelius et al. 2007), i.e. does not necessarily involve precipitation from an aqueous solution. In Fig. 8b, the uraninite is intersected by a network of micro-cracks filled with calcite and uranophane. The uraninite fragments are isolated by this network of calcite

veinlets. Small (1 mm in diameter) orange-colored grains in altered areas of the uraninite (Fig. 8c and d) are interpreted as becquerelite formed by oxidation of the uraninite.

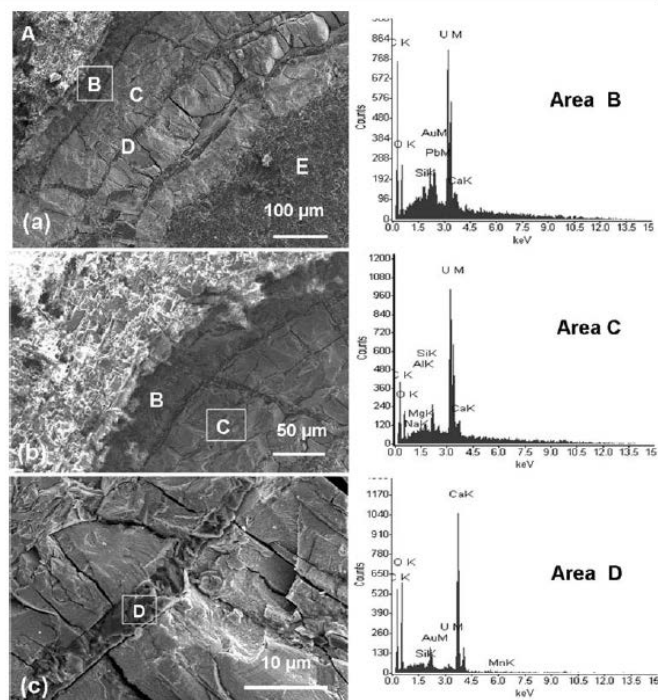
Masuyite $Pb(UO_2)_3O_3(OH)_2 \cdot 3(H_2O)$

Many samples from the Victorino deposit contain uraninite with a botryoidal structure and curved fractures sub-parallel to the surface. The elemental maps of these samples show no evidence of V, but Pb is present in a scattered, irregular pattern and may be linked to masuyite (Fig. 6). This mineral was not observed by OM.

Metatyuyamunite $Ca(UO_2)_2(V_2O_8) \cdot 3(H_2O)$

Metatyuyamunite was identified by OM and XRD. It was only observed in the San Marcos I deposit, in an area of fractured rock with micro-cracks filled with calcite and iron-oxy hydroxides.

Fig. 5 a Photomicrographs of botryoidal uraninite from Victorino sample SMV-25. The top layer (A) corresponds to the carbonatized rock, the immediate lower strip (B) is an area containing an anomalous Pb content, layer (C) is the main body of uraninite. The dark thin stripes (D) are micro-cracks filled with calcite and becquerelite and area (E) corresponds to the host rock. a The EDS spectrum on the right corresponds to area (B), uraninite with Pb. b Detail of (a). The EDS spectrum on the right corresponds to area C consisting of uraninite. c Detail of (a). The EDS spectrum on the right corresponds to zone D, which includes a veinlet filled with Ca and U mineral (possibly calcite and becquerelite)



