The reduced uraniferous mineralizations associated with the volcanic rocks of the Sierra Pena Blanca (Chihuahua, Mexico)

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Abstract

The uraniferous mineralizations of the Nopal I deposit (Sierra Pena Blanca, Chihuahua, Mexico) are related to a breccia pipe in a tertiary vitroclastic tuff (Nopal Formation). Detailed mineralogical and fluid inclusion studies led to the discovery of a primary mineralization stage of tetravalent uranium as part of an ilmenite-hematite phase. This stage occurs soon after the deposition of the tuff and is related to H₂O–CO₂–N₂ fluids, similar to those of the vapor phase, under temperatures ranging from 300 to 350°C. The well developed kaolinitization of the Nopal tuff is associated with a second tetravalent uranium stage (pitchblende-pyrite association). Fluids are aqueous and their temperature ranges from 250 to 200°C. The precipitation of pitchblende with pyrite within the pipe is due to a H₂S activity increase strictly limited to this structure. The remainder of mineralizing events, either hydrothermal or supergene, led to the hexavalent uranium minerals that prevail today.

Introduction

The uraniferous minerals mined in the Pena Blanca district, north of Chihuahua city, Mexico, are commonly oxidized minerals (uranophane, weeksite, haweeite, margaritaitite, metatyuyamunite, soddyite) (Calas, 1977; Uramex, 1980; Goodell, 1981; Wenrich et al., 1982). However tetravalent U minerals (pitchblende) have been described, but presently are only known in the Nopal I deposit (Rodriguez, 1976; Calas, 1977; Uramex, 1980; Goodell, 1981; Aniel, 1983). The relations between pitchblende, oxidized minerals, and wall-rocks alterations in this Nopal I deposit have not been clearly defined. According to Calas (1977), pitchblende may have the same age as the oxidized minerals and may have resulted from a local reaction between uraniferous solutions and already present pyrite.

Detailed mineralogical and chemical studies of Nopal I mineralizations (Aniel, 1983) led to the discovery of a primary depositional stage of tetravalent uranium minerals (stage 1) before the development of the previously mentioned pitchblende (stage 2). The purpose of this paper is to describe these two tetravalent U stages and their relationship with alteration products such as kaolinite and montmorillonite in the Nopal I deposit.

Geologic setting

The mining district is located in the eastern border of the central part of Sierra Pena Blanca, 50 km to the northeast of Chihuahua city. This Sierra belongs to the north–south trending Basin and Range Province of Mexico (Fig. 1). It roughly consists of a tertiary volcanic pile (ryholitic vitroclastic tuffs) overlying a calcareous basement of cretaceous age (Alba and Chavez, 1974; Cardenas-Flores, 1984; Magonetier, 1984a, 1984b). The Nopal I deposit looks like a breccia pipe and the mineralization is strictly located within this structure. A barren ring of altered tuffs (kaolinitization and locally development of montmorillonite) is observed up to 100 meters horizontally away from the "pipe" (Aniel, 1983; George-Aniel et al., 1984).

The unaltered Nopal formation is a partially melted vitroclastic tuff. Phenocrysts of Na–K feldspars (anorthoclase), quartz and oxide minerals (Ti-magnetite and ilmenite) with zircon inclusions and hematite exsolutions (Fig. 2A and 2B), are disseminated in a crystalline matrix, characterized by cristobalite and feldspar shards with axiolitic texture. In the Nopal Formation, vapor phase minerals (quartz and K feldspar) are locally observed (Aniel, 1983). In the altered ring, feldspar phenocrysts are progressively replaced by kaolinite; Fe–Ti and Fe minerals are stable. Within the pipe, both phenocrysts and matrix feldspars are completely kaolinized. The ilmenite and magnetite are no longer stable. The magnetites are replaced by a pitchblende-pyrite phase (Fig. 2C). Ilmenites appear to be stable (Fig. 2D), but detailed mineralogical and chemical studies of these minerals within the pipe led to the dis-
covery of a primary stage of uranium deposition, before the development of the present pitchblende-pyrite phase.