Discussion

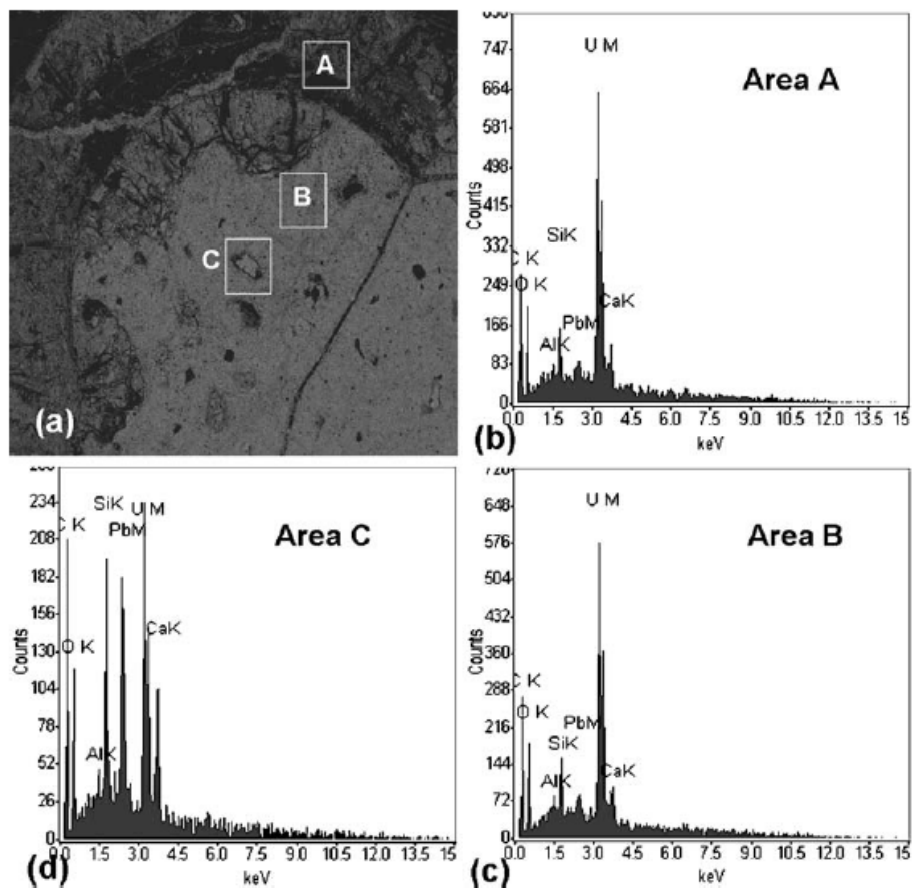
Uranium deposits in volcanic rocks commonly occur in alkaline to peralkaline rocks and the host rock is usually albitized, argillized and hematized or altered by carbonation. Examples include: rhyolite associated with the Michelin deposit in Labrador, Canada; trachyte associated with the Rexpa deposits in British Columbia, Canada (Gandhi and Bell 1995); and welded tuffs of Peña Blanca, Chihuahua, Mexico (Goodell 1985; Percy et al. 1994). This last deposit is located 50 km east of San Marcos and belongs to the same physiographic province. The rocks hosting both the Sierra de San Marcos and Victorino-San Marcos I uranium deposits are alkaline (Mauger and McDowell 1981). In the present work, it has been established that the rocks hosting the Victorino and San Marcos I uranium deposits have undergone argillization and hematization with the later deposit being more intensely altered. In addition, some of the host rocks have undergone carbonation.

Some uranium deposits in volcanic rocks are associated with large calderas (Chabiron et al. 2001) and may be located in distal or proximal volcanic facies of the caldera, ignimbrites, domes, volcanoclastic basins or caldera sediments (Plant et al. 1999). One example is the Moonlight Mine in the McDermitt caldera, northwestern Nevada (Castor and Henry 2000), where both peralkaline and metaluminous rhyolites have high background U and Th contents, which are generally slightly higher in the peralkaline rocks. Uraniferous zircon in that locality is hydrothermal, occurring in the breccia matrix and as crustiform layers in banded quartz–adularia–calcite veins. At the McDermitt caldera, U mineralization is located at different structural and topographic levels within the caldera system. The San Marcos area is thought to be part of a caldera

and Ferríz (1985) has suggested that the Victorino formation and Ignimbrite Quintas are intracaldera formations because of their structure and thickness, which totals more than 400 m.

The age of the Unidad Quintas in Sierra de San Marcos is 45–46 m.y. (Mauger and McDowell 1981), which correlates with the age of the nearby Nopal formation in Peña Blanca (43.8 m.y.) (Alba and Chávez 1974).

Fig. 6 a SEM image of Victorino sample SMV-27. The EDS spectra were taken in the areas corresponding to the lettered boxes. b EDS spectrum of the coating composed of massive micro-crystalline uraninite (*area A*). c EDS spectrum of the botryoidal uraninite matrix (*area B*). d EDS spectrum of an inclusion and its surrounding area, U and Pb indicate the presence of masuyite (*area C*)