**Primary hydrothermal uranium oxides-ilmenite phase (phase I)**

Within the pipe, ilmenite phenocrysts seem to be similar to those of the fresh Nopal tuff, with the same elongation ratio (2.3) and the same zircon inclusions. However, they can be distinguished by their reflectance, their chemical composition, and by small pitchblende veinlets within crystals.

Polished sections were used to make measurements of reflectance (Standard SiC with $R = 20.4\%$ for $\lambda = 540$ nm). Outside the zones of pitchblende veinlets, these minerals have reflectance values ranging from 12.5 to 17.5%, whereas the ilmenites of the non-mineralized rocks have values between 19 and 21%. In hematite-enriched zones (exsolution lamellae and the crystal rim) the reflectance values are from 21 to 26% (Fig. 3). The decrease of reflectance in the ilmenites of mineralized samples does not result from increase in Ti or decrease in Fe content, or from exsolution or inclusions of hematite, magnetite or rutile. Such variations in Ti or Fe would, in fact, produce the opposite effect, an increase in the reflectance.

After a magnetic separation of minerals, powder diffraction patterns were made on ilmenites from the non-altered rocks and from the altered rocks located within the breccia pipe (Debye-Scherrer and Guinier de Wolf Cameras).

The positions of the X-ray powder lines obtained for the two types of ilmenite are identical and are close to those of ilmenite. For the same time (48 hours) the only difference between the two diffraction patterns is the width and the clearness of the lines. For ilmenites from the barren rock, lines are well defined, indicating well-crystallized material. In contrast, lines from ilmenites located within the pipe are diffuse. No other mineral phase is present in the diffraction pattern. If one exists, it is amorphous (metamict). Thus, X-ray diffraction studies confirm the existence, in both mineralized and barren rocks, of a phase with an ilmenite-type structure.

Analyses of these ilmenite-type structure minerals were obtained with an electron microprobe (automated Camebax electron microprobe). The chemical composition of this mineral is very homogeneous (Table 1) away from the pitchblende veinlets. The three most abundant elements are...
Fig. 2. Photomicrographs of phases occurring in the unaltered Nopal formation (A and B) and in the Nopal I deposit (C, D, E and F). (A) Stable microphenocryst of magnetite (Mt) (reflected light photomicrograph). (B) Ilmenite (Ilm) microphenocryst with zircon inclusions (Z) (reflected light photomicrograph). (C) Pitchblende (Pe) and pyrite (Py) pseudomorphs after magnetite (reflected light photomicrographs). (D) Ilmenite–uranium oxide phase (Ilm) with 3 zircon inclusions (Z), surrounded by pitchblende (Pe) and pyrite (Py). The pitchblende apparently formed prior to the pyrite (backscatter electron photomicrograph). (E) Backscatter electron photo of ilmenite–uranium oxide phase: (Z) zircon; (Pe) pitchblende; (1) boxworks after uranium was leached. (F) Backscatter electron photo of pitchblende (Pe) in fracture; (1) ilmenite–uranium oxide association where UO₂ content is about 62%; (2) uranium poor zone.

uranium (locally up to 67 wt.%), iron, and titanium (Fig. 4).

Minor elements are Ca, Pb and Zr. Th and the rare earth elements Ce and Y are less than the limit of detection. The Fe/Ti ratio in these uranium-rich minerals ranges from 0.30 to 0.47 instead of 0.90 to 1.25 as in ilmenites from the fresh tuff. This change in Fe/Ti ratio is interpreted as an iron loss during the uranium enrichment.

Traverses were performed on single crystals with a
CAMECA MS 46 electron microprobe to study the distribution of U, Ti, and Fe (Fig. 5A). It was found that significant concentrations of uranium (as pitchblende) and of titanium (as titanium oxides) clearly appear in the veinlets occurring in the ilmenite-type structure mineral (Fig. 5B). Outside these veinlets, the distribution of U, Ti, and Fe is rather homogeneous.

In backscatter electron microscope photomicrographs (Figs. 2E and F), heavy elements, such as uranium, are lighter in color. Areas enriched in titanium and iron, which are lighter elements, are greyish. In the apparently homogeneous zones, (as seen with the electron microprobe analyses), light and heavy elements are distributed in a uniform pattern. Uranium rich zones have a constant orientation which is independent of the pitchblende veinlets. They reflect the direction of the exsolution lamellae (hematite lamellae) in the ilmenites from the unaltered tuff.

Table 1. Representative analyses by automated Camebax electron microprobe (wt.%): (1) ilmenite from the fresh Nopal tuff; (2) pitchblende from the Nopal I deposit; (3) ilmenite-uranium oxide association; (4) U-depleted zones in association 1 from both sides of pitchblende veinlets (stage 2).

<table>
<thead>
<tr>
<th></th>
<th>Ilmenite (1)</th>
<th>Pitchblende (2)</th>
<th>U-oxide-Ilmenite (association 1) (3)</th>
<th>U-oxide-Ilmenite (association 1) (4)</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>0.45</td>
<td>0.16</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.30</td>
<td>0.16</td>
<td>0.06</td>
<td>0.06</td>
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<tr>
<td>Fe₂O₃</td>
<td>3.25</td>
<td>2.06</td>
<td>1.77</td>
<td>1.77</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.55</td>
<td>2.06</td>
<td>1.77</td>
<td>1.77</td>
</tr>
<tr>
<td>FeO</td>
<td>1.45</td>
<td>0.98</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>MnO</td>
<td>0.56</td>
<td>0.44</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.45</td>
<td>2.92</td>
<td>2.35</td>
<td>2.35</td>
</tr>
<tr>
<td>C₂O</td>
<td>4.45</td>
<td>2.92</td>
<td>2.35</td>
<td>2.35</td>
</tr>
<tr>
<td>Mn₂O₇</td>
<td>1.45</td>
<td>0.98</td>
<td>1.00</td>
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<tr>
<td>FeO</td>
<td>1.45</td>
<td>0.98</td>
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<td>C₂O</td>
<td>4.45</td>
<td>2.92</td>
<td>2.35</td>
<td>2.35</td>
</tr>
<tr>
<td>Numbers of ions on the basis of 2(01)</td>
<td>3(01)</td>
<td>2(01)</td>
<td>2(01)</td>
<td>2(01)</td>
</tr>
</tbody>
</table>

Fig. 3. Reflectance measurements vs. TiO₂ content in wt.% in different oxides. IIm: ilmenites; Pit: pitchblende; Mt: magnetite; Hm: hematite. Ia, Ib: magmatic phase; II: association 1; IIIa, IIIb and IIIc: association 2.

Fig. 4. Microprobe analyses of different oxides in a UO₂-TiO₂-FeO diagram (wt.%) (Aniel, 1983). (A) samples located within the Nopal I deposit; (B) oxides coming from the unaltered Nopal Formation.
Fig. 5. Traverses for U, Ti and Fe obtained with a CAMECA MS 46 electron microprobe (A) on the ilmenite–uranium oxide association (B).

These uranium-rich minerals are interpreted as a uranium oxide–ilmenite phase. It corresponds to a first concentration of uranium within the Nopal I pipe. Uranium precipitated within volcanic ilmenites, perhaps in micro-fractures controlled by the hematite exsolution lamellae lattice.

Such a uranium–iron and/or titanium phase has already been described in the literature. Zielinski (1978) mentions this phase in rhyolites of the western United States, but he did not determine the exact relations between uranium and the Fe–Ti–Mn oxides. In the mineralized systems of Duoblon (Sweden) (Lindros and Smellie, 1979; Smellie, 1982), the uranium released during the devitrification of the ignimbrites precipitates as fine-grained pitchblende in contact with ilmenite and ilmeno-magnetite. The destabilization of this phase leads to the formation of urano-titanate complexes. Elsewhere, Caruso et al. (1982) describe pitchblende deposition in micro-fractures occurring in ilmenites and in hematized feldspars. This deposition would result from an adsorption of uranium species on iron oxides such as hematite.

Pitchblende–pyrite phase (phase 2)

The pitchblende–pyrite phase (phase 2) occurs as disseminations in the kaolinized matrix, pseudomorphs of magnetites, or rings around the uranium oxides–ilmenite phase (phase 1). Pitchblende, without pyrite but with local TiO₂ concentrations, is also observed as small veinlets within phase 1. As for phase 1, the pitchblende–pyrite phase is strictly located within the pipe.