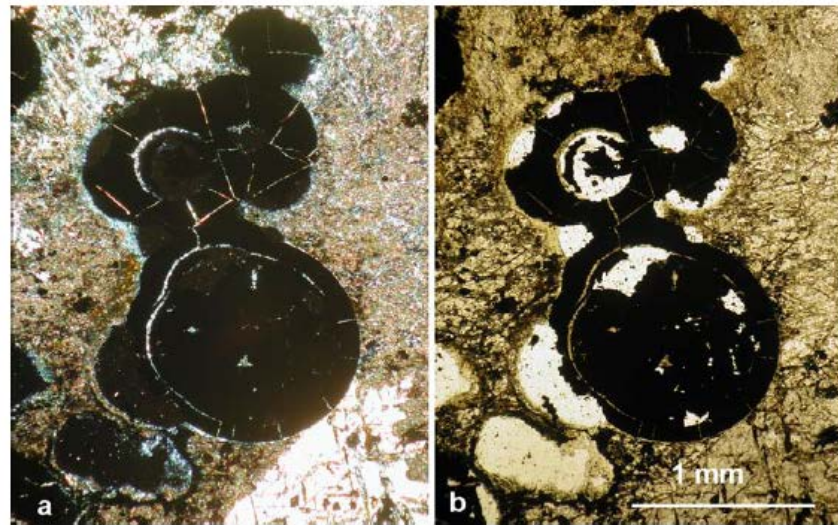
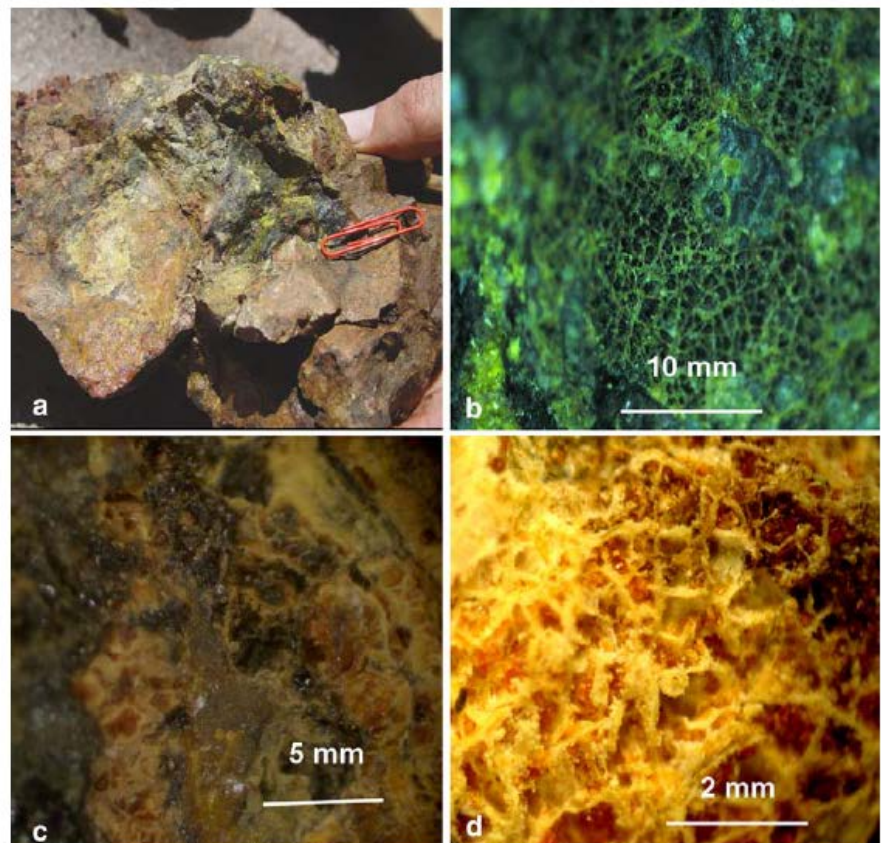


Fig. 7 Optical micrographs of Victorino sample SMV-34 showing botryoidal colloform uraninite (*black*) forming intergrowths with recrystallized calcite (*light-colored*) that fill empty spaces. a Crossed polars, b Plane-polarized light

Fig. 8 a Victorino breccia sample SMV-15 consisting of a matrix of uranium minerals. b Uraninite showing a network of micro-cracks filled with calcite and uranophane. c and d Orange grains of becquerelite encased by calcite and uranophane