This pitchblende has a reflectance ranging from 12 to 14% (Standard SIC, R = 20.4% for \( \lambda = 540 \) nm) (Fig. 3) and the value of the unit cell, \( a \), determined by X-ray diffraction is 5.42Å. The pitchblende composition shows no systematic variation with its distribution in the mineralized tuff. Ca is the main trace element in this pitchblende (from 1.50 to 3.80 wt.% CaO) (Table 1). Pb content is also variable (0.06 to 2.35 wt.% PbO).

Microscope observations of altered and mineralized tuffs from the Nopal I deposit (Aniel, 1983) indicate that this pitchblende–pyrite phase is related to the kaolinization of the Nopal tuff. Hexavalent uranium minerals precipitated after this stage under oxidizing conditions; iron sulfides were transformed to oxides and hydroxides at the same time.

The relations between the two reduced phases, 1 and 2, can be seen on pseudomorphs after ilmenite where they both coexist. The pitchblende veinlets (phase 2) intersect phase 1 and are connected to the pitchblende–pyrite rings around the ilmenites (Fig. 5B). On both sides of these veinlets, there is a U-depleted zone (Fig. 6). Ti is also leached but to a lesser degree. This zone shows a regular lattice of lens-shaped holes as seen by scanning electron microscopy (Fig. 2E). Their orientation, shape, and size are constant and similar to the U-enriched zones in the ilmenite (phase 1). These holes (boxworks) are considered to have been the sites of the primary uranium deposition in the magmatic ilmenites (phase 1, Figs. 2E and 2F).
Fluid inclusion studies and genesis of the reduced uranium phases

Fluid inclusions are relatively rare in the Nopal I deposit and their study could only be performed on three types of minerals: the vapor phase quartz, the rhyolitic quartz within the altered tuff, and the late opal associated with uranophane.

The upper level of the Nopal tuff is characterized by vapor phase crystallization. The quartz is associated with euhedral potassic feldspars in small vugs. The fluid inclusions observed in the quartz are polygonal-shaped two-
phase inclusions with a high vapor/liquid volume ratio (±0.90).

In the rhyolitic quartz, fluid inclusions only appear when the tuff is altered. The one or two-phase inclusions are either disseminated with variable vapor/liquid volume ratios or distributed in healed fractures. For this latter type of occurrence, the vapor/liquid volume ratio remains constant (±0.20).

Lastly, fluid inclusions were observed in the opal which coats euhedral uranophane crystals. This opal precipitated during the latest hydrothermal event recognized by Aniel (1983) in the Nopal I deposit. The fluids are trapped in protoplasmic shaped one or two phase inclusions located between the opal spherules.

Two analytical techniques were used to define the composition of the trapped fluids. Small quartz or opal grains were crushed under the microscope with a crushing stage (Roedder, 1970) in anhydrous glycerin to detect the presence of insoluble gases such as CO₂ and CH₄. If gas bubbles appear in the glycerin another grain of the same sample was then crushed in Ba(OH)₂ to check for the presence of CO₂. The fluid inclusions were then studied with a Chaixmeca microthermometry apparatus as described by Poty et al. (1976).

Figure 7 illustrates the variations in the CO₂ content of fluids obtained by crushing of the different samples. The main results are: (1) CO₂ is very abundant in the vapor phase quartz (Fig. 7Ba); (2) CO₂ is also present in samples collected in the shear zones which limit the breccia pipe and its content decreases with increasing distance to the pipe; (3) no CO₂ is observed in opal (Fig. 7Be). All the results regarding salt contents and homogenization temperatures are given in Table 2.

Fluid inclusions from the vapor phase quartz have homogenization temperatures of about 400°C. The salt content of the liquid phase of these was not determined because of the large volume of the vapor phase (±0.90). The fluids in the rhyolitic quartz are salt-poor (0 to 5 equivalent wt.% NaCl) and the homogenization temperatures vary from 350 to 150°C: the salt content in the opal is lower (0 to 1.7 equiv. wt.% NaCl) and the homogenization temperatures do not exceed 150°C.