The uranium deposit in Victorino is part of a collapse breccia in Unidad Quintas. In addition, there is a number of dikes and rhyolitic domes with strongly distorted vertical flow structures, which can sometimes be confused with this unit. In Nopal I, the mineralization is within a breccia zone, and alteration extends for a short distance into the welded tuff, the mineralized zone beneath the ignimbrite is reported to be cone-shaped with apex downward (Goodell 1981). However, the age of the San Marcos rocks is not necessarily the age of the uranium mineralization and can be correlated with the age of the dikes intruded after the ignimbrites and the tectonism that caused the brecciation. Indeed, Pickett and Murphy (1997) have concluded that in Peña Blanca, the isotopic and chemical data record a history of uraninite deposition several million years ago, followed by the deposition of uranyl silicates during a single episode around 3 Ma, and finally a complicated episodic U remobilization in the past few hundred thousand years. The uranium mineralization in the San Marcos district may have a similarly complex history.

Based on the petrographic observations and analysis of rock samples from the Victorino deposit, the uraninite was precipitated and then altered to oxy-hydroxydes and silicates by a combination of hydrothermal and supergene alteration. The feldspathization, recrystallization of spherulitic orthoclase and adularia replacing glassy matrix and feldspar phenocrysts are associated with the fluids responsible for the early alteration. Micro-fractures contain pyrite pseudo-morphs, goethite, hematite and uranium minerals. The abundances of these minerals decrease with distance from the deposit. All these features are very similar to the character of pyrite distribution in Nopal I (Peña Blanca), where fractures contain goethite, hematite, amorphous

Feoxyhydroxides, and jarosite $[KFe_3(SO_4)_2(OH)_6]$ produced by chemical weathering of pyrite. These fractures also contain anomalous U concentrations that decrease with distance from the deposit. This feature strongly suggests that U was mobilized and transported away from the deposit (Prikryl et al. 1997).

The ash flow tuff in the Unidad Quintas was devitrified and altered by a vapor phase. This process produced locally disseminated chlorite and pyrite, common recrystallization and dissolution structures, as well as alteration envelopes around quartz–feldspar (orthoclase)–hematite veinlets. Based on the available textural evidence, open spaces within the breccia were filled with primary and/or secondary uranium minerals. Uraninite also replaced feldspar phenocrysts and glassy matrix. We speculate that the dissolution of feldspar and U(IV) mineralization have occurred at a relatively high temperature. Fluid inclusion studies of similar types of veins in the Victorino deposit yielded a vein-forming temperature of $\sim 340^\circ\text{C}$ (Ferríz 1985).

Kaolinization and argillization of feldspars would result in an increase in pH and, thus, should have aided the absorption and precipitation of U(IV) (Fig. 2). The higher alkalinity of the mineralized breccia (samples SMV-34 and SMV-35) relative to the unaltered Unidad Quintas rocks (samples SMV-37 SMV-42 and SMV-49, Table 2), indicated by the significant differences in (Na + K)/Al ratio, supports this suggestion. Subsequent hematization and argillization suggest low temperatures and a high f_{O_2} value. Groundwater under supergene and geothermal conditions could have been responsible for the argillization. Furthermore, the paragenesis of uranium minerals at Nopal I in Peña Blanca has been proposed to be relatively simple, consisting of a primary uraninite–kaolinite–pyrite–quartz assemblage followed by uranyl oxide hydrates

and finally by uranyl silicates (Pearcy et al. 1995; Prikryl 2009). These mineralization processes have been described by several authors. Prikryl (2009) suggested that primary uraninite in the ore deposits at Peña Blanca has been almost entirely transformed to a suite of more stable, oxidized U(VI)- bearing mineral phases through several stages of groundwater alteration, which may have occurred over a period of several millions years. Some of the important alteration minerals (uranyl silicates) at Peña Blanca are soddyite, uranophane and weeksite. Earlier, Pearcy et al. (1994) and Pickett and Murphy (1997) concluded that the natural alteration of Nopal I uraninite was dominated by uranophane, the most abundant uranyl phase, with lesser amounts of soddyite and other uranyl minerals. Coincidentally, the most abundant uranium mineral in the San Marcos area deposits is uranophane. Fayek et al. (2006) have observed that at Nopal I, there are apparently at least two stages of uranium precipitation: at stage 1, uranium minerals precipitated from low-temperature fluids that interacted with the igneous silicate minerals in the welded tuff. These uranium minerals were mainly precipitated along cleavages of feldspars. At stage 2, uranium minerals were concentrated along fractures in the tuff. In contrast, at the Victorino deposit, the secondary minerals were formed by two processes: (1) oxidation of the uraninite in situ (Fig. 5) and (2) transport of uranium in hydrothermal solutions and its co-precipitation with calcite and hematite. In the later case, the geothermal solutions deposited uranium in a glassy matrix and in argillized feldspars in the rhyolitic rock (Fig. 2). The inferred paragenetic sequence at Victorino is (Table 3): deposition of uraninite, followed by precipitation of uranyl oxyhydroxides (masuyite, becquerelite) and, finally uranyl silicate (uranophane).