Combining these results with accurate petrological and mineralogical studies, Aniel (1983) shows that phase 1 developed in an environment rich in complex H₂O–CO₂–N₂ fluids, as indicated by gas chromatography analyses, and under temperatures ranging from 300 to 350°C. Uranium was leached by these complex fluids, probably within the breccia pipe, and transported as uranyl carbonate complexes. The precipitation of uranium oxides is due to a change in oxygen fugacity of the fluids which were in contact with the more reduced ilmenite–hematite phase (ilmenite with hematite exsolution). Such complex fluids are only found in relation to the vapor phase and the phase 1. The chemical compositions and temperatures are similar in both cases. This means that the primary concentration stage of uranium was early and occurred soon after the deposition of the tuff, during its cooling.

The kaolinization of the tuff and the precipitation of the pitchblende–pyrite phase within the pipe were related to aqueous salt-poor fluids (2.5 wt.% NaCl). The temperatures ranged from 300 to 150 with the most common temperature about 250°C. The crystallization of pyrite with pitchblende during kaolinization indicates the presence of H₂S in the fluids circulating within the pipe. Outside the pipe, similar kaolinization occurred without any transformation of the volcanic ilmenite–magnetite association. This means that outside the pipe the H₂S activity was low. These variations of H₂S activity explain the different behavior of Fe minerals. U was leached with the kaolinization (4 ppm U in kaolinized rock instead of 8 ppm U in fresh rock) and precipitated as pitchblende within the main structure (the pipe) in relation to the local H₂S activity increase which led to a pH decrease. The quantity of leached U in the kaolinized tuff is sufficient to explain the origin of the Nopal I deposit.

**Conclusion**

Detailed mineralogical and fluid inclusion studies of the Nopal I deposit (Sierra Pena Blanca, Chihuahua, Mexico) suggest that two stages of tetravalent uranium mineralization occurred prior to the development of hexavalent uranium minerals that prevail today.

Phase 1 (uranium oxides–ilmenite): the primary uranium mineralization occurred in contact with the volcanic ilmenites of the breccia pipe and seem to have been controlled by their hematite exsolution lamellae. The leaching of U is related to H₂O–CO₂–N₂ fluids at a temperature of 300–350°C. U may have precipitated due to an oxygen fugacity change when the fluids encountered the ilmenite–hematite phase.

Phase 2 (pitchblende–pyrite): this second stage is related to the kaolinization of the tuff. Uranium from the kaolinized tuff and from phase 1 was leached. Uranium then precipitated as pitchblende within the pipe, probably in response to a local H₂S activity increase (pH variation). Fluids were aqueous with a low salt content (2.5 wt.%), and the temperature ranged from 200 to 250°C.

All the following stages, either hydrothermal or supergene, occurred under oxidizing conditions and led to the

Table 2. Main results of the crushing and of the microthermometric studies.

<table>
<thead>
<tr>
<th>Type of event</th>
<th>Solution</th>
<th>Salinity (wt % NaCl)</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor phase</td>
<td>H₂O + H₂CO₃ + N₂</td>
<td>n.d.*</td>
<td>420-150°C</td>
</tr>
<tr>
<td>Breccia pipe</td>
<td>H₂O + CO₂ + N₂</td>
<td>0.5</td>
<td>350-300°C</td>
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<tr>
<td>Formation</td>
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</tr>
<tr>
<td>Kaolinization</td>
<td>H₂O + CO₂ + N₂</td>
<td>0.5</td>
<td>350-180°C</td>
</tr>
<tr>
<td>+ pitchblende</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinization</td>
<td>H₂O</td>
<td>0.5</td>
<td>300-150°C</td>
</tr>
<tr>
<td>+ uranophane</td>
<td>H₂O</td>
<td>0.1</td>
<td>150°C</td>
</tr>
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</table>

* n.d. not determined
hexavalent uranium mineralization, primarily uranophane, but also soddyite, weeksite (Aniel, 1983), haweeite, boltwoodite, and becquerelite.

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