Becquerelite in the Victorino deposit was formed in situ by alteration of the microcrystalline uraninite by carbonate-bearing solutions. Oxidation of granular uraninite can produce uranyl-Ca complexes, which are precipitated as becquerelite to replace the altered feldspar (Wogelius et al. 2007). Becquerelite may have existed in greater amounts at Victorino and its current scarcity may be due to the fact that it is highly soluble in bicarbonate solutions. It was also observed by Sowder et al. (2001).

Although masuyite was not observed with a petrographic microscope, it was detected in the XRD patterns of concentrated samples (Fig. 4) and also by SEM / EDS (Fig. 6). Under oxidizing conditions, Pb^{2+} can combine with $(UO_2)^{2+}$ to form one of the more than 25 known uranyl-Pb minerals. Many of these minerals form by decay of uranium to lead but many others do not (Finch and Murakami 1999). The presence of hydrothermal Pb is likely to occur because the daughter products of U can escape from crystalline U-bearing solids and be transported by fluids. Therefore, the Pb concentrations can show significant local variations, unless the system is considered to be closed (Bourdon et al. 2003), which is not the case for the deposit described in the present work.

In the San Marcos I deposit, tetravalent uranium was not observed; U mineralization is present in the form of uranophane and metatyuyamunite. As evident from Table 2, $(Na + K)/Al$ ratio indicates that the host rock at San Marcos I area underwent a significant loss of alkalis due to intense hydrothermal alteration. One possibility is that uranium was initially deposited in tetravalent form, but was subsequently completely leached out as U(VI). Another possibility is that only U(VI) minerals were deposited, because of the intense argillization of the host rock.

Table 3 Paragenetic sequence of uranium minerals at Victorino

Mineral		Time →
Oxides	Uraninite	+++++
	Masuyite	-----
Oxi-hydroxides	Becquerelite	-----
Silicates	Uranophane	#####
-----	minor	+++++ abundant
		##### very abundant

Relative time sequence of formation and abundance of uranium minerals in the Victorino deposit

Conclusions

The following uranium minerals were identified in the deposits of the San Marcos area: uraninite, uranophane, metatyuyamunite, becquerelite and a uranium–lead oxy hydroxide (probably masuyite).

The occurrence of becquerelite is the second one reported in a Mexican uranium deposit. In contrast to the previously-made brief description of this mineral from Peña Blanca (Pearcy et al. 1994), the identification of becquerelite in the present work is based on convincing analytical evidence.

The uranium deposits of the San Marcos area in Chihuahua, Mexico, are similar to other uranium deposits associated with rhyolitic rocks (NEA 1998). Particularly, the main characteristics of the Victorino deposit are similar to those of the Nopal I deposit at Peña Blanca.

At the Victorino deposit, the U-enriched rock occurs in an area of approximately 3,000 m² in the southwestern part of the San Marcos area. The U mineralization occurs in breccia in ash flow tuff near its contact with a rhyolitic dome. At San Marcos I, U ore occurs in veins up to 2 cm in width cross-cutting altered tuff of the Unidad Quintas. The extent of the secondary mineralization decreases with distance from the deposit.

Similarities in mineralogy and alteration patterns in both deposits suggest that they are different manifestations of the same mineralizing system. The secondary mineralization is interpreted to have occurred through a combination of hydrothermal and supergene alteration events.

Based on mineralogical and textural evidence, the development and subsequent evolution of the U mineralization involved the following events: (1) uraninite deposition, (2) alteration of uraninite to masuyite (in zones of anomalously high Pb concentrations), (3) micro-cracking, (4) calcite deposition in the micro-cracks, and (5) formation of metatyuyamunite, becquerelite and uranophane. Becquerelite was formed in situ by geothermal alteration of the uraninite which had been almost totally leached away.

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